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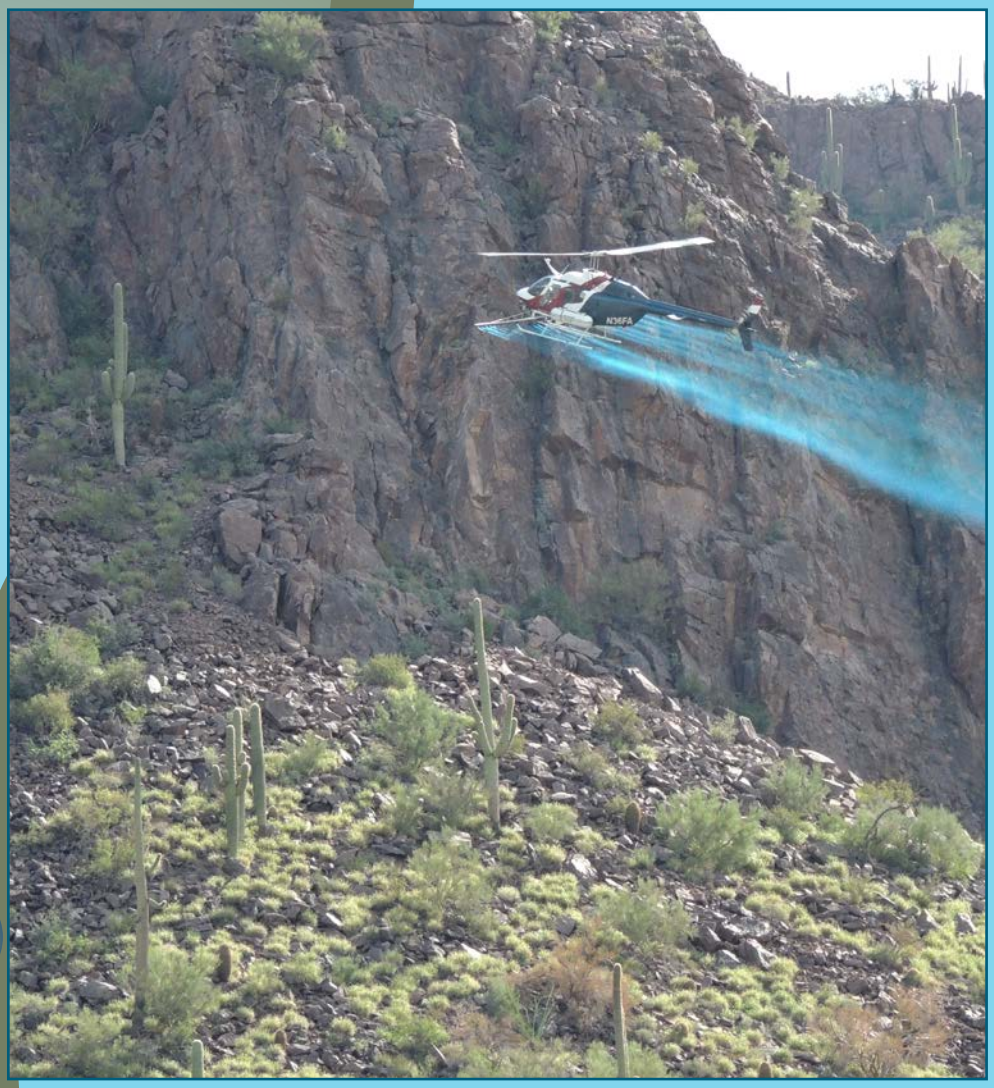
Occurrence, Fate, and Transport of Aerially Applied Herbicides to Control Invasive Buffelgrass within Saguaro National Park Rincon Mountain District, Arizona, 2015–18



Scientific Investigations Report 2021–5039

U.S. Department of the Interior
U.S. Geological Survey

Cover. Glyphosate-based herbicide treatment of buffelgrass patches, National Park Service, Saguaro National Park Tucson Mountain District.

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By Nicholas V. Paretti, Kimberly R. Beisner, Bruce Gungle, Michael T. Meyer, Bethany K. Kunz, Edyth Hermosillo, Jay R. Cederberg, and Justine P. Mayo

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We would also like to thank Petra Pitonak for granting us access to Saguaro National Park through her property and accommodating deployments of sampling equipment.

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Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Flow rate	
grams per year (g/yr)	0.00220462	pounds per year (lb/yr)
	Mass	
gram (g)	0.00220462	pound (lb)

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
	Area	
acre	4,047	square meter (m^2)
acre	0.4047	hectare (ha)
square mile (mi^2)	259	hectare (ha)
square mile (mi^2)	2.59	square kilometer (km^2)
	Flow rate	
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F = (1.8 \times °C) + 32.$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C = (°F - 32) / 1.8.$$

Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in solids and water are given in micrograms per kilogram (µg/kg) or micrograms per liter (µg/L), respectively. Dissolved oxygen concentration is given in milligrams per liter (mg/L).

Isotope Unit Explanation

Per mil: A unit commonly used to express the ratio of stable isotope abundance of an element in a sample to the abundance of the same element in a standard material. Per mil units are equivalent to parts per thousand. Stable isotope ratios are computed as follows (Kendall and McDonnell, 1998):

$$\delta X = \{(R_{sample} - R_{standard}) / R_{standard}\} \times 1{,}000$$

where

δ is the "delta" notation,

X is the heavier stable isotope, and

R is the ratio of the heavier, less abundant isotope to the lighter, stable isotope in a sample or standard.

The δ values for stable isotope ratios discussed in this report are referenced to the following standard materials:

Element	R	Standard identity and reference
Hydrogen	Hydrogen-2/hydrogen-1 (δ^2H)	Vienna Standard Mean Ocean Water (Fritz and Fontes, 1980)
Oxygen	Oxygen-18/oxygen-16 ($\delta^{18}O$)	Vienna Standard Mean Ocean Water

Stable isotope ratios of oxygen ($^{18}O/^{16}O$) and hydrogen (^2H [deuterium]/^1H) are shown in delta (δ) notation as $\delta^{18}O$ and δ^2H, in per mil (parts per thousand).

Abbreviations

a.i.	active ingredient
a.e.	acid equivalent
AMPA	aminomethylphosphonic acid
$\delta^{2}H$	a measure of the ratio of stable isotopes hydrogen-2 and hydrogen-1
$\delta^{18}O$	a measure of the ratio of stable isotopes oxygen-18 and oxygen-16
GBH	glyphosate-based herbicide
K_{ow}	octanol-water partitioning coefficient
LC50	Acute toxicity testing determines what constitutes a lethal concentration of a substance for 50 percent of a given animal population
LOAEC	lowest-observed-adverse-effect concentration
NOAEC	no-observed-adverse-effect concentration
NPS	National Park Service
POEA	polyoxyethylene tallow amine
USGS	U.S. Geological Survey

Occurrence, Fate, and Transport of Aerially Applied Herbicides to Control Invasive Buffelgrass within Saguaro National Park Rincon Mountain District, Arizona, 2015–18

By Nicholas V. Paretti, Kimberly R. Beisner, Bruce Gungle, Michael T. Meyer, Bethany K. Kunz, Edyth Hermosillo, Jay R. Cederberg, and Justine P. Mayo

Abstract

The spread of the invasive and fire-adapted buffelgrass (*Cenchrus ciliaris* L.) threatens desert ecosystems by competing for resources, increasing fuel loads, and creating wildfire connectivity. The Rincon Mountain District of Saguaro National Park addressed this natural resource threat with the use of glyphosate-based herbicides (GBHs). In 2010, the Rincon Mountain District initiated an aerial restoration plan to control dense buffelgrass patches in remote areas and implemented a trial project to evaluate the effects of aerial restoration techniques that included the helicopter application of GBHs. In 2014, more than 250 acres of buffelgrass in the Rincon Mountain District were treated with the aerial application of GBHs. This widespread aerial application of GBHs continued through 2018, but the potential transport and effects to aquatic ecosystems were unknown.

In 2015–18, the U.S. Geological Survey, in cooperation with the National Park Service, studied the occurrence, distribution, fate, and transport of glyphosate in surface water and sediments derived from areas that were treated during past and current aerial herbicide applications. Three watersheds, treated with different regimens of GBHs, were sampled for glyphosate and the primary metabolite of glyphosate, aminomethylphosphonic acid (AMPA), during various hydrologic flow conditions. Water and aquatic sediment were collected from three watersheds, each in a different stage of application during the U.S. Geological Survey study. The unnamed watershed above the Loma Verde Trailhead referred to by the National Park Service as "Loma Verde canyon" had received no aerial treatment since 2014, whereas the Box Canyon watershed was aerially treated every year beginning in 2014. The Madrona Canyon watershed was first sprayed in 2016 and aerial application continued once a year though the entirety of the study. In addition, terrestrial soil samples were sampled from areas sprayed to understand dissipation rates and herbicide transport via sediments washing away during rainfall runoff. The concentrations present in water and sediment samples were compared to ecological benchmarks and characterized within the context of the environmental conditions of the park setting.

Of the 48 water samples collected and analyzed for glyphosate and AMPA, 10.4 percent and 14.6 percent were detected above the laboratory minimum detection limit, respectively. Mean water concentrations, calculated using specific statistical methods for non-detects, were equal to the laboratory minimum detection limit of 0.02 microgram per liter for samples collected in all the watersheds. In aquatic sediments, glyphosate and AMPA were detected in 10.7 and 25.0 percent of the samples, whereas 89.5 and 100 percent of the terrestrial soil samples had detections for glyphosate and AMPA, respectively. Mean aquatic sediment concentrations were 1.13 and 4.42 micrograms per kilogram (µg/kg) for glyphosate and AMPA, respectively. Mean terrestrial soil concentrations were orders of magnitude greater than water and aquatic sediment with concentrations of 678 µg/kg for AMPA and 1,240 µg/kg for glyphosate. Hours after glyphosate-based herbicide was applied, the concentrations of glyphosate and AMPA were present in terrestrial soil samples near or above the laboratory maximum detection limit of 5,000 µg/kg. The Box Canyon watershed was the most intensively treated watershed in terms of total land area treated, total amount of GBH applied, and number of years treated. The frequent and large volume of treatment resulted in the highest number of detections of glyphosate and AMPA in water (3 and 7 detections, respectively) and in aquatic sediment (2 and 6 detections, respectively) samples. In comparison, the other two watersheds had two or fewer detections for glyphosate and AMPA in water and aquatic sediment.

Glyphosate detected in pools was associated with increased rainfall closer in time to the last herbicide treatment. Glyphosate and AMPA concentration ratios above one, along with stable-isotope and tritium results, indicated that runoff processes were the primary transport mechanism for the two compounds when found in streams and pools rather than subsurface recharge or deeper flow paths. One pool in a small tributary of Box Canyon consistently had detections of glyphosate and AMPA in aquatic sediments, but these frequent concentrations were likely related to the intensive application upstream, near the steep terrain above the head of the channel that supplies the downstream pool. Intense flows during summer rainfall events move treated sediments into this

channel where vegetation and the incised bedrock banks of the pool retained those sediments and ultimately led to frequent detections of both compounds. Isotope results in most of the pools and tinajas indicated that the water source had residence time representative of recently recharged waters, on the order of years.

No water concentrations exceeded published criteria for human health or aquatic life. Median and maximum glyphosate and AMPA water concentrations were lower than those reported in other national assessments, but maximum concentrations observed in individual runoff samples were higher than median concentrations measured in the national assessments. A similar finding was observed with aquatic sediment concentrations measured in the Rincon Mountain District. Results from the study were compared and assessed in the context of other studies examining GBHs and their effects on amphibians, fish, and macroinvertebrates. This comparison was used to generalize the potential risk to aquatic species similar to those species in the Rincon Mountain District. Concentrations of published effect levels were several orders of magnitude greater than the highest concentration detected in water at the Rincon Mountain District. Most published studies evaluate acute and chronic toxicity for glyphosate and GBHs, and these criteria may not be representative of environmental conditions in the Rincon Mountain District. The classic lethal dose studies conducted in a controlled laboratory setting may not be suitable for comparison to the longer, variable, low-dose exposure conditions in the pools and tinajas in the Rincon Mountain District. However, this study determined that the fate of GBHs transported from treated areas to potential aquatic habitat was highly variable in occurrence, timing, and concentrations. This variability in glyphosate concentrations was too high, and the potential exposure was determined to be far too complex to directly compare with the results from controlled studies.

This study provides the first information collected on GBHs used to control invasive buffelgrass in a remote, mountainous, and semiarid setting. The information about the transport and fate of herbicide application near aquatic habitat will help to inform managers about the broader ecosystem implications and provide useful information to other agencies implementing buffelgrass remediation strategies near aquatic habitat.

Introduction

Saguaro National Monument was established by President Herbert Hoover on March 1, 1933, and the U.S. Congress designated it a national park in 1994. This mountainous park has two districts—the Rincon Mountain District (east) and the Tucson Mountain District (west)—separated by the City of Tucson, Arizona (fig. 1). The park manages 87,526 acres in Federal ownership of which 71,400 acres are designated wilderness. Management priorities of the park include preserving and protecting the iconic saguaro (*Carnegiea gigantea*) and promoting the diversity of biotic communities including the Sonoran Desert and associated mountain and aquatic ecosystems (National Park Service, 2007). The Rincon Mountain District (Saguaro National Park) supports many endangered and threatened species as well as several sensitive species of concern, including the lowland leopard frog (*Lithobates yavapaiensis*), whose remaining high-quality habitat in southern Arizona is within the Rincon Mountain District. These plant and animal species evolved in a landscape free of wildfire, and are highly threatened by the spread of buffelgrass (*Cenchrus ciliaris* L.), an invasive African plant species that burns vigorously and thrives in a wide range of ecosystems. Buffelgrass competes with native plant species for nutrients and water, produces dense monoculture infestations, and increases the connectivity of dry fuels that carry wildfires (D'Antonio and Vitousek, 1992; Marshall and others, 2012; Olsson and others, 2012). A buffelgrass-fueled fire will destroy many of the native species in the Rincon Mountain District while promoting fire-adapted regeneration of buffelgrass and opening space for other non-native plants to invade, thus resulting in a feedback cycle that accelerates an invasive process that is hard to disrupt (D'Antonio and Vitousek, 1992; Búrquez-Montijo and others, 2002; Franklin and others, 2006; Esque and others, 2007; Olsson and others, 2012). Other negative effects of these buffelgrass-compounded fires include accelerated erosion on steep slopes and increased sedimentation, filling of tinajas and other pools with sediment, and destruction of scarce aquatic habitat (Parker, 2006).

Tinajas, meaning "small jars" in Spanish, are perennial or quasi-perennial surface waters present in bedrock erosional features of a few feet to tens of feet in diameter (McIntyre and others, 2018). A tinaja is a pool that may be in or adjacent to a stream channel, is made of impermeable bedrock, is shaped more or less like a bowl, and for most of the year is a function of surface evaporation unless it is fed by a spring or seep. Springs and seeps that supply tinajas may be related to local fracture systems where groundwater maintains perennial and intermittent flow (National Park Service, 2017b). Tinajas are otherwise refilled periodically by high flows and (or) precipitation. A non-bedrock pool, however, is an in-stream deep and slow-velocity water feature that has a sandy or cobbled bottom with a water volume that is a function of streamflow. When streamflow decreases, water velocity decreases, surface area decreases, and eventually the pool disappears. Tinajas in stream channels have been formed over time by scouring fluvial processes, whereas those outside of stream channels have been formed by in situ weathering and erosional processes (McIntyre and others, 2018). Although the term "tinaja" is commonly used in the American Southwest, a variety of terms are used to describe these natural bedrock depressions, including pothole, natural tank, plunge pool, water pocket, and sand tank (McIntyre and others, 2018). In this study tinajas are considered a type of pool; a reference to "pools" in this report, therefore, includes non-bedrock pools and tinajas.

Proximity of the Rincon Mountain District to the Tucson urban environment facilitates the reseeding and spread of buffelgrass into the park through soil disturbance and seed transport, precluding permanent eradication. The spread of

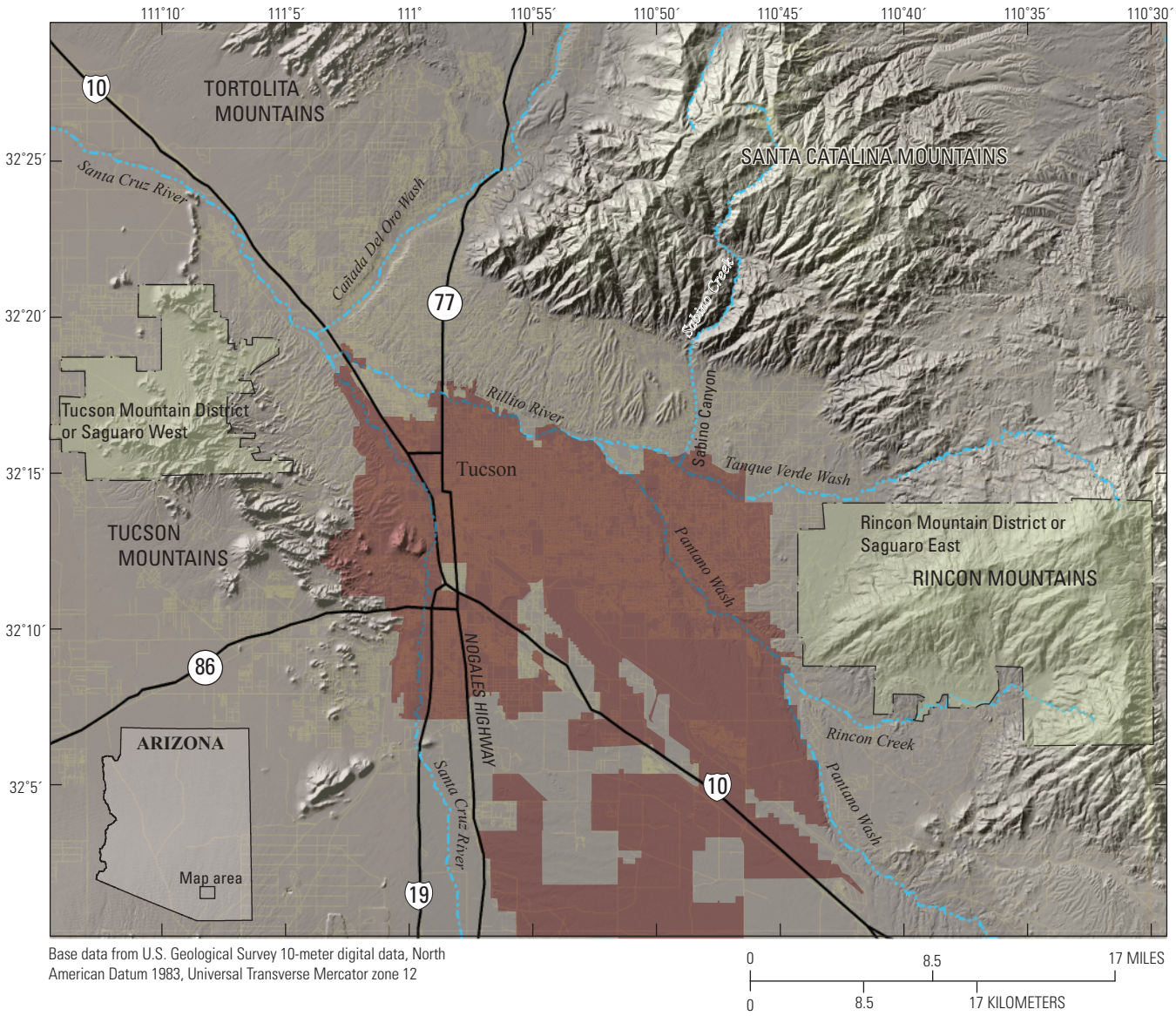

Figure 1. Saguaro National Park eastern Rincon and western Tucson Mountain Districts and Tucson, Arizona.

buffelgrass has been identified as a primary and imminent threat to Sonoran Desert ecosystems because of its rapid propagation and broad dispersal throughout southern Arizona and northern Sonora, and the Rincon Mountain District has identified buffelgrass as the number one threat to the natural and cultural resources of the park (Rogstad, 2008; Saunders and others, 2009). Buffelgrass has been so pervasive in the Southwest that the U.S. Department of the Interior issued a declaration in a 2010 testimony that was referenced as the war on buffelgrass (Frost, 2010). In 2008, the Rincon Mountain District developed and enacted a restoration strategy to remediate the spread of buffelgrass that utilized manual removal as well as ground-based herbicide treatments using a glyphosate formulation applied by individuals using backpack sprayers. However, these methods were not viable options for areas where buffelgrass was growing in remote, steep, rocky terrain within the Rincon Mountain District.

In 2010, the Rincon Mountain District initiated an aerial restoration plan for buffelgrass-infested areas that included a preliminary demonstration project that included different areas of Tucson, as well as the necessary compliance process to evaluate the effects of aerial restoration techniques that include helicopter application of glyphosate-based herbicides (GBHs; White and Baldwin, 2010). The program continued after the demonstration project, and by 2014 more than 250 acres of buffelgrass in Saguaro National Park Rincon and Tucson Mountain Districts were treated by aerial application. In the Rincon Mountain District, with the success of managing large buffelgrass patches, aerial application continued yearly through 2018, but the potential effects to aquatic ecosystems were unknown and were not included in the management plan. An assessment of the potential effects to aquatic environments was not included owing to the limitations of the analytical capabilities for analyzing glyphosate in the environment.

Glyphosate itself has not been shown to be highly toxic for several species, but most toxicity testing is conducted in a laboratory setting where lethal concentrations are identified at fixed intervals. The toxicity of trademarked glyphosate formulations that include surfactants, however, has been shown to have effects on different species, many of which are amphibians (Howe and others, 2004; Relyea and Jones, 2009; Jones and others, 2010; Edge and others, 2014; Navarro-Martín and others, 2014). These documented effects do not always address ecologically relevant concentrations or the broader implications to the ecosystem health and no studies have looked at the effects to semiarid aquatic ecosystems or to the lowland leopard frog specifically, which is one of the primary concerns of the Rincon Mountain District.

Purpose and Scope

Since 2014, the National Park Service (NPS) has been aerially applying GBHs on a yearly basis to eliminate the spread of buffelgrass in the Rincon Mountain District. However, comprehensive information regarding the fate and transport of GBHs in a semiarid environment was not available at the time of the environmental assessment for their aerial application. The water resources in the Rincon Mountain District are scarce and therefore critical to the survival of native aquatic species, such as the sensitive lowland leopard frog. The potential for contamination of aquatic resources resulting from surface runoff and (or) aerial drift is a primary concern and in need of further investigation.

A 4-year U.S. Geological Survey (USGS) study was implemented to increase understanding of the occurrence, distribution, fate, and transport of glyphosate in surface water derived from past and current aerial herbicide applications. Sediment and water were sampled for glyphosate and its primary metabolite, aminomethylphosphonic acid (AMPA), during various hydrologic flow conditions in three watersheds at different stages of herbicide treatment. The potential for transport of herbicide from within the park boundary was assessed. Concentrations in water and sediment samples were related to ecologically sensitive organisms within the context of the park setting. The information gained through the study provides the Rincon Mountain District with the information needed to evaluate the specifics of the herbicide application strategy by identifying any unanticipated side effects of the application program and mitigating any negative effects of the program on the broader Rincon Mountain District aquatic ecosystem. The broader ecosystem implications are also important for other agencies when assessing their own buffelgrass remediation strategies.

Description of Study Area

The Rincon Mountain District of Saguaro National Park encompasses a diverse and rugged landscape that contains a portion of the Sonoran Desert as well as the oak and pine-forested peaks of the Rincon Mountains (fig. 2). The Rincon Mountains make up most of the terrain within the eastern park district and are one of several mountain ranges of southern Arizona. Collectively the mountain ranges are known as the “Madrean Archipelago” or “Madrean Sky Islands” and together these mountain ranges offer a mechanism for genetic exchange and support a complex and unique biodiversity. A major reason for this biodiversity is a mixing of different life zones on the relatively isolated mountain ranges, distinguished by the large elevation and climatological change within a short horizontal distance. The semiarid desert at the bottom is connected to mountain-top forest ecosystem, which promotes unique adaptive characteristics and life-zone mixing of the ecological communities (Bezy, 2016). Elevations range from 2,670 feet (ft) along the western edge of the park district to 8,666 ft at the summit of Mica Mountain. There are extensive stands of saguaro cactus, prickly pear and cholla (*Opuntia* spp.), ocotillo (*Fouquieria splendens*), various agave (*Agave* spp.), yucca species (*Yucca* spp.), and woody shrubs covering the lower elevations and bajadas. Higher elevation hillslopes are vegetated with grassland, scrubland, manzanita (*Arctostaphylos* spp.), oak (*Quercus* spp.), and juniper woodlands (*Juniperus* spp.). The upper elevation mountainous terrain is covered with mixed conifer forest, mostly ponderosa pine (*Pinus ponderosa*) and Douglas-fir (*Pseudotsuga menziesii*) (Powell and others, 2006).

Stream channels within the study area are mostly bedrock controlled and the geometry, sinuosity, and substrate depend on the local geologic structure and lithology of the terrain over which the stream flows. In the higher elevations, stream channels are generally narrow and high gradient, with cobble and large and small boulders that shape the channel morphology in the mountainous landscape of the study area. The lower elevation channel sections are more alluvial, with channel banks and bed substrates that are more mobile than in the higher elevations and channel morphology that is primarily controlled by stream discharge (Parker, 2006). The alluvial reaches are characterized by sand- and gravel-bed channels with discontinuous alluvial banks, and frequent expressions of bedrock sections on the channel bottom, which expose the thin alluvial depositional layer. Tinajas and pools can form in narrow bedrock sections where a fragment breaks from the bottom of the channel along joint planes or a trough has been eroded into the narrow channel bottom by continuous fluvial incision or abrasion (Parker, 2006). The carved bedrock tinajas are generally round or oval shaped, frequently occur in multiples that continuously step down a sharp channel gradient, and have a wide range of lengths and depths, ranging from a few feet to more than 20 ft across, and from less than a foot to more than 10 ft deep (Parker, 2006). The recharge and flowpaths maintaining and replenishing these tinajas have been a topic of ongoing geochemical studies in the Rincon Mountains (Eastoe and others, 2004; Eastoe, 2012).

Soils generally are thin (7 to 20 inches to bedrock) except on some ridge tops and small upland basins. The general soil classification of the ridges and bajadas for the study area is the Lampshire-Romero-rock outcrop complex (Cochran and Richardson, 2003). This soil classification unit is 45 percent

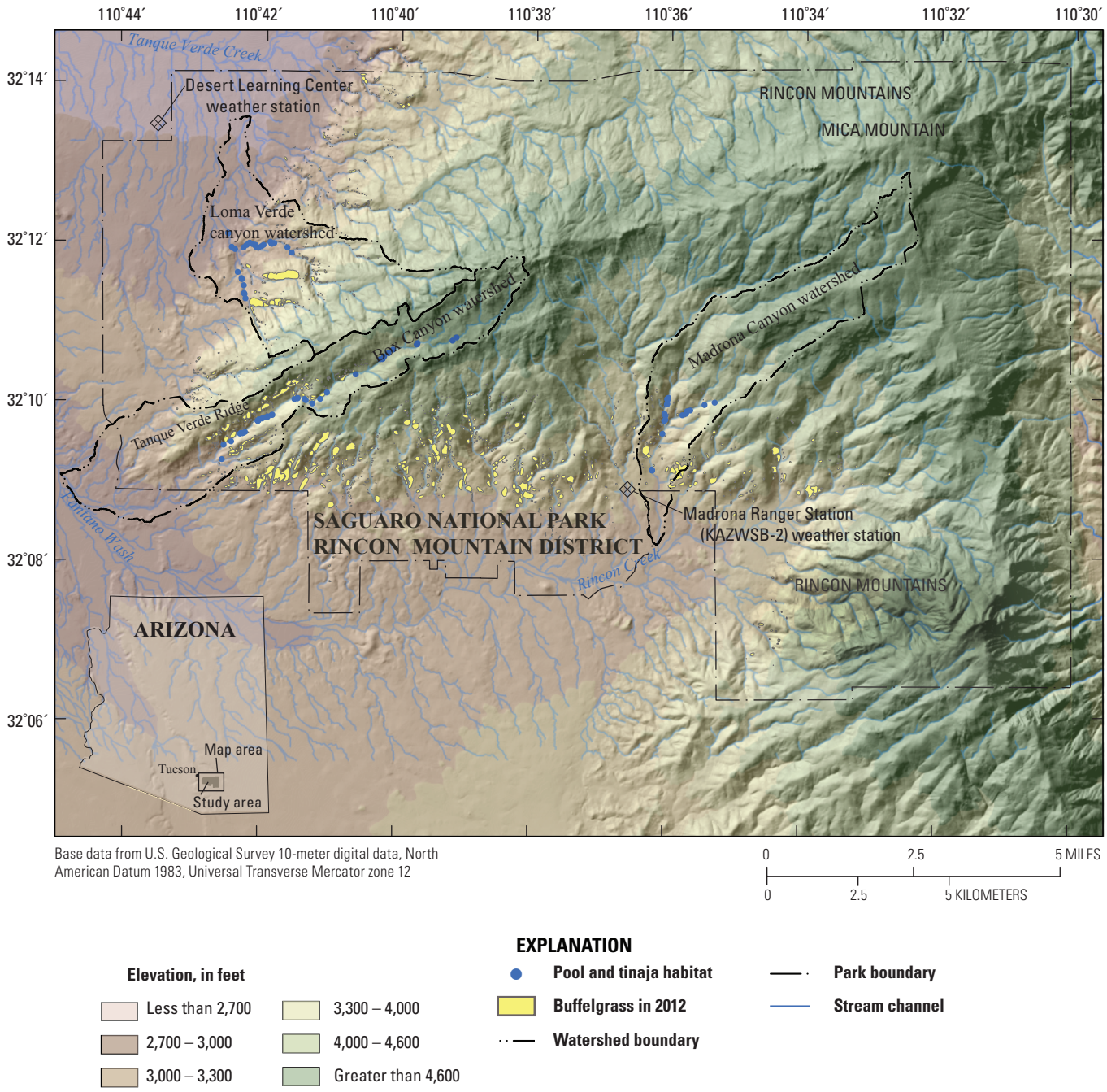

Figure 2. Saguaro National Park-Rincon Mountain District, Arizona, and Loma Verde canyon, Box Canyon, and Madrona Canyon watersheds. Elevation gradation is shown with a color gradient.

Lampshire (gravelly loam), 20 percent Romero (gravelly sandy loam), 15 percent Rock outcrop, and 20 percent other soil types covering small areas (Cochran and Richardson, 2003). Lampshire-Romero is neutral to alkaline and organic matter averages 1 to 5 percent. It is well drained, with medium rates of runoff, a moderately permeable complex, and a low soil-erosion tolerance factor (Cochran and Richardson, 2003). In the study area, the highest density of buffelgrass patches grow in this soil unit and therefore it receives the most herbicide application (fig. 3).

Parker (2006) described channel alluvium and sediment transport as mostly substrate consisting of small cobble-size gravel (2–128 millimeters [mm] diameter) and sand (0.0625–2 mm diameter). Channel bottoms and tinaja sites with deposits generally contain poorly sorted sandy gravels, with a silt-clay content of less than 5 percent. The low content of fine-grained sediments (particle size less than [<] 0.0625 mm) in the Rincon Mountains indicates that hillslope sediments in the study area are nearly cohesionless, consisting of sands and gravels, and that fine silts may get trapped prior

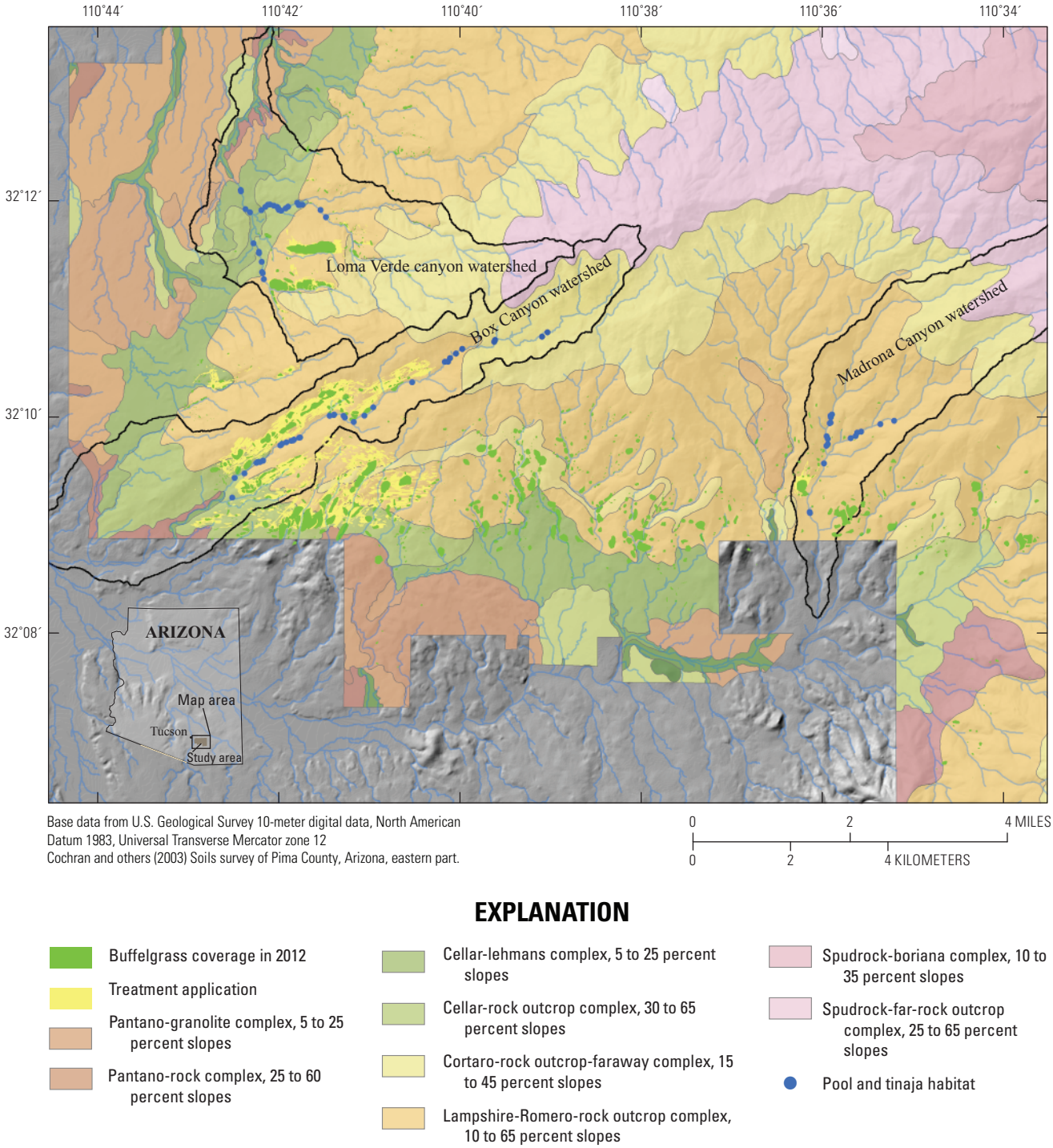

Figure 3. Soil classifications, 2012 buffelgrass coverage, glyphosate-based herbicide treatment coverage 2014–18, and pool and tinaja habitat for the Loma Verde canyon, Box Canyon, and Madrona Canyon watersheds, Rincon District of Saguaro National Park.

to reaching to the stream channel, thus leading to suspended sediment flow that is supply limited in fine particles, resulting in very little deposition downstream (Parker, 2006).

Most of the Rincon Mountain District is located within the larger Rillito-Pantano Wash watershed (920 square miles). Drainage of the southern- and western-facing portion of the Rincon Mountains in the park flows towards Rincon Creek (45 square miles), which in turn flows west toward Pantano Wash (fig. 1). Rincon Creek is the most consistently flowing drainage in the park. Except for a portion of the pools and tinajas, there are no perennial stream reaches in the park; streamflow is often intermittent at higher elevations and ephemeral at lower elevations. Several tinajas are considered perennial and these are crucial habitat for aquatic and terrestrial species' survival during dry periods. Streams flow mainly in response to runoff from the intense convective rainfall that falls during the North American monsoon (July through September) and from winter precipitation and spring

snowmelt. In some years, tropical moisture from decaying tropical cyclones can also cause heavy rainfall in the mountains from late September to early November. Overall, the most consistent sources of surface water are the deep tinajas shaded by canyon walls and riparian vegetation that minimize evaporation. Tinajas may receive additional inflow from springs or seeps that discharge groundwater from the fractured rock that encloses the pools (Parker, 2006). The hydrogeology of the Rincon Mountain District is complex and a complete understanding of the source waters to springs and pools has not been developed, but geochemical studies and surface-water monitoring are helping to provide this information (Eastoe and others, 2004). This greater regional understanding, however, is complicated and exacerbated by changing climate conditions, such as long-term trends toward less precipitation and warmer temperatures in an already arid climate (Zylstra and others, 2015).

Loma Verde canyon, Box Canyon, and Madrona Canyon watersheds are the focus and primary treatment areas of this study, and they are contained mostly within the Rincon Mountain District boundary. The watershed above the Loma Verde Trailhead is an unnamed canyon but referred to by the National Park Service as "Loma Verde canyon" and hereafter referred to "Loma Verde canyon" in this report. The watersheds are roughly 1.36, 6.53, and 5.70 square miles, respectively (fig. 2, table 1). The land use of these three watersheds is primarily classified as lower shrubland including desert, and the higher elevation portions of the watershed are classified as forest. A small percentage (less than 2 percent) has some degree of urbanization (low, medium, and high density), but urbanized area is lower in the watershed outside of the park boundary. Mean basin elevation for Loma Verde canyon, Box Canyon, and Madrona Canyon is 3,990, 4,290, and 5,640 ft, respectively (table 1). The terrain in the watersheds is steep with average slopes exceeding 30 percent. Much of the area draining from Madrona and Box Canyon is above 5,000 ft (64 and 33 percent, respectively). These high elevation areas enhance precipitation orographically and increase winter and spring runoff, contributing to subsurface flow of water to pools and tinajas. The mean annual precipitation for the Rincon Mountain District area is around 20 inches per year (U.S. Geological Survey, 2018; table 1), but the park measured average annual precipitation as approximately 16.8 inches from February 2014 to February 2018. Local precipitation for the sampling period was obtained from rain gages at the Madrona Ranger Station (KAZWSB-2, elevation 3,425 ft) and the Desert Learning Center (elevation 2,750 ft) (Walking Shadow Ecology, 2021). Values from the two locations were averaged. The 2014–15 winter was particularly wet with about 16.3 inches of precipitation recorded (average of Desert Learning Center and Madrona Ranger Station rain gages). Patterns during the study were representative of recent historical averages and patterns. The steep slopes and high elevation areas of the study area commonly result in rapid runoff and high energy floods capable of moving debris and substrate. Estimated magnitude and frequency of floods are similar

Table 1. Watershed characteristics, flood frequency, and rainfall statistics.

[DEM, digital elevation model; NED, National Elevation Dataset; NLCD, National Land Cover Dataset; SEP, standard error of prediction; Paretti and others, 2014; U.S. Geological Survey, 2018]

Basin characteristic or percent annual exceedance probability	Madrona Canyon	Box Canyon	Loma Verde canyon
Area that contributes flow to a point on a stream, in square miles (drainage area)	5.70	6.53	1.36
Mean annual precipitation, in inches	23.6	19.1	17.9
Mean annual temperature, in degrees Fahrenheit	57.9	63.1	64.8
Mean basin elevation, in feet	5,640	4,290	3,990
Percent of area above 5,000 feet, in percent	64	33	12
Mean basin slope computed from 10-meter DEM, in percent	34.8	27.4	38.8
Percent area with slopes greater than 30 percent from 10-meter NED, in percent	59	39	63
Percentage of forest from NLCD 2001 classes 41–43, in percent	40	6	1
Percentage of shrubland from NLCD 2001 classes 51–52, in percent	58	90	95
Percent basin surface area containing high permeability aquifer units as defined for Arizona in SIR 2014–5211, in percent	0	13	0
2-Year peak flood (SEP 86.6), in cubic feet per second	258	278	114
5-Year peak flood (SEP 61.5, in percent), in cubic feet per second	657	709	280
10-Year peak flood (SEP 52.4, in percent), in cubic feet per second	1,060	1,150	444
50-Year peak flood (SEP 43.5, in percent), in cubic feet per second	2,440	2,640	986
100-Year peak flood (SEP 42.6, in percent), in cubic feet per second	3,260	3,530	1,300
500-Year peak flood (SEP 43.2, in percent), in cubic feet per second	5,680	6,160	2,220

between the Box Canyon and Madrona Canyon watersheds. The Loma Verde canyon watershed flood estimates are lower because of watershed size. The 50-percent exceedance probability peak flow (also known as the 2-year flood) ranges between 114 and 278 cubic feet per second and the 1-percent annual exceedance probability peak flow (100-year flood) ranges between 1,300 and 3,530 cubic feet per second (Paretti and others, 2014; U.S. Geological Survey, 2018).

Related Glyphosate-Based Herbicide-Use Studies for Resource Management Purposes

In the last 20 years, resource managers have been using more aggressive approaches that involve the use of herbicidal applications to manage invasive non-native plant species. Most often herbicides are used in conjunction with physical methods, such as burning, cutting, or uprooting. Herbicides are used worldwide in natural resource management settings to prepare forest sites for planting or to control competing vegetation after the tree crop has been planted, but research related to ecological implications has been limited (Rolando and others, 2017). The herbicide application in the setting of the Rincon Mountain District, where it is being used to control buffelgrass in a mostly upland desert and semiarid climate, is somewhat unique relative to other uses in the United States and other countries where it is used to control tamarisk (*Tamarix* spp.), giant reed (*Arundo donax*), and various weeds in forests and along river corridors (Feng and others, 1990; Bakke, 2001; Dixon and others, 2003; Briggs, 2009; Gresham, 2010; U.S. Department of Agriculture, 2012; Thistle and others, 2014; Rolando and others, 2017; González and others, 2017).

In U.S. Forest Service programs, GBHs are used primarily for conifer release situations, site preparation, and noxious weed control (Durkin, 2011). In silviculture and forest management, herbicides are mostly used to reduce competitive stresses exerted by undesirable weeds and other broad-leafed vegetation on small conifer plants. The GBHs are also used to control weeds in nursery settings without injuring hardwood seedlings.

Assessments have been conducted to better understand the effects of drift during ground-based glyphosate applications, especially in proximity to water (Feng and others, 1990). In one case study, Bakke (2001) reported that with one exception, there were no glyphosate detections in water and sediment sampling from riparian zones conducted after ground-based applications targeting noxious weeds in reforestation projects. A review by Rolando and others (2017) led to the conclusion that GBHs, as typically employed in planted forest management, did not pose a significant risk to humans or the terrestrial and aquatic environments.

Tamarisk and giant cane are extremely invasive in riparian communities and, in many areas of the southwestern United States, have completely replaced native vegetation during the past several decades. Governmental and non-profit agencies have tested several weed control strategies including chemical eradication with the use of the herbicides imazapyr, triclopyr, and glyphosate. Although glyphosate has proven effective at eradicating unwanted plant species in many situations and is seemingly successful as part of a restoration strategy, there have been some unanticipated issues documented such as some noxious weeds developing glyphosate resistance as well as the introduction of herbicides to river waters (Briggs, 2009; González and others, 2017).

Herbicide applications for a resource management action often are specific to the regional setting, but because the environmental conditions in which they are implemented may differ, the fate and potential effects are not known. For example, an intermittent stream treated with an herbicide in the Southwest would result in a different degradation process and environmental fate compared to a wet and colder boreal forest in the Pacific Northwest. These environmental conditions determine the concentrations that are bioavailable and the exposure potential. These differences could affect species of different regions in different ways and ultimately change the risk to a similar species living in different habitats. A common approach to addressing animal species risk is to defer to regulatory agency standards such as the U.S. Environmental Protection Agency's acute and chronic pesticide criteria, toxic effects levels, or reregistration eligibility decision (U.S. Environmental Protection Agency, 1993, 2004). However, these blanket effect levels may not represent all the conditions described above and likely only address an upper threshold for single species, which may not be relevant to the environmental setting, exposure, or multiple species types present in specific types of habitat.

Overview and History of Buffelgrass in Saguaro National Park

Buffelgrass (*Cenchrus ciliaris* L.) is a drought-tolerant, perennial bunchgrass introduced into southern Arizona beginning in the 1930s for erosion control and for livestock forage. Numerous strains have been collected throughout its range (stretching from Africa to India) in attempts to find species and cultivars to improve forage production and soil conservation. The common type T-4464 (collected from Kenya) is recognized as the most abundant type in the wild in southern Arizona (Van Devender and others, 1997). The grass has a bushy stem that can grow more than 3.5 ft tall and as much as 3 ft in diameter, with roots multiple feet in depth and seeds that can be viable in the soil for as many as 5 years (Marshall and others, 2012; U.S. Department of Agriculture, 2014). Buffelgrass is most successful in areas with average precipitation above 8 inches and where minimum average temperatures do not consistently fall below freezing. In Arizona, growth is during the rainy season. The grass is brown and dormant until seasonal precipitation increases when the grass becomes mostly green, indicating new growth at about 12 days after a 3-week period of cumulative rainfall totals of at least 1 to 2 inches (Wallace and others, 2016). The grass grows best on rocky hillsides and desert washes and disperses seeds by wind, water, or by attaching to passing animals. It grows densely and

rapidly converts complex biological communities into monocultural grasslands by outcompeting most native plants for resources. Buffelgrass is fire adapted and evolved in a setting prone to fires. The bushy, almost woody stems easily burn and create fuel loads of 1 to 4 tons per acre, thousands-fold more than normal Sonoran Desert fuel loads (Esque and others, 2007; McDonald and McPherson, 2011, 2013; Marshall and others, 2012).

Buffelgrass was first recorded in Saguaro National Park in 1989, but it was not recognized as a threat until the early 1990s. Buffelgrass extent in Saguaro National Park has been doubling about every 2 to 7 years since 1988 (Olsson and others, 2012). In the 1970s, buffelgrass was widely planted in areas near Saguaro National Park for erosion control, and by 2002 an NPS survey estimated there were 175 acres of buffelgrass in both park districts. By 2012, coverage had increased to more than 2,000 acres, a rate of increase of roughly 35 percent per year (National Park Service, 2011, 2017a; fig. 3). Historically the Sonoran Desert burned infrequently, and when it did the fires were patchy and not very intense (McDonald and McPherson, 2013). Buffelgrass has increased fuel loads several orders of magnitude from those historically observed in both park districts. The increased frequency of large, high-temperature buffelgrass fires is extremely likely without mitigation, and the Sonoran Desert has not experienced such a threat before, putting native vegetation and long-lived species such as saguaro cacti at risk.

A manual control program for buffelgrass in Saguaro National Park was started in 1993. Manual or mechanical removal is very laborious and time consuming and was not adequate for the high rate of buffelgrass expansion in the park. In 2004, Saguaro National Park managers developed an Environmental Assessment and Exotic Plant Management Plan (National Park Service, 2004) to address this rapidly expanding threat. The Environmental Assessment introduced the approach to use herbicides in conjunction with manual removal to control buffelgrass. Managers quickly realized the logistical complications associated with areas too remote or too rugged for ground treatments, and the potential use of aerial spraying was evaluated. In 2014, aerial spraying of the GBH was used to manage buffelgrass with numerous mitigations to protect human safety and natural resources. A related issue considered but not fully investigated was the potential for herbicides to move into the aquatic ecosystem or groundwater resources that provide water to pools and tinajas. Glyphosate has generally been shown to have lower acute toxicity, shorter half-life, and lower mobility than most herbicides (Giesy and others, 2000), but the chemical behavior is tied closely to environmental factors. To date, little research has been carried out on the chemical behavior of glyphosate in a semiarid environment with thin soils such as on mountain flanks in the Sonoran Desert. Since recognizing the threat of buffelgrass to the Sonoran Desert landscape, many innovative approaches to modeling its presence, spread, and timing of emergence have been implemented to give park managers the tools necessary to manage buffelgrass (Olsson and others, 2012; Bean, 2014; Wallace and others, 2016; Jarnevich and others, 2018). However, none of these tools specifically addresses the potential of GBH persistence, transport, fate, or ecotoxicological effects in aquatic habitat.

Glyphosate-Based Herbicides

In the last 20 years, land managers have utilized herbicidal treatments to control invasive plant species (Kettenring and Adams, 2011; Rolando and others, 2017). Often chemical treatments are more cost effective than manual removal, or they are considered the only remaining option owing to the scale of invasion or remote location of the target species. One of the major issues for natural resource managers is the vast number of herbicides and additives available on the market. Also, the propriety nature of the ingredients and alteration of formulations creates challenges for users trying to understand the unintended consequences of non-point source effects of the parent chemicals and metabolites, and their fate lower in the watershed.

The efficacy of several herbicides for controlling buffelgrass has been analyzed by resource managers in Australia and the United States, but primarily in Arizona and Texas national parks (Dixon and others, 2003; Tjelmeland and others, 2008; U.S. Department of Agriculture, 2012; Bean, 2014; Thistle and others, 2014; Rolando and others, 2017). At the Rincon Mountain District, various treatment types and mixtures of herbicides were tested with backpack and aerial spray methods. Glyphosate-based herbicides (GBHs), generally in the form of Roundup, were selected by the Rincon Mountain District owing to its effectiveness and low potential for non-target species damage (U.S. Department of Agriculture, 2012; Thistle and others, 2014; Bean, 2014). However, there are several types of Roundup with unknown additives and surfactants in addition to the many ways the user can prepare mixtures for different uses. A surfactant is commonly added to improve the efficacy of the glyphosate. This mélange of chemicals makes it difficult to measure the various constituents of the GBHs in the environment, especially at a non-point source. In urban and agricultural settings, the research focus has been on measuring glyphosate and the primary metabolite of glyphosate to assess the effects of GBH application. Surfactants are more difficult to measure directly, but the presence of glyphosate generally indicates a higher likelihood that the surfactant or other additives are present as well.

The compounds described in the current study are glyphosate, the active ingredient in most Roundup formulations; AMPA, a weak organic acid with a phosphonic acid group and the primary metabolite of glyphosate; and polyoxyethylene tallow amine (POEA), a common non-ionic surfactant used in many GBH formulations. Many types of surfactants are used in GBHs and although POEA was not specifically analyzed in this study, it is a common surfactant and assumed to have many similar properties to other ethoxylated surfactants used in the herbicide formulations applied in the Rincon Mountain District.

Glyphosate is the active ingredient used in Roundup herbicide formulations. Glyphosate ($C_3H_8NO_5P$), or N-phosphonomethyl glycine is a nonselective or broad-spectrum contact herbicide that kills plants by inhibiting the synthesis of aromatic amino acids (Franz and others, 1997). Glyphosate was first synthesized in 1950, but because it showed no pharmaceutical prospects, the chemical was ignored until more than a decade later when it was noticed by Monsanto Company while testing AMPA-related substances during the development of phosphonic acid type water-softening agents (Székács and Darvas, 2012). Its herbicidal properties were not fully recognized until J.E. Franz of the Monsanto Company synthesized glyphosate yet again in 1970 as part of a program focused on development of a systemic perennial herbicide (Franz and others, 1997). It was introduced as the herbicide product Roundup (formulation of the isopropylamine salt of glyphosate with a surfactant). When sprayed on plant surfaces, glyphosate is absorbed by the foliage and then moves to the roots, rhizomes, and apical tissues. Inside the plant, glyphosate inhibits an enzyme (5-enolpyruvylshikimate-3-phosphate) synthase required for synthesizing certain aromatic amino acids necessary for plant growth, specifically protein formation and the production of secondary plant products (Franz and others, 1997). This process results in the wilting and yellowing of the plant that becomes complete browning with deterioration of underground parts. These effects develop more slowly than with other contact herbicides, requiring as many as 4 days for effects to become obvious with most annuals, and 7 days or more with most perennials (Cheminova, Inc., 2004; Monsanto Company, 2007). Glyphosate does not penetrate the woody stems of trees, and some plants are resistant to glyphosate when dormant (for example, Bermuda grass and conifers; Franz and others, 1997).

Since its introduction in the mid-seventies, glyphosate has become the largest-selling pesticide in the world (Franz and others, 1997; Baylis, 2000; Veiga and others, 2001; Kolpin and others, 2006). Much of this success is due to the low toxicity to non-target organisms that do not have the 5-enolpyruvylshikimate-3-phosphate synthase and the increased use of glyphosate-tolerant genetically modified crops. Glyphosate is used in more than 130 countries and is the most heavily used pesticide in the United States (Aspelin, 1997; Giesy and others, 2000; Székács and Darvas, 2012; Battaglin and others, 2014). China is the largest glyphosate supplier in the world, using thousands of tons of GBHs each year (Dill, 2005; Zhang and others, 2011; Yang and others, 2015). Non-agriculture use of glyphosate in the United States was less than 1 million pounds in 1974 and reached more than 20 million pounds in 2004. As of 2014, non-agriculture glyphosate use was 26.5 million pounds (Aspelin, 1997; Kiely and others, 2004; Grube and others, 2011; Battaglin and others, 2014; Benbrook, 2016). In general, glyphosate by itself has been shown to be low in acute toxicity testing to birds, fish, and aquatic invertebrates with low oral and dermal acute toxicity to humans (U.S. Environmental Protection Agency, 1993). The active ingredient alone does not persist in a bioactive form in the environment, does not readily bioaccumulate or biomagnify, and is generally considered to pose minimal ecological risk (Giesy and others, 2000; Rodriguez-Gil, 2015). More recent studies have suggested or shown the potential for endocrine disrupting effects (Gasnier and others, 2009; Myers and others, 2016).

Aminomethylphosphonic acid (AMPA) is a product resulting from phosphonate degradation and is the primary metabolite of glyphosate microbial degradation (Franz and others, 1997, Giesy and others, 2000; Borggaard and Gimsing, 2008; Székács and Darvas, 2012; Wang and others, 2016). It can also be a photodegradation product of aminopolyphosphonates in water or wastewater from commonly used industrial and household applications, such as detergents, fire retardants, and anticorrosives (Nowack, 2003; Lesueur and others, 2005), but concentrations of AMPA measured during this study are attributed to the microbial degradation of glyphosate because there are no wastewater sources in the study area. Aminomethylphosphonic acid (AMPA) has properties and a toxicity comparable to that of glyphosate and it is therefore considered to be of similar toxicological concern. However, few studies have done direct comparisons of the toxicity of glyphosate and AMPA on non-target species (Battaglin and others, 2014), although one study did determine that AMPA was equally or more toxic as glyphosate to some algae, invertebrate, and mammal species (Giesy and others, 2000).

Polyoxyethylene tallow amine (POEA) was not measured in the study owing to the difficulties in the laboratory method capabilities that are described below. POEA is a non-ionic surfactant related to alkylamine ethoxylates (Tush and others, 2013) and is a common surfactant added to many glyphosate formulations to increase the efficacy of glyphosate. POEA is added to glyphosate to facilitate effective penetration of water-soluble glyphosate across plant cuticles, which are waxy and hydrophobic, and POEA reduces the amount of glyphosate washed off target plants. Additives such as POEA are listed as inert ingredients when included by the manufacturer and considered adjuvants when mixed by the user. However, this labeling can be misleading since the surfactant is typically as much as 15 percent by weight of some glyphosate formulations and potentially very harmful to aquatic organisms (Giesy and others, 2000; Tush and Meyer, 2016). Although Monsanto Company and other glyphosate producers indicate that glyphosate herbicides typically include a surfactant blend, the exact formulations are generally considered proprietary (Tush and others, 2013; Tush and Meyer, 2016), which prevents most researchers from identifying specific surfactants in glyphosate formulations (Relyea, 2005; Bureau of Land Management, 2007; Durkin, 2011).

Properties, Mobility, and Fate of Glyphosate, Aminomethylphosphonic Acid, and Polyoxyethylene Tallow Amine

Glyphosate is extremely water soluble with a low vapor pressure and a low octanol-water partitioning coefficient (K_{ow}), which means the compound will preferentially be in the water phase rather than volatilizing (table 2). Likewise, biota exposed to glyphosate will preferentially metabolize or excrete the compound rather than bioaccumulate it in fatty tissues, although bioaccumulation has been documented in worms (Contardo-Jara and others, 2009). The reported half-life in water of glyphosate averages 20 days on the low end (minimum, 2 days) and 60 days on the high end (maximum, 180 days) (Goldsborough and Brown, 1993; U.S. Environmental Protection Agency, 1993; Schuette, 1998; Giesy and others, 2000; Coupe and others, 2012; Battaglin and others, 2014; Yadav and others, 2017; table 2). Several factors affect this half-life range; specifically, pH, specific

Table 2. Chemical, physical, and environmental fate behavior of glyphosate, aminomethylphosphonic acid, and polyoxyethylene tallow amine.

[C, carbon; H, hydrogen; N, nitrogen; O, oxygen; P, phosphorus; --, no data; <, less than; %, percent; Compiled from Battaglin and others, 2014; Coupe and others, 2012; Durkin, 2011; Giesy and others, 2000; Goldsborough and Brown, 1993; Grandcoin and others, 2017; Grunewald and others, 2001; Henderson and others, 2010; Schuette, 1998; Rodriguez-Gil, 2015; U.S. Environmental Protection Agency, 1993, 2008; Traas and Smit, 2003; Yadav, and others, 2017]

Description	Characteristic	Value	Comments
		Glyphosate	
Common name and forms	Glyphosate ($C_3H_8NO_5P$)	Chemical Abstracts Service Number 1071–83–6	--
	N-(Phosphonomethyl) glycine (acid)	--	--
	Glyphosate isopropyl amine salt (IPA salt)	Chemical Abstracts Service Number 38641–94–0	Other common salts include Monoammonium, Dimethyl amine, and Potassium.
Physical and chemical properties (acid unless specified otherwise)	Molecular weight (grams per mole)	169 (acid); 228 (IPA salt)	Physical state crystalline powder, white.
	Melting point (degrees Celsius)[a]	190–230	--
	Water solubility (milligrams per liter at 25 degrees Celsius)[b]	10,000–15,700 (acid); 900,000 (IPA salt)	--
	Vapor pressure (pascals at 25 degrees Celsius)[c]	$1.31–2.59 \times 10^{-5}$ (acid); 2.1×10^{-6} (IPA salt)	--
	Octanol/water partition coefficient (K_{ow} near neutral or pH 7)[d,e]	−4.85–−1.6	--
	Sorption partition coefficient (K_d in liters per kilogram)[f]	1, 3–1,188; 2, 18–1,000	1, range of agricultural and forest soils; 2, sand to silty clay loam.
	Sorption partition coefficient (K_{oc} in liters per kilogram)[g]	1, 9–60,000; 2, 3,100–58,000	1, range of agricultural and forest soils; 2, sand to silty clay loam.
	Henry's law constant (pascal-cubic meters per mol)[h]	1.41×10^{-5}–$<2.1 \times 10^{-7}$	--
Half-lives (acid unless specified)	Water	2–180 days (average low and high, 20–60 days)	--
	Sediment (aerobic)	14.1 days	Water-silty clay loam sediment.
	Sediment (anaerobic)	208 days	Silty clay loam sediment.
	Soil (not specific)	1–215 days (average low and high, 12–60 days)	--
	– aerobic	1.8–180 days	--
	– anaerobic	0.9–1,000 days	--
	Field dissipation half-life, terrestrial in Arizona	17 days	--

Table 2. Chemical, physical, and environmental fate behavior of glyphosate, aminomethylphosphonic acid, and polyoxyethylene tallow amine. —Continued

[C, carbon; H, hydrogen; N, nitrogen; O, oxygen; P, phosphorus; --, no data; <, less than; %, percent; Compiled from Battaglin and others, 2014; Coupe and others, 2012; Durkin, 2011; Giesy and others, 2000; Goldsborough and Brown, 1993; Grandcoin and others, 2017; Grunewald and others, 2001; Henderson and others, 2010; Schuette, 1998; Rodriguez-Gil, 2015; U.S. Environmental Protection Agency, 1993, 2008; Traas and Smit, 2003; Yadav, and others, 2017]

Description	Characteristic	Value	Comments
		Aminomethylphosphonic acid (AMPA)	
Common name and forms	Aminomethyl phosphonate	--	--
	AMPA (CH_6NO_3P)	Chemical Abstracts Service Number 1066–51–9	--
Physical and chemical properties	Molecular weight (grams per mole)	111.04	Physical state crystalline powder, white.
	Melting point (degrees Celsius)[a]	338−344	--
	Water solubility (milligrams per liter at 25 degrees Celsius)[b]	1,470–5,800	--
	Vapor pressure (pascals at 25 degrees Celsius)[c]	Similar to glyphosate	--
	Octanol/water partition coefficient (K_{ow} near neutral or pH 7)[d,e]	−2.36–−1.36	--
	Sorption partition coefficient (K_d in liters per kilogram)[f]	Similar to glyphosate	--
	Sorption partition coefficient (K_{oc} in liters per kilogram)[g]	Similar to glyphosate	--
	Henry's law constant (pascal-cubic meters per mol)[h]	Similar to glyphosate	--
Half-lives	Water	60–240 days	--
	Sediment (aerobic)	7 (19%)–30 (25%) days	Water- silty clay loam sediment system.
	Sediment (anaerobic)	15 (25%) days	Water- silty clay loam sediment system.
	Soil (not specific)	10–958 days (average low and high, 42–265 days)	--
	Field dissipation half-life, terrestrial in Arizona	142 days	--
		Polyoxyethylene tallow amine or polyethoxylated tallowamine	
Common name and forms	POEA, MON 0818, polyoxyethyleneamine (R-N(CH_2CH_2O)H_m(CH_2CH_2O)H_n	Chemical Abstracts Service Number 61791-26-2; *n*: Number of carbons in alkyl chain (hydrophobic contribution); *m*: number of ethylene oxide groups (hydrophilic contribution); N, signifies that the substituent is connected to the nitrogen; R, group is an abbreviation for any group in which a carbon or hydrogen atom is attached to the rest of the molecule.	MON 0818 is a code designation for the commercial blend of POEA surfactants used in Roundup® and other glyphosate-based herbicide formulations marketed by the Monsanto Company. The exact composition of MON 0818 is confidential information.
Physical and chemical properties	Molecular weight (grams per mole)	Varies based on polyethylene chain length	Physical state liquid, amber-yellow.
	Melting point (degrees Celsius)[a]	12	--
	Sorption partition coefficient (K_{oc} in liters per kilogram)[g]	2,500–9,600	Silt loam, silt clay loam, and sandy loam.

Table 2. Chemical, physical, and environmental fate behavior of glyphosate, aminomethylphosphonic acid, and polyoxyethylene tallow amine. —Continued

[C, carbon; H, hydrogen; N, nitrogen; O, oxygen; P, phosphorus; --, no data; <, less than; %, percent; Compiled from Battaglin and others, 2014; Coupe and others, 2012; Durkin, 2011; Giesy and others, 2000; Goldsborough and Brown, 1993; Grandcoin and others, 2017; Grunewald and others, 2001; Henderson and others, 2010; Schuette, 1998; Rodriguez-Gil, 2015; U.S. Environmental Protection Agency, 1993, 2008; Traas and Smit, 2003; Yadav, and others, 2017]

Description	Characteristic	Value	Comments
Polyoxyethylene tallow amine or polyethoxylated tallowamine—Continued			
Half-lives	Water	Estimated 5 hours–42 days; hours if total organic concentrations were high	--
	Sediment (aerobic)	1–9 days during first phase decay and second decay phase 21 days	--
	Soil	Estimated 7–14 days	--

[a]The temperature at which the given substance changes its physical state from solid to liquid (Agricultural Substances Databases Agriculture and Environment Research Unit, 2016).

[b]The mass of a given substance (the solute) that can dissolve in a given volume of water. Some chemicals solubility may be pH sensitive (Agricultural Substances Databases Agriculture and Environment Research Unit, 2016).

[c]The pressure at which a liquid is in equilibrium with its vapor at 25 degrees Celsius. It is a measure of the tendency of a material to vaporize (Agricultural Substances Databases Agriculture and Environment Research Unit, 2016).

[d]Very pH dependent.

[e]The logarithm (base-10) of the partition coefficient between n-octanol and water. It is used in environmental fate studies and large values (+4 or higher) are regarded as an indicator that a substance will bioaccumulate. For some substances K_{ow} will be very sensitive to pH (Agricultural Substances Databases Agriculture and Environment Research Unit, 2016).

[f]The adsorption-desorption distribution coefficient (K_d) is an important parameter for understanding the mobility of a compound in the environment (partitioning) and its distribution between water, sludge, soil and sediment phases (Agricultural Substances Databases Agriculture and Environment Research Unit, 2016).

[g]Sorption coefficient data are a measure of the tendency of a chemical to bind to soils, corrected for soil organic carbon content. Values can vary substantially, depending on soil type, soil pH, the acid-base properties of the pesticide and the type of organic matter in the soil (Agricultural Substances Databases Agriculture and Environment Research Unit, 2016).

[h]The amount of gas absorbed by a given volume of liquid at a given temperature is directly proportional to the partial pressure of that gas in equilibrium with that liquid. As such it provides an indication of the preference of a chemical for air relative to water that means, its volatility (Agricultural Substances Databases Agriculture and Environment Research Unit, 2016).

conductance, temperature, and sunlight have all been shown to change the half-life magnitude (Yadav and others, 2017). For example, increased pH and specific conductance (a more basic environment with more salts), lower temperatures, and less sunlight have been shown to increase the half-life to months rather than days (U.S. Environmental Protection Agency, 1993; Yadav and others, 2017). Increased dissolved organic compounds also likely play an important role in reducing the half-life as well (Rodriguez-Gil, 2015). Studies have demonstrated that dissipation kinetics follow a first order decay model (Giesy and others, 2000; Yadav and others, 2017; Carles, and others, 2019).

There is general agreement that the variability of remnant glyphosate and metabolites is linked to microbial characteristics, temperature, physicochemical chemistry parameters, and soil moisture (Bento and others, 2016). Microbial activity—primarily *Pseudomonas* species—which is closely tied to the factors listed previously, is the primary determinant in degradation or dissipation rates. Glyphosate degradation by bacteria occurs primarily by two enzymatic digestion pathways. The first and more common pathway is cleavage of the carbon-nitrogen bond (enzyme glyphosate oxidoreductase) where the decarboxylation results in intermediate metabolites AMPA and glyoxylate, and is ultimately metabolized as phosphate, carbon dioxide, and microbial biomass (Franz and others, 1997; Giesy and others, 2000; Székács and Darvas, 2012; Sviridov and others, 2015). Similar to glyphosate, AMPA is also very water soluble with a low K_{ow} and vapor pressure (table 2), but the half-life of AMPA in aquatic environments can be much more persistent than glyphosate, months to a year, depending on the environmental conditions (Giesy and others, 2000; Meyer and others, 2009; Coupe and others, 2012; Grandcoin and others, 2017; table 2). The second degradation pathway, dephosphorylation, involves the cleavage of the carbon-phosphorous bond, resulting in inorganic phosphate and sarcosine, which is transformed to glycine. This pathway has been observed with isolated soil bacteria and strongly depends on the concentrations of environmental phosphate and therefore would most likely occur in conditions of a phosphorus deficiency (Sviridov and others, 2015). Chemical processes, such as photolysis

and hydrolysis of degradation are less effective because of the presence of a highly stable carbon-phosphorus bond in the compound (Gimsing and others, 2004b).

Glyphosate and AMPA are mostly immobile in soil environments because of their strong adsorption to soil particles by interacting with clay minerals and forming tight complexes with cations in solution followed by adsorption on soil particles (Carlisle and Trevors, 1988). It is mainly the phosphonic acid moiety that participates in the cation complexation process, and therefore it may compete for surface sites on these minerals. For example, the main glyphosate soil sorption sites are on the surfaces of aluminum oxide, iron oxide, and aluminum silicates allophane and imogolite, and on the edges of layer silicates (Gimsing and Borggaard, 2001; Gimsing and Borggaard, 2002; Sheals and others, 2002; Dideriksen and Stipp, 2003; Barja and dos Santos Afonso, 2005; Gimsing and Borggaard, 2007). Soils enriched with these minerals have been determined to be effective glyphosate sorbents; however, soils rich in illite, smectite, and vermiculite are less effective sorbents (De Jonge and others, 2001; Gimsing and others, 2004a, c; Vereecken, 2005; Gimsing and others, 2007). Shallow leaching has been reported between 2 to 100 centimeters, but the prevailing consensus indicates that risk of groundwater pollution at depth is low (Laitinen and others, 2006; Borggaard and Gimsing, 2008; Napoli and others, 2015; Yang and others, 2015). The strong adsorption on clay particles and organic matter contributes to the varying lengths of time and persistence of glyphosate after application (Peñaloza-Vazquez and others, 1995).

Excess phosphorus can also play an important role in the degradation of glyphosate, and the excess availability of phosphorus will reduce the microbial degradation efficacy and induce an accumulation of AMPA (Carles and others, 2019). Phosphate-rich soils may reduce glyphosate sorption and potentially increase mobility as a result (Borggaard and Gimsing, 2008). Studies have shown that glyphosate persists much longer in soil with drier conditions and lower temperatures (Strange-Hansen and others, 2004; Stenrød and others, 2005; Vereecken, 2005; Borggaard and Gimsing, 2008; Napoli and others, 2015; Bento and others, 2016). In addition, the dissipation rates will increase with increased soil moisture, which also promotes the microbial activity that is metabolizing the glyphosate.

The reported half-life of glyphosate in soil averages 12 days on the low end (minimum, 1 day) and 60 days on the high end (maximum, 215 days) (Goldsborough and Brown, 1993; U.S. Environmental Protection Agency, 1993; Schuette, 1998; Giesy and others, 2000; Coupe and others, 2012; Battaglin and others, 2014; Yadav and others, 2017). Studies have determined detectable amounts in soil 8 months to multiple years beyond the initial application (Borggaard and Gimsing, 2008; Laitinen and others, 2009). Aminomethylphosphonic acid (AMPA) does have on average a longer half-life in soil than glyphosate. Many studies have documented the occurrence of AMPA in environmental soils and aquatic sediments with average half-lives around 42 days on the low end (minimum, 10 days) and 265 days on the high end (maximum, 958 days) (Goldsborough and Brown, 1993; U.S. Environmental Protection Agency, 1993; Schuette, 1998; Giesy and others, 2000; Grunewald and others, 2001; Bergström and others, 2011; Coupe and others, 2012; Battaglin and others, 2014; Bento and others, 2016; Yadav and others, 2017). The microbial degradation of AMPA in soil is primarily affected by temperature and soil moisture and eventually metabolizes to carbon dioxide and inorganic phosphate as well as ammonium (Battaglin and others, 2014; Wang and others, 2016). Aminomethylphosphonic acid (AMPA) is more persistent than glyphosate, and the degradation of both compounds is slower in colder and drier conditions (Bento and others, 2016). The slower degradation rates may be related to stronger adsorption onto soil particles than glyphosate, possibly affecting bioavailability to microorganisms (Araújo and others, 2003).

The proprietary nature of glyphosate formulations has resulted in a lack of published information about the surfactants and possible analytical methods used to identify different surfactants in environmental samples. This lack of information in turn limits studies about the environmental fate and transport of POEA. In addition, the analytical procedures for chemical constituent identification and quantification can be quite complex (Tush and others, 2013). The environmental fate of POEA has not been adequately studied or modeled in freshwater systems, but POEA is thought to act like other non-ionic-cationic surfactants in environmental samples, transporting via runoff from erosional processes of treated soil and potentially redistributing in bottom sediments of surface waters (Giesy and others, 2000; Wang and others, 2005; Rankine, 2015; Tush and Meyer, 2016). The strong adsorption properties indicate that POEA does not leach from soils and it would not be readily transported through the unsaturated zone.

It is possible that POEA may accumulate with certain soil sorption characteristics. Rankine (2015) determined that POEA rapidly dissipated from water but persisted in sediment, and Rodriguez-Gil and others (2016) likewise determined rapid dissipation of POEA (within hours) from the water column, whereas sediment acted as a significant POEA sink. In general, however, there is limited research about the fate and transport of POEA in the environment (Tush and others, 2013). Tush and others (2013) is considered one of the first to begin to investigate the environmental fate of POEA when packaged with herbicides, but in an agricultural setting.

In natural waters containing suspended sediment, such as lakes, ponds, and rivers, POEA is degraded through microbial processes (Giesy and others, 2000). The half-life of POEA is estimated to be as many as 4 weeks and as short as a week. In one study, the mineralization of 40 to 50 percent of the applied POEA was demonstrated to disappear in 14 weeks (Giesy and others, 2000; table 2). The aquatic half-life range for POEA is estimated to be 21 to 42 days, but can be on the order of hours with high dissolved organic concentrations.

Glyphosate-Based Herbicide Application Methods in Saguaro National Park

In 2010, the NPS, in cooperation with other State and Federal agencies, used an aerial demonstration project to understand the best methods for aerially spraying an herbicide, to evaluate the aircraft efficiency, and to evaluate spray techniques to minimize drift and non-target impacts (White and Baldwin, 2010; National Park Service, 2012; U.S. Department of Agriculture, 2012; Thistle and others, 2014). In 2013, the NPS received a 3-year grant for aerial herbicide application in the Rincon Mountain District and initiated the project in 2014. A helicopter with a 40-ft boom sprayer, coarse sprayer nozzles with 500–1,000-micrometer volume median diameter (the average droplet size by volume of spray cloud), and a programmable differential correction global position system navigation guidance system was used to spray a GBH on plots in the Loma Verde canyon watershed as well as the Box Canyon watershed in the Rincon Mountain District (fig. 4*A*). The Madrona Canyon watershed was sprayed later as part of this study. This aircraft and setup were chosen to provide greater flexibility for applications over relatively small areas and to target invasive species while minimizing damage to non-target species. Spray timing is based on buffelgrass greenness and generally applied mid- to late August. Herbicide mixtures have varied year to year but all were glyphosate based in the form

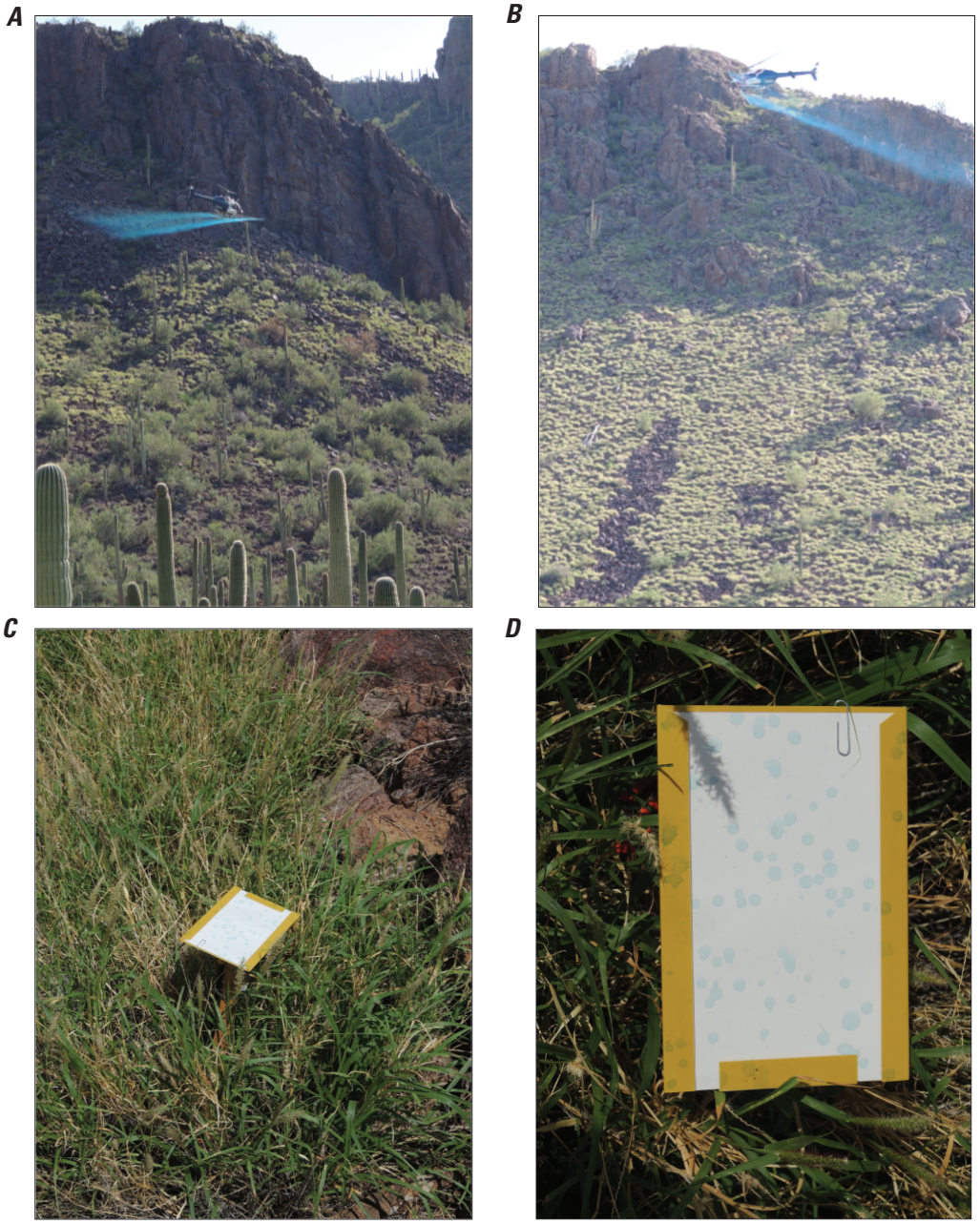

Figure 4. Glyphosate-based herbicide treatment of buffelgrass patches in Tucson Mountains, Arizona. *A,* Helicopter with a boom sprayer treating a small patch along the mountain slope. *B,* Helicopter treating a large patch along the mountain slope. *C,* Example of spray distribution as quantified by a drift card in a new growth buffelgrass patch in Saguaro National Park. *D,* A zoomed in view of the glyphosate-based herbicide spray and dye on the drift card.

of isopropylamine salt with 41 percent active ingredient and 59 percent other ingredients, including the surfactant. Prior to the USGS study (2014), Roundup Pro and KleenUp Pro were applied. In 2015 to 2017, there was a more consistent use of Ranger Pro and KleenUp Pro (table 3). Glyphosate works optimally at a pH of 5 to 6. Native water is basic (pH greater than 7) with an average hardness of 50–200 milligrams per liter (mg/L), and therefore an adjuvant, ammonium sulfate water conditioner was used to reduce the pH of the native water. In 2014 and 2015, Choice Weather Master was added to the mixture, followed by AMS-Supreme in 2016 and 2017. A blue indicator dye (Hi-Light) was added to the solution to mark where the herbicide solution was applied and to allow colorimetric analysis to obtain a detailed understanding of mass of active ingredient per area (fig. 4*B*). The glyphosate base products include a surfactant that is proprietary, but it is likely a nonionic ethoxylated tallow amine surfactant that is or is like POEA. In 2014 and 2015, an additional nonionic lecithin-based alcohol ethoxylate surfactant, LI-700, and Liberate were added to the spray mixture to reduce drift. These products have all been registered with the U.S. Environmental Protection Agency and the labels of these products and all other registered chemicals were strictly followed by the park personnel.

Glyphosate is a weak acid but normally is sold as a salt and the formulations differ owing to the chemistry of the salt and different adjuvants used by the various manufacturers. The glyphosate in the weak acid form is not as effective as the salt, which is better able to penetrate the plant tissues than the acid form. The various salt forms will have different molecular weights and the amount of glyphosate salt in the formulation will be listed as the active ingredient (a.i.) in pounds of a.i. per gallon. However, units of the glyphosate salt make it hard to compare different formulations and is somewhat less intuitive because the user is interested in the amount of glyphosate acid or constituent that is actually affecting the plants (not glyphosate salt). A more appropriate way to compare and analyze information is through an acid equivalent (a.e.), which is defined as the portion of a formulation that theoretically could be converted back to the corresponding or parent acid (Hanson and others, 2013). The Rincon Mountain District purchased three parent glyphosate products from the manufacturers all indicated 3 a.e. pounds per gallon on the label. These products were mixed in different concentrations during the study.

During the aerial demonstration, the NPS tested two treatment concentrations and two carrier rates, and adjustments were continually made to improve the spray efficiency. Starting in 2014, only Box Canyon and Loma Verde canyon were sprayed. The concentration changed slightly during the USGS study—from around 2.48 pounds a.e. per acre in 2014 and 2015 to around 3.75 pounds a.e. per acre in 2016 and 2017. The carrier rate, which includes the formulation, adjuvants, and water, was 10 gallons per acre. A helicopter load generally carried 50 gallons per flight, which covered around 5 acres per flight. The total acres treated in Loma Verde canyon were approximately 63, 59, and 38 in 2014, 2015, and 2017, respectively. Box Canyon was approximately 95, 244, 68, and 289 acres in 2014, 2015, 2016, and 2017, respectively; and Madrona Canyon was approximately 13 and 9 acres in 2016 and 2017, respectively.

Methods

Sampling and analytical methods include the collection and analysis of water, aquatic fine sediment, and terrestrial soil. Water samples were analyzed for glyphosate, AMPA, glufosinate, tritium isotopes, deuterium isotopes (δ^2H), oxygen-18 isotopes ($\delta^{18}O$), and general water chemistry parameters (temperature, dissolved oxygen, pH, and specific conductance). Analysis was sample dependent, and samples were analyzed for fewer constituents depending on season and collection method.

Procedures and methods are described in published USGS techniques and methods (U.S. Geological Survey, 2006; Wilde, 2008; Sandstrom and Wilde, 2014; Révész and Coplen, 2008a, b; Meyer and others, 2009). Field quality-control and laboratory quality assurance measures were also implemented following the same published USGS techniques and methods (Mueller and others, 2015).

Sample Design, Site Description, and Approach

At the initiation of the current USGS study, the GBH treatment of watersheds was ongoing. The Loma Verde canyon, Box Canyon, and Madrona Canyon watersheds were at different stages of treatment regimens. The USGS study sampling focused on the most heavily treated watershed, Box Canyon (fig. 5*A*), and the Madrona Canyon watershed, which had not yet been treated prior to the 2014 start of the study. The Box Canyon watershed was used to monitor the occurrence and extent of glyphosate and AMPA of residual GBHs from previous treatments as well as newer 2015 to 2018 treatments (13 locations; table 4). The Madrona Canyon watershed was used as a controlled setting where samples were collected before and after the very first treatment (fig. 5*B*). Samples were also collected during rainfall runoff events to monitor the transport of glyphosate and AMPA from treated areas (five GBH collection locations; table 4). The Loma Verde Canyon watershed had no aerial treatment after September 2015 (figs. 5*C*, 6). This watershed was only sampled once in April 2017, and was used to evaluate the legacy effects of treatment (4 locations; table 4). The primary interest was to know if glyphosate and AMPA could still be detected more than a year after treatment. Primary flow paths or larger tributary catchments (greater than 0.05 square mile) were identified as areas of increased transport from spray area to downstream pools (fig. 5*A–C*). The larger watershed boundaries are identified in figure 5 to show flow direction and potential transport pathways from spray area to downstream areas. Pools were frequently sampled below these areas susceptible of increased GBH transport.

Table 3. Glyphosate-based herbicide treatment description for Saguaro National Park, 2014–17.

[NA, not applicable]

Drainage	Date range	Application	Herbicide[a]	Gallons	Adjuvants[a]	Gallons	Total amount of chemical applied (includes herbicide, adjuvant, and water), in gallons	Acres treated per year	Percentage of watershed sprayed per year
Loma Verde Canyon	8/22/2017	Aerial	Kleenup Pro	48	AMS Premium or AMS Supreme	1.92	384	38.4	4.41
Loma Verde Canyon	8/27–8/28/2015	Aerial	Round Up Pro Concentrate	48.5	Choice Weather Master and Liberate (2:1 ratio)	4.41	588	58.8	6.76
Loma Verde Canyon	8/21/2014	Aerial	Kleenup Pro	52.3	Choice Weather Master and LI-700 (2:1 ratio)	4.76	634	63.4	7.28
Madrona Canyon	8/22/2017	Aerial	Kleenup Pro	11.6	AMS Premium or AMS Supreme	0.464	92.8	9.28	0.254
Madrona Canyon	8/19/2016	Aerial	Ranger Pro	16.1	AMS Premium or AMS Supreme	0.645	129	12.9	0.354
Box Canyon	8/18–8/22/2017	Aerial	Ranger Pro and Kleenup Pro (2:1 ratio)	510	AMS Premium or AMS Supreme	14.5	2,890	289	6.92
Box Canyon	8/19–8/22/2016	Aerial	Ranger Pro	85.1	AMS Premium or AMS Supreme	3.4	681	68.1	1.63
Box Canyon	8/24–8/28/2015	Aerial	Round Up Pro Concentrate and Ranger Pro (4.4:1 ratio)	415	Choice Weather Master and Liberate (2:1 ratio)	18.3	2,440	244	5.83
Box Canyon	8/22–8/23/2014	Aerial	Kleenup Pro	119	Choice Weather Master and LI-700 (2:1 ratio)	10.5	953	95.3	2.28
Total cumulative per watershed for 2014–17									
Loma Verde Canyon	NA	NA	NA	149	NA	11.1	1,610	161	18.5
Madrona Canyon	NA	NA	NA	27.7	NA	1.11	222	22.2	0.61
Box Canyon	NA	NA	NA	1,130	NA	46.7	6,960	696	16.7

[a]Proprietary trademark name or copyright.

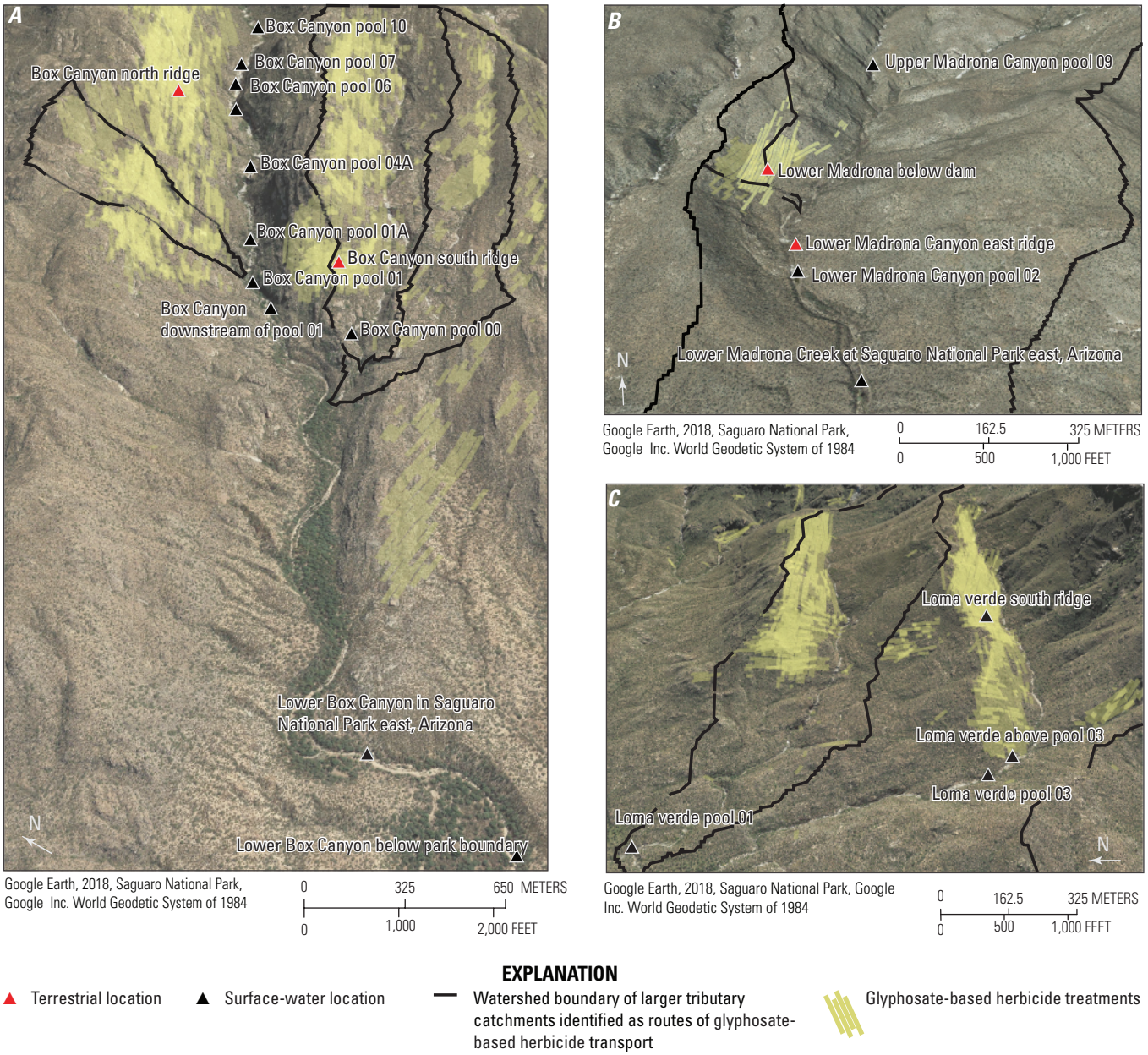

Figure 5. Sample locations in the three watersheds in the Rincon Mountain District of Saguaro National Park. *A*, Box Canyon watershed pool and terrestrial sampling locations and location of automatic sampler installations. *B*, Madrona Canyon watershed pool and terrestrial sampling locations and location of automatic sampler installation. *C*, Loma Verde canyon watershed pool and terrestrial sampling locations.

Water, aquatic sediment, and terrestrial sediment were collected seasonally during the study period (fig. 6) and the sampling was determined by timing of GBH treatments, seasonal climatic conditions, and flow events. The station naming convention was established by the Rincon Mountain District during pool and tinaja inventories. A number was assigned to the primary pool or tinaja and the next distinct pool increased sequentially with distance up the watershed. Some pools are closely connected with flow in a series of pools and water parameters (specific conductance, dissolved oxygen, and pH) were indistinguishable. In these instances, the primary pool number was changed to an alphanumeric name. For example, the primary pool is "Pool 01" and the related downstream Pool is named "Pool 1A." During this study, low-flow conditions sometimes caused a shift in the previously known location of the primary pool and that resulted in a new station that included a down or upstream reference to the primary pool in the name. For example, the new pool would be named "downstream of Pool 01." Water and aquatic sediment were mostly collected from pools during times of base flow, which could vary greatly depending on seasonal conditions. During the winter and spring, rainfall and snowmelt created base-flow

Table 4. Station/sample location descriptions for Saguaro National Park-Rincon Mountain District, Arizona.

[Data collected for this study by the U.S. Geological Survey are available from https://doi.org/10.5066/F7P55KJN (U.S. Geological Survey, 2020) by using the 15-digit station numbers. NAD 83, North American Datum of 1983; WS, surface water; SB, aquatic sediments; SO, soil; --, not available]

Station number	Station name	Sample type and number of samples	Latitude, in decimal degrees (NAD 83)	Longitude, in decimal degrees (NAD 83)
	Loma Verde canyon			
321145110421601	Loma Verde Canyon pool 01	WS, 1	32.19594	−110.70447
321116110421001	Loma Verde Canyon pool 03	WS, 1	32.18789	−110.70278
321114110420801	Loma Verde Canyon above pool 03	WS, 1; SB, 1	32.18722	−110.70219
321114110414801	Loma Verde Canyon south ridge	SO, 1	32.18717	−110.69658
	Box Canyon			
320839110435301	Jeremy wash near Old Spanish Trail	WS, 1	32.14413	−110.73136
320847110431201	Lower Box Canyon below Saguaro National Park boundary	WS, 2	32.14633	−110.71989
320856110431001	Lower Box Canyon in Saguaro National Park	WS, 3; SB, 3	32.14889	−110.71942
320915110423101	Box Canyon pool 00	WS, 5; SB, 6	32.15425	−110.70867
320920110422401	Box Canyon south ridge	SO, 7	32.15553	−110.70681
320923110423201	Box Canyon downstream of pool 01	WS, 2; SB, 2	32.15643	−110.70879
320926110422901	Box Canyon pool 01	WS, 2; SB, 2	32.15728	−110.70806
320929110422401	Box Canyon pool 1A	WS, 3; SB, 3	32.15817	−110.70658
320935110421301	Box Canyon pool 4A	WS, 2; SB, 2	32.15981	−110.70353
320945110421001	Box Canyon north ridge	SO, 6	32.1625	−110.70286
320945110415901	Box Canyon pool 06	WS, 1; SB, 1	32.1625	−110.69967
320946110415501	Box Canyon pool 07	WS, 1; SB, 1	32.16283	−110.69867
320949110414601	Box Canyon pool 10	WS, 1	32.16367	−110.69603
	Madrona Canyon			
320855110360300	Lower Madrona Creek at Saguaro National Park	WS, 20; SB, 1	32.14861	−110.60081
320907110360801	Lower Madrona Canyon pool 02	WS, 5; SB, 5	32.15183	−110.60233
320910110360901	Lower Madrona below dam	WS, 2	32.15281	−110.60247
320922110361301	Lower Madrona Canyon east ridge	SO, 6	32.15625	−110.60356
320950110355701	Upper Madrona Canyon pool 09	WS, 2; SB, 2	32.16375	−110.59919
[a]KAZWSB-2	Madrona weather station	--	32.1524	−110.6081
	Near Loma Verde canyon			
--	Desert Research Learning Center	--	32.222	−110.72333

[a]National Park Service station; data accessible at http://www.climateanalyzer.us/raws/KA7WSB-2.

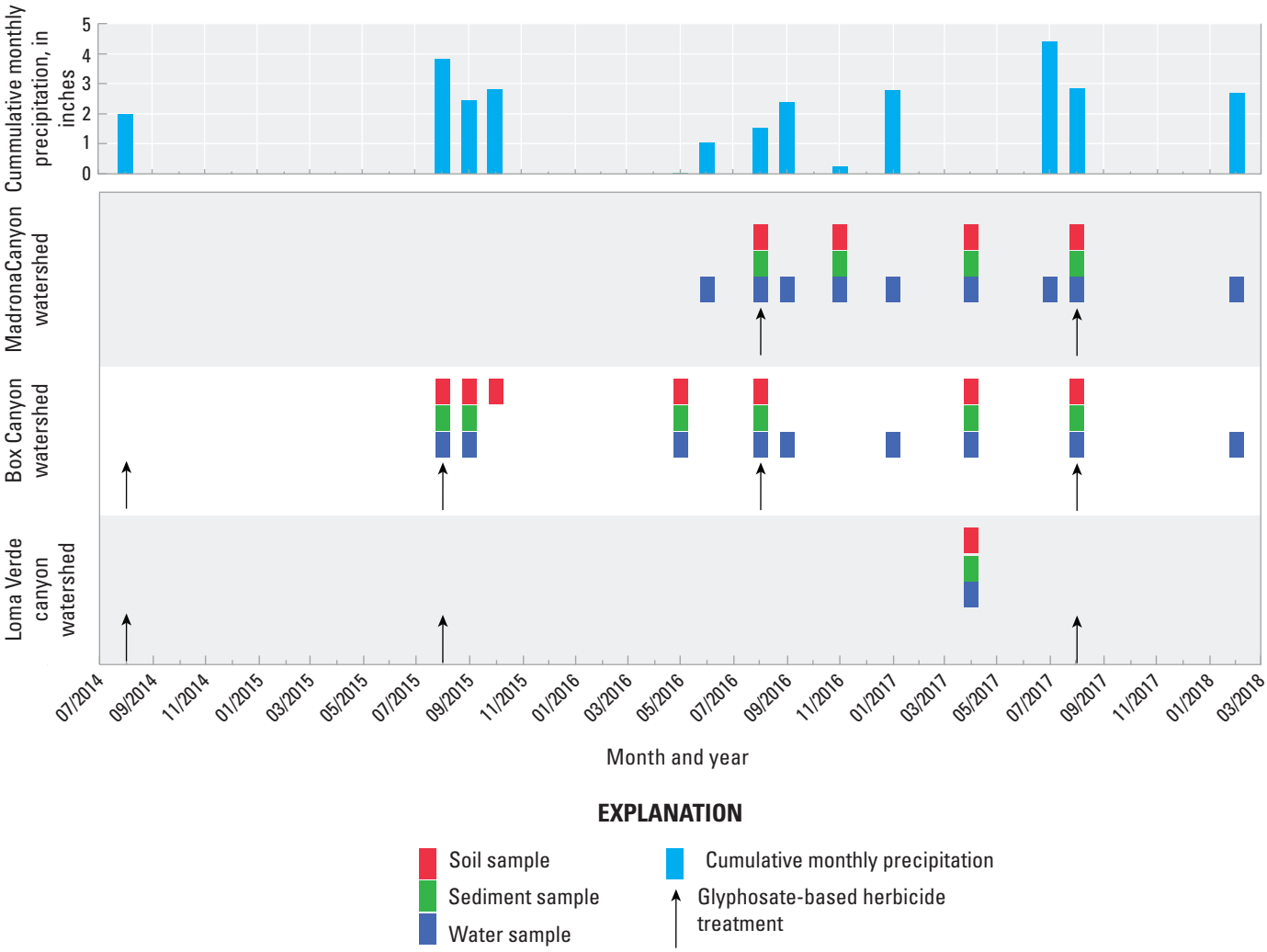

Figure 6. Sample collection types and dates for the Box Canyon, Madrona Canyon and Loma Verde canyon watersheds in relation to the timing of the cumulative monthly precipitation.

conditions that would lead to continuous flow between the pools and cause homogenous water chemistry throughout the main stream channel. During dry periods of the study, very few pools were full or flowing and conditions could be different depending on recent deposition of debris and sediment, which could prevent repeat sampling at some locations.

In the Box Canyon watershed, Box Canyon pool 10 (USGS station 320949110414601; hereafter referred to as "Pool 10") was sampled once (for isotopes only); Pools 06 and 07 (USGS stations 320945110415901 and 320946110415501, respectively; hereafter referred to as "Pool 06" and "Pool 07") were sampled once for water and aquatic sediment; and Pools 4A, 1A, 01, and downstream of pool 01 (USGS stations 320935110421301, 320929110422401, 320926110422901, and 320923110423201, respectively; hereafter referred to the pool common names) were sampled multiple times for water and aquatic sediment (fig. 7*A*–*G*). Pool 00 (USGS station 320915110423101; hereafter referred to as "Pool 00") was sampled frequently for water and aquatic sediment owing to the consistent presence of standing water in a small tributary to the main Box Canyon stream channel (fig. 7*H*). The Madrona Canyon watershed had two of the larger perennial

Figure 7 (page 21). Box Canyon sampling locations starting with the most upper portion of the watershed sampled. *A*, Pool 10 looking northeast (site number 320949110414601), April 13, 2017; *B*, Pool 07 looking northeast (site number 320946110415501), April 13, 2017; *C*, Pool 06 looking northeast (site number 320945110415901), August 19, 2015; *D*, Pool 4A looking southwest (site number 320935110421301), August 19, 2015; *E*, Pool 1A looking northeast (site number 320929110422401), April 13, 2017; *F*, Pool 01 looking east and (site number 32092611042290), September 24, 2015; *G*, downstream from Pool 01 looking north (site number 320923110423201), August 31, 2017; *H*, Pool 00, looking northeast (site number 320915110423101), August 19, 2015.


A
B
C
D
E
F
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H

tinajas of this study. Upper Madrona Canyon pool 09 (USGS station 320950110355701; hereafter referred to as "Pool 09") was far from any GBH treatment and used as a reference sample, whereas Lower Madrona Canyon pool 02 (USGS station 320907110360801; hereafter referred to as "Pool 02") was below the treatment area (fig. 8*A–B*). An old shallow concrete impoundment filled with sediment between Pools 02 and 09 created a downstream discharge point that was sampled on two visits and named Lower Madrona below dam (USGS station 320910110360901) (fig. 8*C*). Runoff was collected from different areas in the lower Box Canyon watershed and rainfall runoff flood-water samples were collected using automatic samplers in Box and Madrona Canyons (fig. 9*A–D*). In the Loma Verde canyon watershed, water and aquatic sediment were collected upstream from Pool 03 or Loma Verde above pool 03 (321114110420801; hereafter referred to as "above pool 03"), whereas isotope samples were collected in Loma Verde pool 03 and Loma Verde pool 01 (USGS stations 321116110421001 and 32114511042160107, respectively; hereafter referred to as "Pool 03 and Pool 01" (fig. 10*A–C*).

Terrestrial soil samples were collected from one location in each of the Loma Verde and Madrona Canyon watersheds and from two locations in the Box Canyon watershed (fig. 11*A–C*; table 4). The sampling was timed to measure conditions prior to herbicide treatment and after treatment, which provided information about the rate of dissipation on the treated soils. The timing of water and aquatic sampling relative to treatment was evaluated in conjunction with rainfall events to quantify glyphosate and AMPA that may runoff with treated sediments.

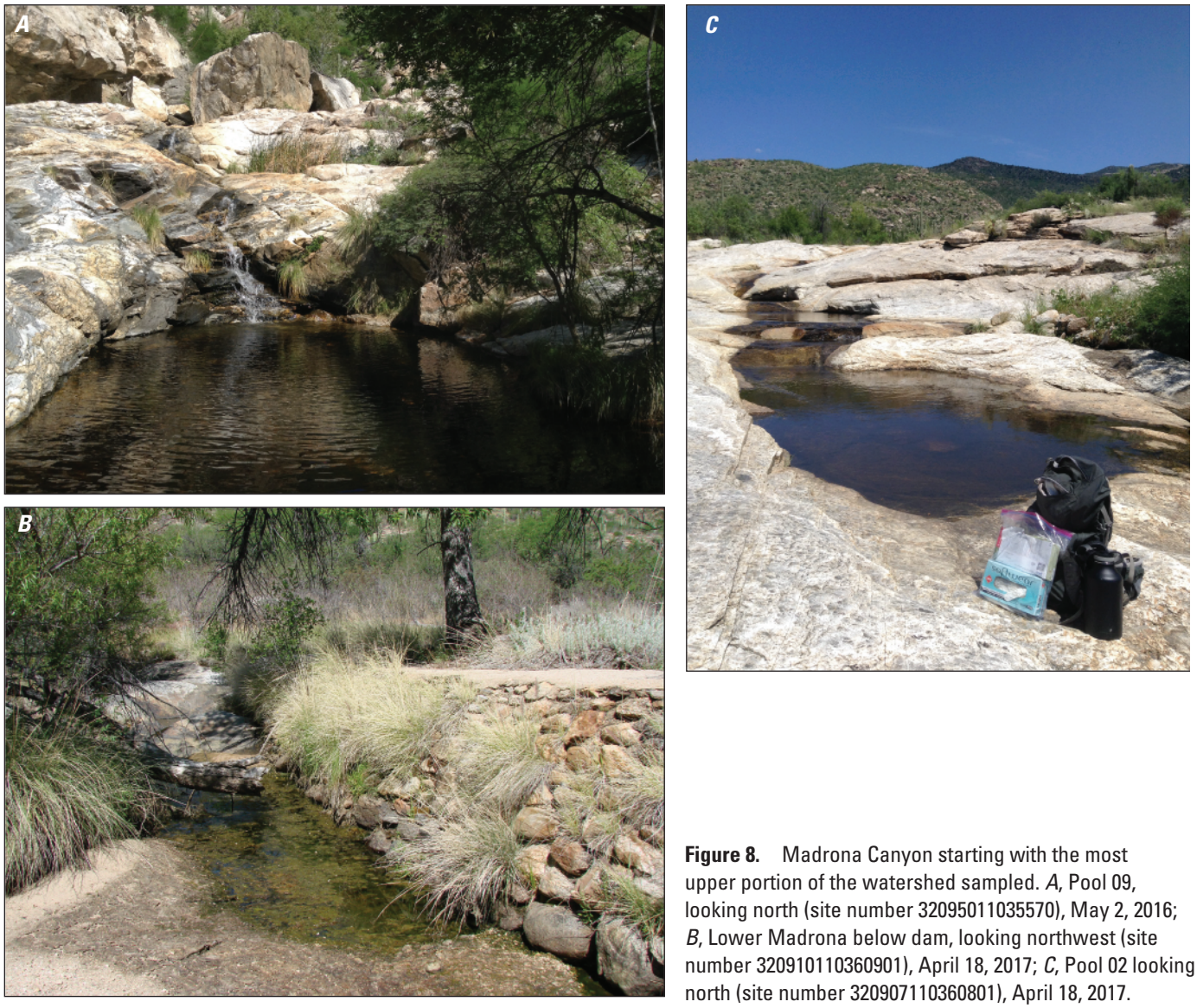

Figure 8. Madrona Canyon starting with the most upper portion of the watershed sampled. *A*, Pool 09, looking north (site number 32095011035570), May 2, 2016; *B*, Lower Madrona below dam, looking northwest (site number 320910110360901), April 18, 2017; *C*, Pool 02 looking north (site number 320907110360801), April 18, 2017.

Figure 9. Examples of automatic sampler installations in Box Canyon and Madrona Canyon watersheds. *A,* Lower Box Canyon in Saguaro National Park automatic sampler installation in dry conditions with no flow (site number 320856110431001), August 31, 2017; *B*, Lower Box Canyon below Saguaro National Park boundary temporary automatic sampler installation during high flow conditions (site number 320847110431201), September 8, 2016; *C,* Lower Madrona Creek at Saguaro National Park automatic sampler installation in dry conditions with no flow (site number 320855110360300), July 12, 2016; *D*, Lower Madrona Creek at Saguaro National Park automatic sampler installation during high flow conditions, January 22, 2017.

Figure 10. Loma Verde canyon watershed sampling locations starting with the most upper portion of the watershed sampled, April 11, 2017. *A*, Upstream from Pool 03, looking southeast (site number 321114110420801); *B*, Pool 03 looking southeast (site number 321116110421001); *C*, Pool 01, looking southeast and USGS scientist collecting water quality parameters (site number 321145110421601).

Sample and Data Collection

Data collection methods, cleaning procedures, and quality assurance followed protocols described in the USGS "National Field Manual Collection of Water-Quality Data" (U.S. Geological Survey, 2006), Wilde (2008), and Shelton and Capel (1994). Water-quality parameters, including temperature, pH, specific conductance, and dissolved oxygen, were measured as conditions permitted for each water-sampling site using an In Situ Inc. smarTROLL multiparameter meter. The multiparameter meter was calibrated daily before field measurements were collected using standards supplied by the USGS National Water Quality Laboratory (U.S. Geological Survey, 2006). Field parameters were only measured during base-flow collections.

Flood surface-water sample collection utilized Teledyne ISCO Avalanche portable refrigerated automatic samplers and a Teledyne ISCO 6700. A refrigerated automatic sampler was operated as a permanent deployment in the Madrona Canyon watershed and temporary deployments (refrigerated or iced) were made in the Box Canyon watershed. The automatic sampler in the Madrona Canyon watershed was configured with a carousel holding twelve 1-liter polyethylene bottles and Box Canyon had a single 2.5-gallon glass container used for a composite sample. The automatic sampler intake consisted of 3/8-inch inner diameter vinyl tubing inside conduit and affixed to a T-post. The height of the intake tubing for the permanent deployments was adjusted to 6 to 10 inches above the dry channel to minimize the pumping of bed material and to sample a representative well-mixed water column during flooding

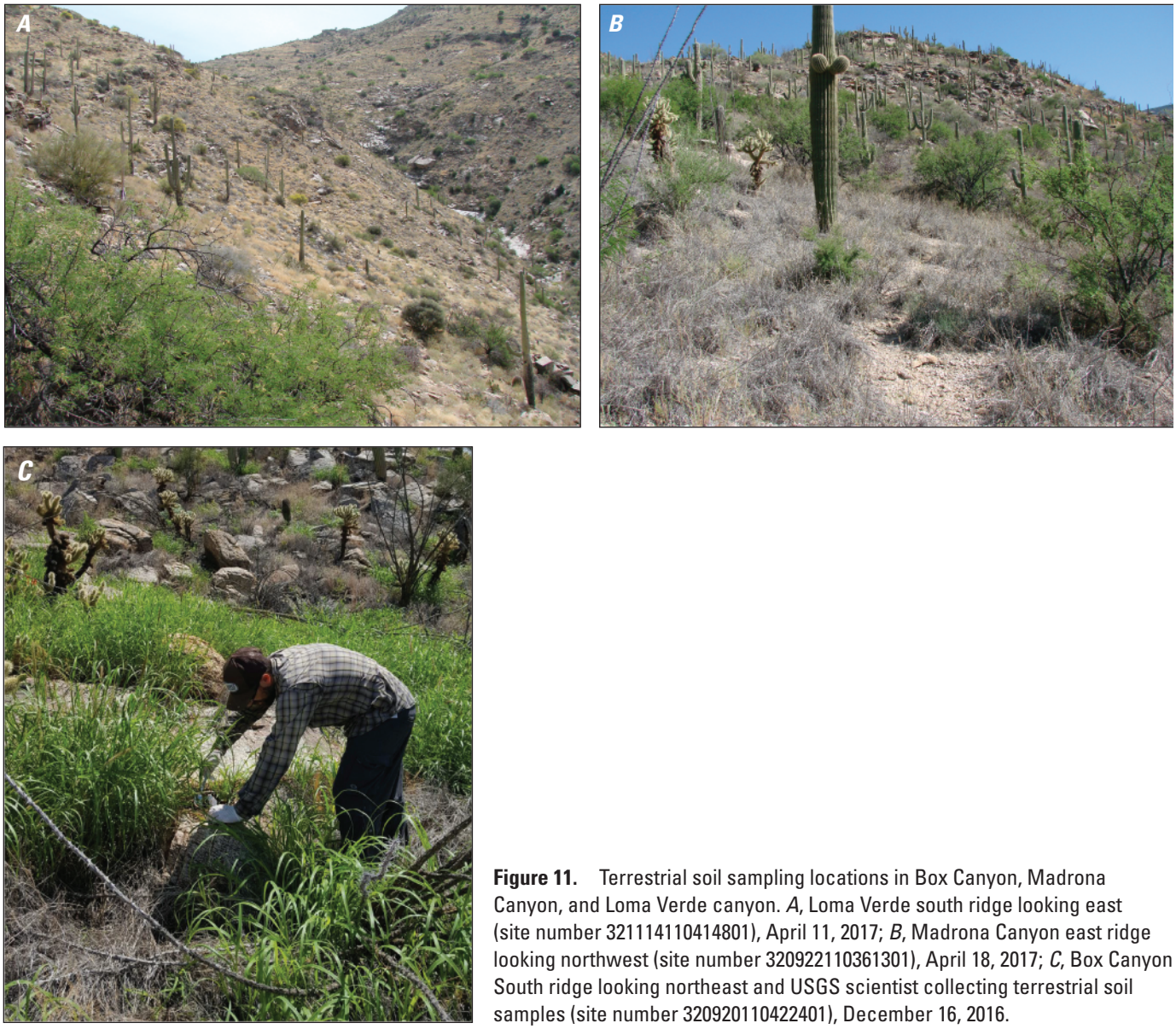

Figure 11. Terrestrial soil sampling locations in Box Canyon, Madrona Canyon, and Loma Verde canyon. *A*, Loma Verde south ridge looking east (site number 321114110414801), April 11, 2017; *B*, Madrona Canyon east ridge looking northwest (site number 320922110361301), April 18, 2017; *C*, Box Canyon South ridge looking northeast and USGS scientist collecting terrestrial soil samples (site number 320920110422401), December 16, 2016.

events. Samplers were initiated using a pressure transducer or liquid-level actuator. After samples were collected, the refrigerated automatic sampler kept samples chilled at 2 to 4 degrees Celsius (°C) and upon retrieval the samples were kept at this temperature until shipped and analyzed. Generally, sample bottles and tubing used for glyphosate collection would be made of polytetrafluoroethylene or glass, but this was not feasible with the automatic sample configuration. To ensure quality control, blank samples were collected with the automatic sampler to test for possible contamination. Flood samples were visibly void of fine sediments, so no suspended sediment samples were collected from surface-water sites.

Water stage height was recorded using an In Situ vented Level TROLL 700 pressure transducer or a non-vented Solinst 3001 Levelogger pressure transducer. The data were logged continuously at 15-minute intervals and transmitted to the USGS National Water Information System (U.S. Geological Survey, 2020) or downloaded manually. The data collected via Levelogger were corrected for atmospheric pressure using a Solinst Barologger.

Discrete water and fine sediment samples were collected in pools for analysis of glyphosate and AMPA. Terrestrial soil samples were collected along canyon ridges where herbicides were directly applied. Water samples collected for glyphosate and AMPA analysis were collected using a 20-milliliter (mL) high density polypropylene syringe. The syringe was rinsed with native water and then a Whatman 25-mm, 0.7-µm pore-size baked glass-fiber Luer-Lock filter was attached to the syringe and the plunger was slowly depressed to force several milliliters of sample water out of the syringe to rinse the filter. Once rinsed, approximately 5 mL of sample was filtered into a 20-mL baked amber glass vial. Aquatic fine-grained

substrates—stream substrates (<2 mm)—consisting primarily of a mixture of clay, muck, and organics, were often difficult to gather owing to their limited presence. When collected, they consisted of 4 to 5 subsamples of fine-grained substrates collected from bottom deposits or along the margins of pools and composited. Sands and fine gravels were avoided. Fine sediments were scooped from upper depositional surfaces with a clean stainless-steel spoon and composited in a baked 125- or 250-mL amber glass jar. Terrestrial soils were scraped from the upper 2 inches of the land surface at 4 to 5 locations and composited in a 125- or 250-mL wide-mouth amber glass baked jar. All samples were shipped to the Kansas Water Science Center's Organic Geochemistry Laboratory and analyzed for glyphosate, AMPA, and glufosinate. Glufosinate is a broad-spectrum herbicide that is used to control certain weeds in agricultural settings. Because the Rincon Mountain District does not use this compound in their mixture, no detections were observed during the study, but laboratory quality control data are presented as a negative control. Discrete isotope samples were collected from pools using a 1-liter polyethylene bottle for tritium and a 60-mL glass bottle for stable isotopes of hydrogen and oxygen (δ^2H and $\delta^{18}O$) and shipped to the University of Miami and the USGS Reston Stable Isotope Laboratory, respectively.

Quality control samples consisted of three water blanks analyzed for glyphosate and AMPA. Automatic samplers were a major concern of possible contamination owing to the inability to use fluoropolymer or glass to collect samples. The infrequent detections in base-flow and flood environmental samples imply that contamination bias was likely not an issue. A background (no herbicide) soil sample was collected as a reference and one soil replicate was collected to determine the variability of the composite style collection approach.

Analytical Laboratory Methods

All analyses were performed by USGS laboratories following published operating procedures. Analytical methods follow Meyer and others (2009) for glyphosate and AMPA analysis, and isotopic methods follow Révész and Coplen (2008a, b).

Glyphosate and Aminomethylphosphonic Acid

All glyphosate and AMPA chemical analyses were conducted by the USGS Kansas Water Science Center's Organic Geochemistry Research Laboratory. Water samples were stored at 2 to 4 °C until derivatization and solid samples were stored at −20 °C until preparation for analysis. Water samples were prepared for derivatization within 36 hours of their receipt or frozen until derivatization. The derivatization procedure described in Meyer and others (2009) was modified to reduce the volume of sample required from 10 to 1 mL.

Laboratory spiked water samples and standard curves were prepared by adding the appropriate amount of either a 0.05 nanogram per microliter (ng/µL) standard mix or a 1:20 dilution of the standard mix to 10 mL of laboratory water to generate 0.01 through 5.0 micrograms per liter (µg/L) standards. For standards and laboratory blanks the procedure was identical to the environmental sample preparation, but used the unmodified volumes described in Meyer and others (2009).

Each sample run consisted of 47 samples including a 9-point standard curve, 22 environmental samples, 8 blanks, 4 check standards, 2 environmental duplicates, and 2 spiked environmental samples. A blank sample was analyzed within each set of 11 environmental samples; after each set of 11 environmental samples, an environmental duplicate, a spiked environmental sample, a blank, two check standards, and another blank sample were analyzed. All standard solutions, blanks, and matrix spikes were treated the same as the environmental water samples.

Solid samples were thawed 24 hours prior to sample processing. Moisture content of each sample was determined by weighing 5 g of sample into a pre-weighed aluminum boat, heating in a 120 °C oven for 24 hours, followed by cooling to room temperature in a desiccator and then reweighing. Samples with high moisture content were freeze-dried before proceeding. Each thawed or freeze-dried sample was placed onto a sheet of clean aluminum foil, broken up, and thoroughly mixed with a clean metal spatula. A representative 5 g aliquot of each sample, subsampled a minimum of 10 times, was weighed out in a 50 mL polyethylene centrifuge tube using a calibrated top-loading balance. Additional 5 g aliquots were obtained from a subset of samples to use for duplicates and environmental spikes.

Glyphosate, AMPA, and glufosinate were extracted from the solid by adding 100 microliters of solution that contains 1 ng/µL of stable isotope labeled glyphosate and AMPA to each sample followed by the addition of 25 mL of 0.5 molar potassium hydroxide into each tube. For environmental spike samples, 100 microliters of a standard mix containing 1 ng/µL of glyphosate, AMPA, and glufosinate was also added to the sample aliquot prior to the addition of the potassium hydroxide.

Derivatized water samples and solids samples were analyzed by ultra-performance liquid chromatography-mass spectrometry. Method detection limits were determined to be 0.02 µg/L and 1.0 microgram per kilogram (µg/kg) for glyphosate, AMPA, and glufosinate in water and solids, respectively.

Isotopes

Stable isotope ratios ($\delta^{18}O$ and δ^2H analysis) were measured at the USGS Reston Stable Isotope Laboratory following methods by Révész and Coplen (2008a, b). The δ^2H-ratio analyses are performed using a hydrogen equilibration technique (Révész and Coplen, 2008a). The hydrogen equilibration technique measures deuterium activity. Water samples are measured for delta $\delta^{18}O$ using the carbon dioxide equilibration technique, which has been automated (Révész and Coplen, 2008b). The 2-sigma uncertainties for the stable isotope analyses are 0.2 per mil for $\delta^{18}O$ and 2 per mil for δ^2H, reported relative to Vienna Standard Mean Ocean Water.

The University of Miami Tritium Laboratory measured tritium using the electrolytic enrichment and gas counting method, with a method detection limit of 0.3 picocurie per liter (pCi/L). Tritium concentrations are normally expressed in tritium units, where 1 tritium unit indicates a T/H abundance ratio of 10^{-18}. The values refer to the tritium scale recommended by U.S. National Institute of Science and Technology and International Atomic Energy Agency. The tritium unit numbers are based on the National Institute of Science and Technology tritium water standard #4926E. Age corrections and conversions are made using the recommended half-life of 12.32 years, which indicates a decay rate of 5.626 percent per year (McCurdy and others, 2008).

Statistical

Censored data analysis was used to analyze the glyphosate and AMPA results. Computing summary statistics on analytical results reported below (non-detected) or above the laboratory detection limit requires a censored data analysis. The Nondetects and Data Analysis for Environmental Data (Helsel, 2012) package in R (Lee, 2015) was used to calculate the median, mean, and standard deviation. The censored regression on order statistics or "cenros" function from Nondetects and Data Analysis for Environmental Data was used to compute the summary statistics. Traditional non-parametric approaches used to graph and compute general statistics were completed using JMP© software (SAS Institute, Inc., 2007). The dissipation kinetics of glyphosate in water were fitted using JMP version 12 software to a simple first-order three parameter exponential decay model, characterized by the following equation:

$$C_t = C_0 e^{-kt} + a, \quad (1)$$

where

t is the time that passed,
C_t is the glyphosate concentration at time t,
C_0 is the initial concentration of glyphosate,
e is the exponential of 2.71828183,
K is the rate constant in day^{-1}, and
a is the asymptote constant.

Results

Quality control results had acceptable bias and variability in field collection methods and laboratory analysis methods. No results were qualified because of poor performance. The GBH detections were infrequent and low in concentrations in the water samples. Aquatic fine sediments were limited in much of the watersheds sampled, but when sediments were collected, the concentrations of glyphosate and AMPA were variable. Glyphosate in aquatic sediment was detected less than the water and AMPA was detected more frequently in sediment than the water samples. Soil concentrations were common and found at the highest concentrations because samples were collected from areas known to be sprayed with GBH. Soil concentrations showed considerable dissipation after application, but compounds were also very persistent and detected 592 days after application.

Quality Control

Field and laboratory blank water samples were all below the detection limit of 0.02 µg/L for glyphosate, AMPA, and glufosinate (table 5). Glufosinate is a separate herbicide associated with agricultural settings and is not expected to be found in the Rincon Mountain District. It was used in this study as a negative control. Sediment sample laboratory blanks consisted of a potassium hydroxide solution and all laboratory blank samples were below the method detection limit of 1.0 µg/kg.

The percent difference of the seven laboratory split replicates was zero for AMPA and glufosinate. One of the seven split replicates analyzed for glyphosate had a difference of 11 percent. A laboratory split replicate was done for one sediment and one soil sample. The glufosinate (not detected) had a 0 percent difference for both replicates, whereas the soil glyphosate and AMPA had percent difference of 6 and 12, respectively. The field concurrent replicate had a relative standard deviation that was 465 µg/kg plus or minus 14 percent for AMPA and 375 µg/kg plus or minus 25 percent for glyphosate. The high variability likely was a result of the aerial application process or uneven spraying and methods used to collect soil composite samples.

The two laboratory spikes for the water samples averaged 106, 165, and 114 percent for AMPA, glufosinate, and glyphosate, respectively. The two aquatic sediment laboratory spikes averaged 138, 220, and 87 percent for AMPA, glufosinate, and glyphosate, respectively. Standard reference standards analyzed for the sediment samples for 10, 50, and 100 µg/kg of glyphosate averaged a percent recovery of 101, 96, and 99 percent, respectively.

Blanks indicated that field and laboratory procedures and analyses were not introducing bias in the form of contamination. In addition, reproducibility in replicate samples showed little variation although most of the water samples collected during the study were below or near the detection limit. Soil samples were more variable than sediment samples, which may be related to different soil types, uneven herbicide distribution, and heterogeneous mixture of particles and organic materials. Laboratory method recovery of glufosinate in water was above 100 percent and biased high for glufosinate although no detections were observed in the study. Internal sediment samples spiked and analyzed for AMPA and glufosinate were biased high but had lower recovery for glyphosate at 83 and 90 percent.

Table 5. Laboratory and field quality control data summary.

[AMPA, aminomethylphosphonic acid; Gluf, glufosinate; Glyph, Glyphosate; µg/L, microgram per liter; µg/kg, microgram per kilogram; %, percent; ±, plus or minus; --, not available; NA, not applicable; <, less than the minimum laboratory detection limit]

Site ID	Site location	Collection date	Sample description	Percent difference			Percent recovery			µg/L water or µg/kg soil			Average percent recovery		
				AMPA	Gluf	Glyph	AMPA	Gluf	Glyph	AMPA	Gluf	Glyph	AMPA	Gluf	Glyph
Split replicate															
320945110415901	Box Canyon pool 6	8/19/2015	Aquatic sediment	0%	0%	0%	--	--	--	--	--	--	--	--	--
320920110422401	Box Canyon south ridge	9/24/2015	Terrestrial soil	12%	0%	6%	--	--	--	--	--	--	--	--	--
320856110431001	Lower Madrona Creek at Saguaro National Park	8/11/2016	Surface water	0%	0%	0%	--	--	--	--	--	--	--	--	--
320950110355701	Upper Madrona Canyon pool 9	11/2/2016	Surface water	0%	0%	0%	--	--	--	--	--	--	--	--	--
320855110360300	Lower Madrona Creek at Saguaro National Park	1/21/2017	Surface water	0%	0%	0%	--	--	--	--	--	--	--	--	--
320915110423101	Box Canyon pool 00	4/13/2017	Surface water	0%	0%	0%	--	--	--	--	--	--	--	--	--
320855110360300	Lower Madrona Creek at Saguaro National Park	7/31/2017	Surface water	0%	0%	0%	--	--	--	--	--	--	--	--	--
320855110360300	Lower Madrona Creek at Saguaro National Park	7/20/2017	Surface water	0%	0%	0%	--	--	--	--	--	--	--	--	--
320856110431001	Lower Box Canyon below Saguaro National Park boundary	2/16/2018	Surface water	0%	0%	11%	--	--	--	--	--	--	--	--	--
Field replicate															
320922110361301	Lower Madrona Canyon east ridge		Terrestrial soil	465 µg/kg±14%	NA	375 µg/kg±25%	--	--	--	--	--	--	--	--	--
Spike recovery															
320915110423101	Box Canyon pool 00	9/24/2015	Aquatic sediment	--	--	--	170%	245%	83%	--	--	--	--	--	--
320929110422401	Box Canyon pool 1A	5/5/2016	Aquatic sediment	--	--	--	105%	195%	90%	--	--	--	--	--	--
320915110423101	Box Canyon pool 00	8/19/2015	Surface water	--	--	--	117%	160%	110%	--	--	--	--	--	--
320855110360300	Lower Madrona Creek at Saguaro National Park	7/29/2017	Surface water	--	--	--	95%	170%	117%	--	--	--	--	--	--

Table 5. Laboratory and field quality control data summary. —Continued

[AMPA, aminomethylphosphonic acid; Gluf, glufosinate; Glyph, Glyphosate; µg/L, microgram per liter; µg/kg, microgram per kilogram; %, percent; ±, plus or minus; --, not available; NA, not applicable; <, less than the minimum laboratory detection limit]

Site ID	Site location	Collection date	Sample description	Percent difference			Percent recovery			µg/L water or µg/kg soil			Average percent recovery		
				AMPA	Gluf	Glyph	AMPA	Gluf	Glyph	AMPA	Gluf	Glyph	AMPA	Gluf	Glyph
Laboratory blanks (8 samples)															
320855110360300	Lower Madrona Creek at Saguaro National Park	NA	Surface water	--	--	--	--	--	--	<0.02	<0.02	<0.02	--	--	--
Laboratory blanks (51 samples)															
NA	NA	NA	Sediment or soil	--	--	--	--	--	--	<1.0	<1.0	<1.0	--	--	--
Field blanks (2 samples)															
NA	NA	NA	Surface water	--	--	--	--	--	--	<0.02	<0.02	<0.02	--	--	--
Standard reference samples in solids (7 samples)															
NA	NA	NA	Soil (10 µg/kg)	--	--	--	--	--	--	--	--	--	97%	124%	101%
Standard reference samples in solids (2 samples)															
NA	NA	NA	Soil (50 µg/kg)	--	--	--	--	--	--	--	--	--	104%	102%	96%
Standard reference samples in solids (7 samples)															
NA	NA	NA	Soil (100 µg/kg)	--	--	--	--	--	--	--	--	--	106%	110%	99%

Surface-Water Pools and Runoff

Water-quality parameters were collected during base-flow conditions with the exception of three sets of parameters collected in flood recession conditions. Mean dissolved oxygen ranged between 5.47 and 10.4 mg/L and the median pH was slightly basic at 7.2 pH units. The largest differences were observed in specific conductance. The Madrona Canyon watershed had the lowest mean concentrations at 70.9 µS/cm, whereas the Loma Verde canyon and Box Canyon watersheds mean concentrations were 395 and 180 µS/cm, respectively (table 6). Evaporation had an increasing effect on pool specific conductance, especially in the dry summer months. Seasonal differences were also related to runoff contributions diluting pool and tinaja water in the spring and fall.

The frequency of detections of glyphosate and AMPA in water samples was low for the 48 total water samples collected. Less than 15 percent of the samples had a detection of glyphosate, AMPA, or both (table 7; fig. 12*A*). The mean water concentrations of glyphosate and AMPA were below the laboratory detection limit of 0.02 µg/L, with the highest glyphosate concentration collected during a flood event in Box Canyon (0.20 µg/L; fig. 12*B*). No measurable glyphosate or AMPA was present in the one sample collected in the Loma Verde canyon watershed. Water detections were more common in the base-flow samples than in flood samples, but the flood sampling was limited in the Box Canyon watershed. Pool 00 had the greatest number of water detections and the pool is located below a steep section in a small side tributary (0.21 square mile) to the main channel of Box Canyon, on the eastern part of the watershed. Six water samples were collected in Pool 00 and all the samples had detections of AMPA and two had detections of glyphosate. The highest AMPA concentration of 0.63 µg/L was measured in Pool 00. All other base-flow water samples collected in Pools 07, 06, 4A, 1A, and 01 did not have any detections of glyphosate or AMPA.

Three flood events were sampled in the Box Canyon watershed, although two of the composites collected by the automatic samplers did not sample the rise and peak of the flood profile. The runoff following treatment can mobilize

Table 6. Summary statistics for water-quality parameters in each watershed.

[*n*, sample size]

Parameter	Statistic	Loma Verde canyon (*n*=3)	Box Canyon (*n*=29)	Madrona Canyon (*n*=24)
Dissolved oxygen, in milligrams per liter	Mean	10.4	5.47	7.32
	Standard deviation	4.06	3.42	1.67
	Median	12.4	6.63	7.23
pH, in standard units	Mean	7.92	7.17	7.26
	Standard deviation	0.862	0.418	0.583
	Median	8.19	7.14	7.19
Specific conductance, in microsiemens per centimeter	Mean	395	180	70.9
	Standard deviation	22.9	96.2	25.9
	Median	389	151	67.7
Water temperature, in degrees Celsius	Mean	20.4	22.8	22.8
	Standard deviation	4.41	4.69	4.78
	Median	21.5	23.8	22.9

Table 7. Summary statistics for aminomethylphosphonic acid and glyphosate concentrations using regression on ordered statistics.

[AMPA, aminomethylphosphonic acid; <, less than; >, greater than]

Medium	Compound	Number of samples	Mean	Median	Standard deviation	Maximum	Number of samples censored[a]	Percentage of samples censored[a,b]
Water, in micrograms per liter	AMPA	48	0.021	0	0.092	0.63	41	85.4
	Glyphosate	48	<0.02	<0.02	0.038	0.2	43	89.6
Aquatic sediment, in micrograms per kilogram	AMPA	28	4.42	<1.0	14.4	76	21	75
	Glyphosate	28	1.13	<1.0	4.2	22	25	89.3
Soil, in micrograms per kilogram	AMPA	19	1,240	410	1,740	5,200	1	5.26
	Glyphosate	19	678	85	1,210	>5,000	3	15.8

[a]Censored or not detected above the laboratory method detection level.

[b]Statistics are unreliable when greater than 80 percent of the data are censored.

higher concentrations of the contaminant with initiation of the flood event, and the leading edge of a peak flow can be correlated with the peak concentration of contaminant (McCarthy, 2006). The February 2018 composite flood sample was the first flow after the 2017 herbicide application and the composite sample had detections of glyphosate and AMPA. The rise, peak, and portion of the recession were sampled as a composite and concentrations of 0.2 µg/L of glyphosate and 0.04 µg/L of AMPA were measured.

In the Madrona Canyon watershed, neither compound was detected in the water of Pool 02 or Pool 09 during base-flow conditions (fig. 12*C*). Between August 1, 2016, and March 1, 2018, eight flood events were recorded in the Madrona Canyon watershed and samples from the automatic sampler were collected at multiple points during the flood hydrograph for seven of those events (15- or 30-minute intervals collected during the rise, peak, or recession limb of the flood hydrograph). Samples collected on the rising and (or)

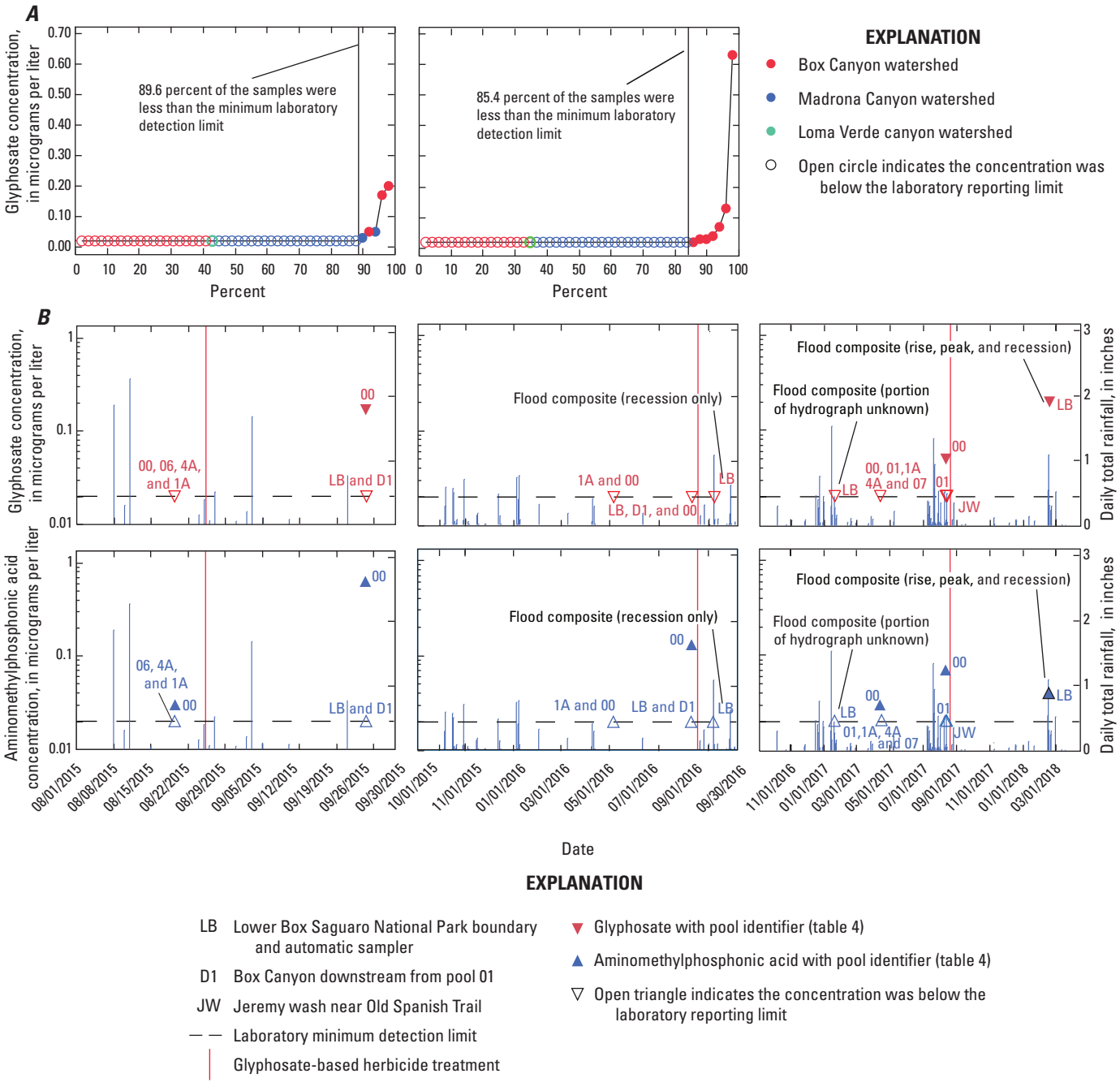

Figure 12. A summary of water samples collected in the Rincon Mountain District. Concentration of glyphosate and aminomethylphosphonic acid (AMPA) in water *A*, ranked and plotted as a percent of total samples collected in the Loma Verde canyon, Box Canyon watershed, and Madrona Canyon watershed. A time series of glyphosate and AMPA concentrations, glyphosate-based herbicide application, and rainfall for *B*, Box Canyon watershed and *C*, Madrona Canyon watershed.

peak portion of the flood were most often sent in for analysis to maximize the probability of detecting compounds at the highest concentration of the flood. A few flood events resulted in multiple peaks during consecutive days and multiple samples were analyzed for glyphosate and AMPA during the same flood event. Only 2 of the 20 samples analyzed during flood events had detections of glyphosate. The two samples were collected during the same flood event on July 29, 2017, with one collected on the rise and the other on the peak of the flood, and the concentrations of glyphosate were 0.05 and 0.03 µg/L,

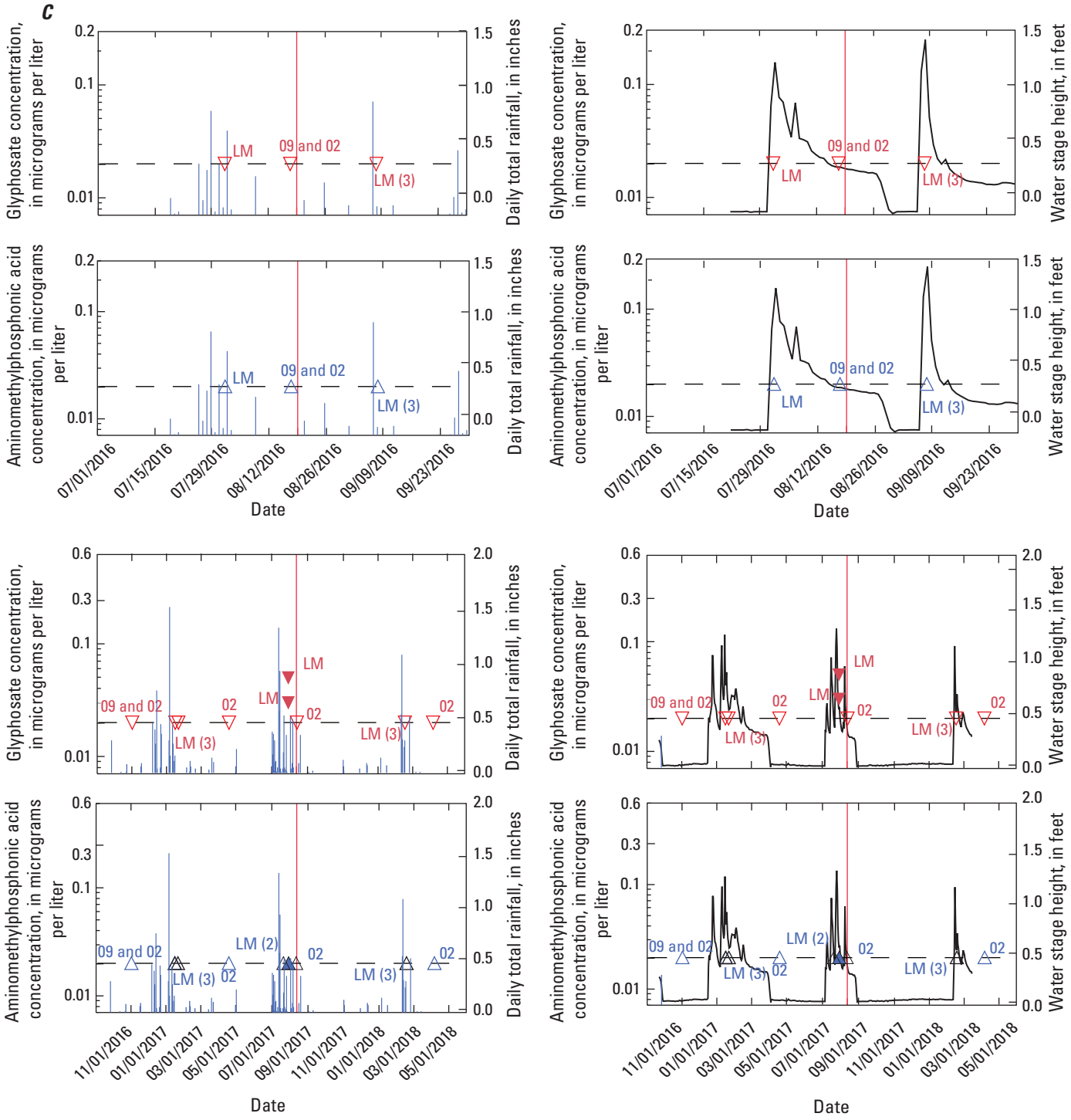

Figure 12.—Continued

respectively. No glyphosate was detected during the recession and AMPA was not detected in any of the three samples. The previous treatment application was sprayed mid-August 2016.

Stable isotope ratios measured on 25 water samples ranged from 0.19 to −16.5 per mil and −18.3 to −122 per mil for $\delta^{18}O$ and $\delta^{2}H$, respectively. Samples at the low end of the range plot near the global meteoric water line (Craig, 1961) and samples near the high end of the range plot near the local meteoric water line (developed by Eastoe and Dettman, 2016; National Park Service, 2017b; fig. 13) were determined using samples collected from rainfall in Tucson, Arizona, and the Santa Catalina Mountains. Samples that plot to the right of the meteoric water lines indicate that the water may have undergone evaporation. Additional samples were collected by Saguaro National Park in cooperation with Chris Eastoe during June 2010 and 2014 (Eastoe, 2012; National Park Service, 2017b) and represent a local meteoric water line for the study area using the following equation:

$$\delta^{2}H = 3.8409 \times \delta^{18}O - 28.757 \quad (2)$$

where

$\delta^{2}H$ is a measure of the ratio of stable isotopes hydrogen-2 and hydrogen-1,

$\delta^{18}O$ is a measure of the ratio of stable isotopes oxygen-18 and oxygen-16.

Most samples collected plotted to right of the global meteoric water line showing a slightly evaporated signal. Madrona Canyon samples follow the trajectory of the global meteoric water line whereas the Box Canyon samples more closely follow the local meteoric water line, although most samples plot to the right of the local meteoric water line with partially evaporated signal and possibly originating from higher-elevation precipitation. Some of these samples represent spring (April) samples collected in Box Canyon. The fall (November) samples from Madrona Canyon and the spring (April) samples from Loma Verde canyon show a less evaporated signal and potentially represent waters from higher elevations.

Seven sites were sampled more than one time and show variability of stable isotope values between samples (table 7). The variation in stable isotopic values may be related to different seasonal precipitation events supplying different isotopic ratio type water to the sampled pools over time. The variation in stable isotopic values over time may indicate that the water supplying the pools, prior to our sample collection, has a short residence time in the system.

Tritium is a useful tracer for determining if there is a component of water recharged during the period of nuclear bomb testing in the 1950s and 1960s, when tritium in the atmosphere peaked and then decreased during the following decades. Tritium values have stopped decreasing in recent precipitation (after 1992), and average recent values of tritium in precipitation in Tucson are 16.7 pCi/L (Eastoe and others, 2012). Tritium values from nine water samples ranged from 9.9 to 18.9 pCi/L. Values between 11.3 and 20.9 pCi/L are considered to represent water with residence time on the order of a few decades (Eastoe and others, 2012). Most of the water samples may represent more recently recharged waters on the order of years.

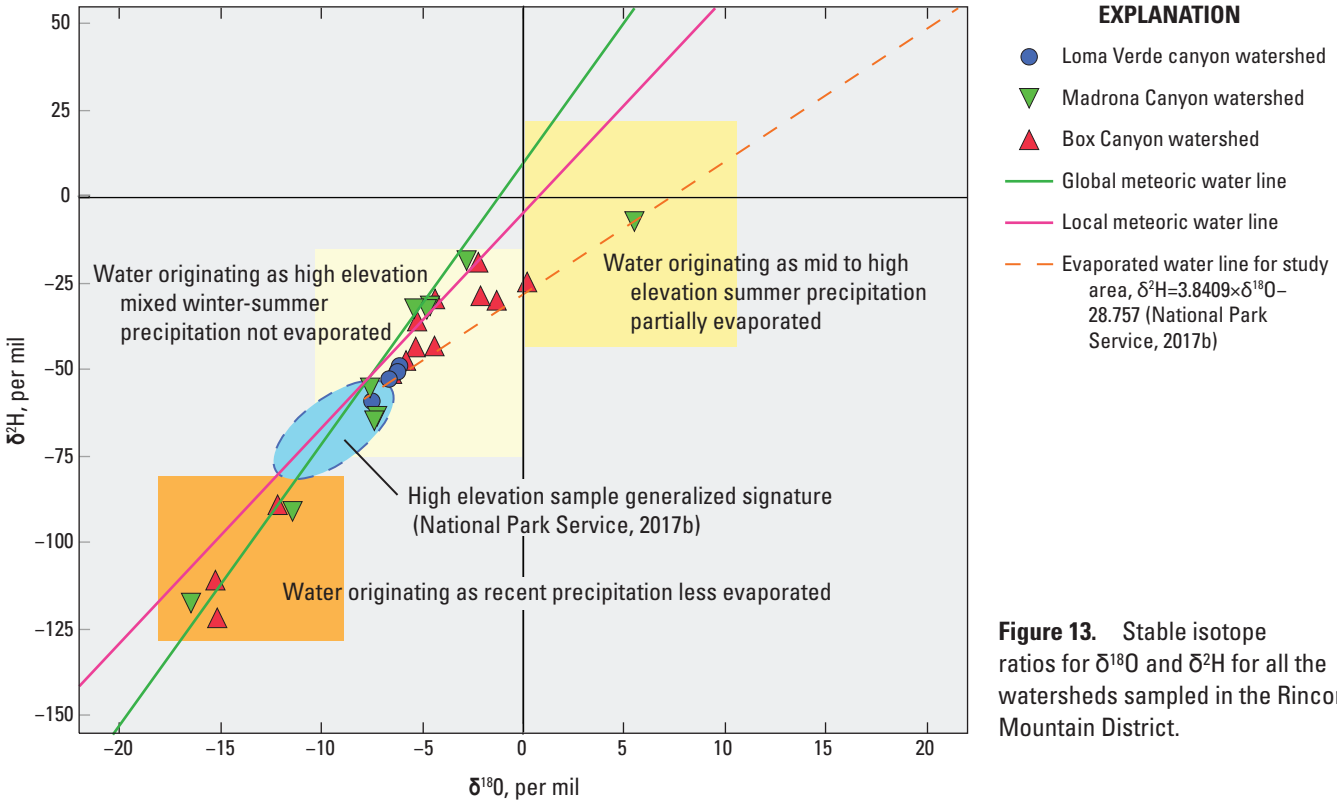

Figure 13. Stable isotope ratios for $\delta^{18}O$ and $\delta^{2}H$ for all the watersheds sampled in the Rincon Mountain District.

Aquatic Sediment

The frequency of glyphosate in aquatic sediment detections was similar to water samples, but AMPA was about 10 percent higher than water samples, detected in 25.0 percent of the 28 samples (fig. 14*A*). Mean aquatic sediment concentrations were 1.13 and 4.42 µg/kg for glyphosate and AMPA, respectively. No measurable glyphosate or AMPA was found in the one sample collected in the Loma Verde canyon watershed. Aquatic sediments sampled in Pool 00 in the Box Canyon watershed had the highest concentrations of the current study at 22 and 76 µg/kg of glyphosate and AMPA, respectively (fig. 14*B*). Pools 1A and 4A in the Box Canyon watershed also had detections of AMPA in aquatic sediment samples but they were closer to the overall mean concentration. Other than Pool 00, glyphosate was only detected in one sample at Pool 1A. In the Madrona Canyon watershed, eight aquatic sediment samples were collected and only one sample in Pool 02 had detections of glyphosate (4.10 µg/kg) and AMPA (7.70 µg/kg; fig. 14*C*).

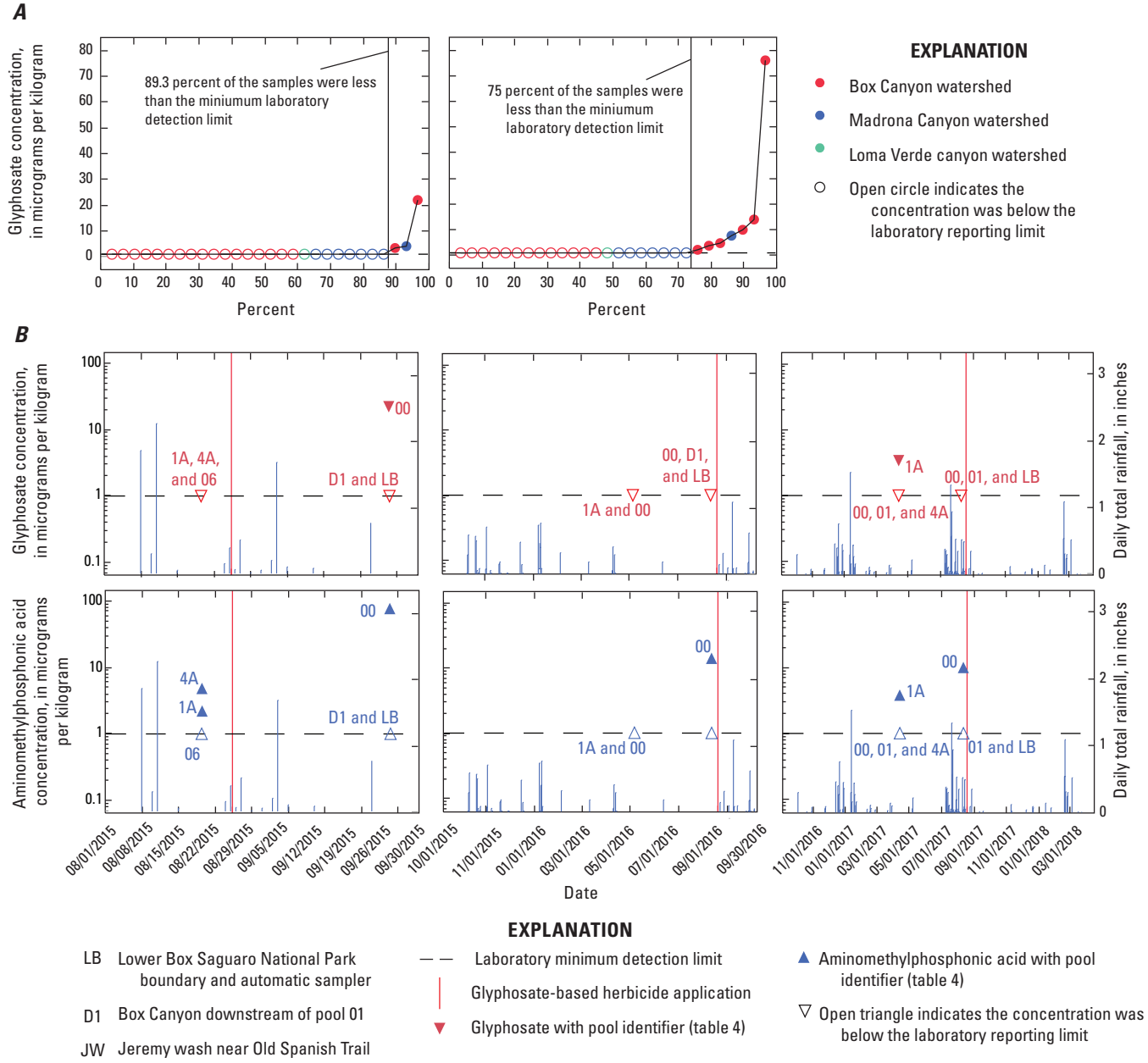

Figure 14. A summary of aquatic sediment samples collected in the Rincon Mountain District. Concentration of glyphosate and aminomethylphosphonic acid (AMPA) in aquatic sediment *A*, ranked and plotted as a percent of total samples collected in the Loma Verde canyon, Box Canyon and Madrona Canyon watersheds. A times series of glyphosate and AMPA concentrations, glyphosate-based herbicide application, and rainfall for *B*, Box Canyon watershed and *C*, Madrona Canyon watershed.

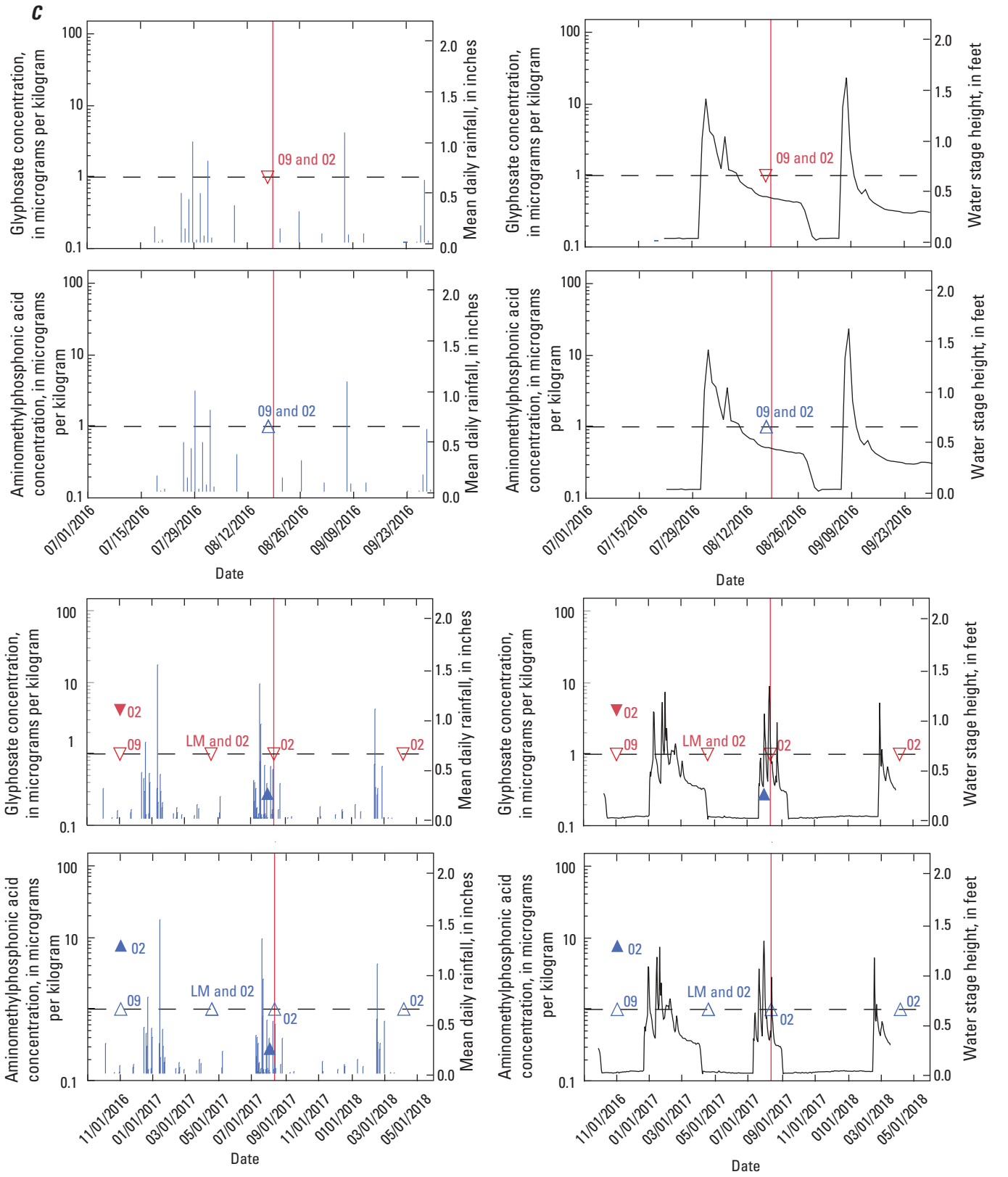

Figure 14.—Continued

Terrestrial Soil

Nineteen terrestrial soil samples were collected from areas treated with GBHs, which coincides with the greater the frequency of detection. Of the 19 soil samples collected, 89.5 percent of the soil samples collected contained glyphosate and 100 percent of the soil samples contained AMPA (fig. 15*A*). Mean concentrations of glyphosate and AMPA were 678 µg/kg and 1,240 µg/kg, respectively. The single terrestrial soil sample collected in the Loma Verde canyon watershed had concentrations of glyphosate (11 µg/kg) and AMPA (150 µg/kg) 592 days after the last

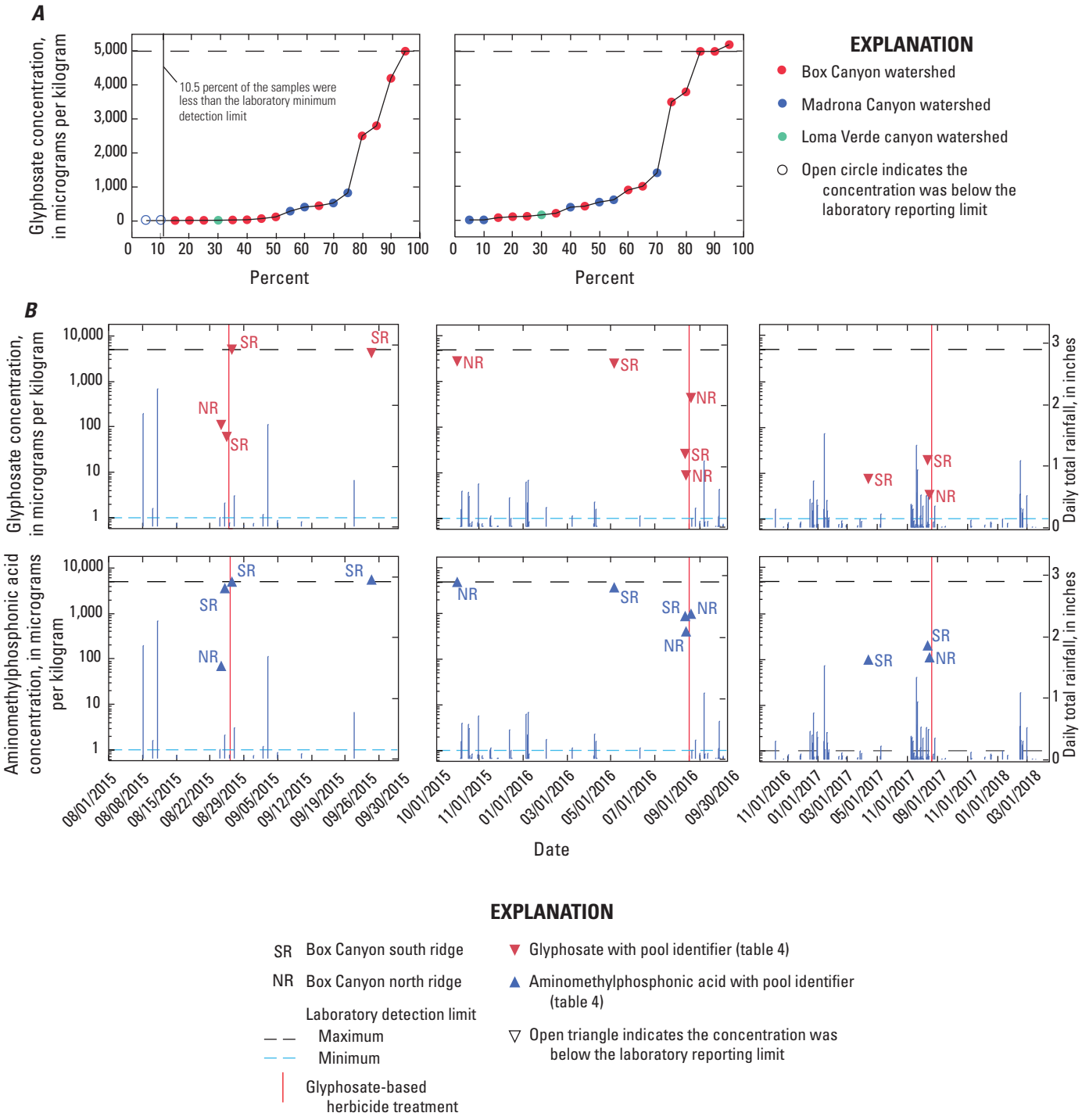

Figure 15. A summary of soil samples collected in the Rincon Mountain District. Concentration of glyphosate and aminomethylphosphonic acid (AMPA) in soil *A*, ranked and plotted as a percent of total samples collected in the Loma Verde canyon, Box Canyon and Madrona Canyon watersheds. A times series of glyphosate and AMPA concentrations, glyphosate-based herbicide application, and rainfall for *B*, Box Canyon watershed and *C*, Madrona Canyon watershed.

treatment application. Terrestrial soil concentrations for both compounds were consistently higher in the Box Canyon watershed (fig. 15*B*). Three samples in the Box Canyon watershed exceeded 5,000 µg/kg for AMPA. The Box Canyon watershed received the greatest volume of GBHs applied and had the greatest extent of coverage. The Madrona Canyon watershed concentrations after treatment were lower than the Box Canyon watershed and never measured greater than 1,000 and 1,500 µg/kg for glyphosate and AMPA, respectively (fig. 15*C*).

Terrestrial soils were sampled a few times per year to measure the changes in glyphosate and AMPA after GBHs were applied. Concentrations of glyphosate and AMPA mostly decreased between applications, but there were differences between sites in the dissipation rates of compounds. Glyphosate dissipated more rapidly than AMPA, but because AMPA is the primary metabolite of glyphosate, degradation likely was simultaneously augmenting and compounding the total AMPA concentrations. Box Canyon north ridge (USGS station 320945110421001; hereafter referred to as the "Box Canyon north ridge") showed more than a 99-percent decrease in glyphosate in about 10 months (2,800 to 8.8 µg/kg) and more than a 90-percent reduction in AMPA concentrations (greater than 5,000 to 410 µg/kg). A similar pattern occurred at Box Canyon south ridge (USGS station 320920110422401; hereafter referred to as the "south ridge of Box Canyon") after about 11 months (greater than 5,000 to 26 µg/kg for glyphosate and 5,200 to 890 µg/kg for AMPA). After the first ever treatment application to the Lower Madrona Canyon east ridge (USGS station 320922110361301; hereafter referred to as the "east ridge of Madrona Canyon"), initial concentrations were lower than those measured in the Box Canyon watershed, although less volume was applied to the area. Samples collected 4 to 5 months later showed increases in both compounds, but after 9 months more than 99 percent of both compounds had dissipated.

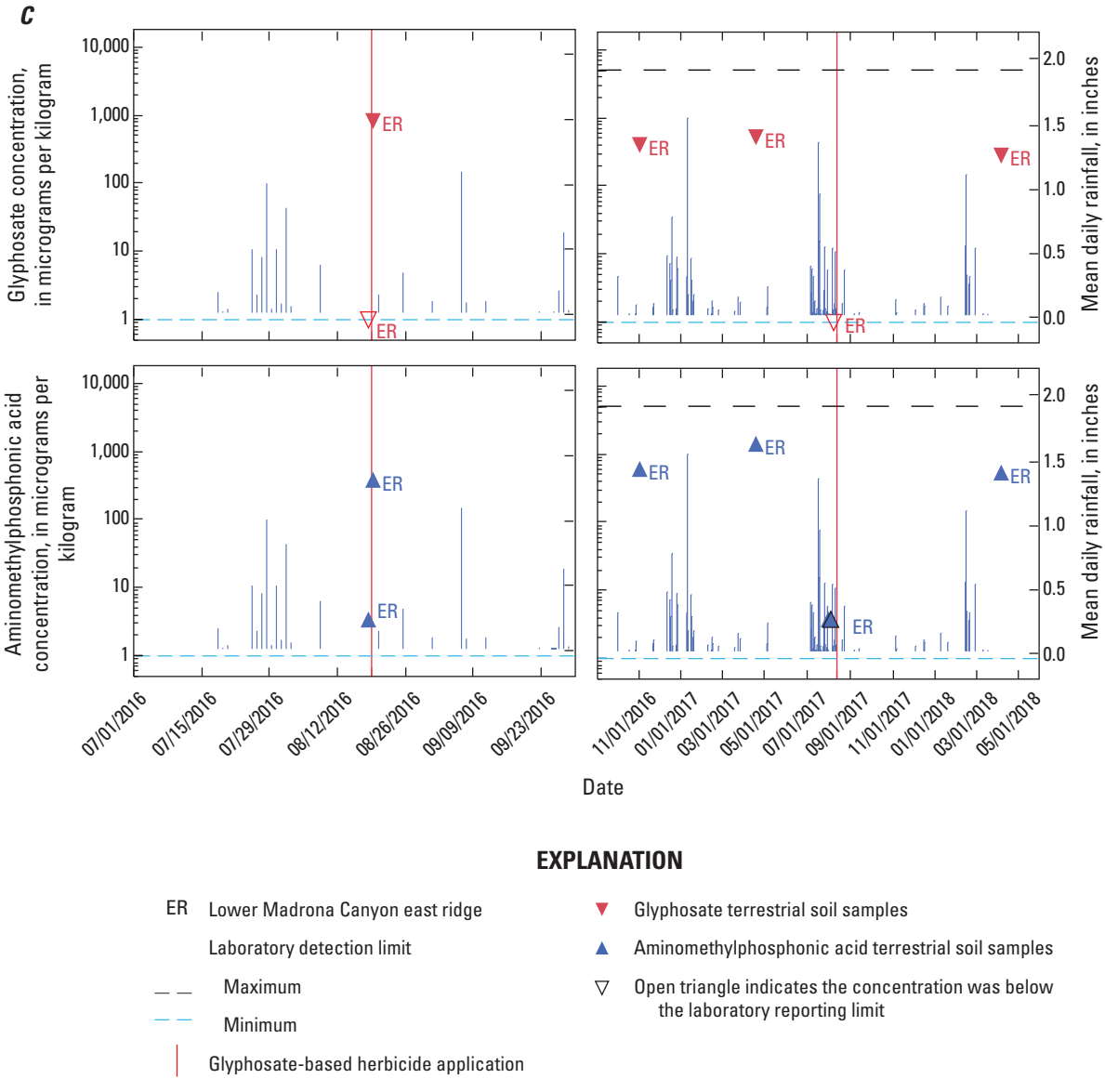

Figure 15.—Continued

Discussion

The hydrologic information collected during the study and the quantification of the magnitude, timing, and frequency of glyphosate and AMPA in the three watersheds helped to characterize the result of GBH usage and the factors involved in the occurrence, transport, and fate of glyphosate and AMPA in the Rincon Mountain District. This information can be used to put the results in the context of other glyphosate-related studies and toxicological studies to better understand the possible risk to aquatic organisms. The study discussion focuses on glyphosate and AMPA occurrence, transport, and fate and how this compares to other glyphosate and AMPA studies as well as to health and aquatic life criteria and published toxicological studies quantifying the effects of GBHs on aquatic organisms. The Box Canyon watershed is a primary focus of discussion because of the intensity and frequency of GBH application. Specifically, the Box Canyon Pool 00 had frequent detections and elevated concentrations that were associated with the timing of GBH application and runoff after precipitation events.

Factors in Occurrence, Transport, and Fate of Glyphosate and Aminomethylphosphonic Acid

The climate, physiography, and soil conditions are important factors in the processes affecting the dissipation and movement of GBHs from treatment areas along the upper terraces and mountain ridges to the waters lower in the watershed. The persistence of glyphosate in an ecosystem is suspected to be primarily affected by microbial biodegradation processes, which are dependent on moisture, temperature, and organic carbon. Giesy and others (2000), Borggaard and Gimsing (2008), and Székács and Darvas (2012) described that when most of the previously listed environmental conditions and resources are limited, like those in a desert ecosystem, glyphosate dissipation will be reduced and ultimately GBHs will be more persistent. This persistence in the treatment areas was observed during the study and the longevity of GBHs was exemplified in the Loma Verde canyon watershed. Glyphosate was still present in the one sample collected 592 days after the last treatment of GBHs. The low ratio of 0.07 (11 to 150 µg/kg of glyphosate to AMPA) indicates that glyphosate was in a late stage of dissipation, but still at levels considered elevated when compared to other studies (Giesy and others, 2000; Battaglin and others, 2014).

Studies have documented that glyphosate dissipation follows a simple first-order decay model in soil (Tang and others, 2019). In the current study, glyphosate and AMPA dissipation in soil was modeled using a simple first-order decay function for samples collected at the Box Canyon south ridge location (USGS station 320920110422401). This area was only treated once during a 2-year period and samples were collected through that period to understand glyphosate dissipation. Dissipation rates and runoff processes affect the downstream Pool 00 where glyphosate and AMPA were frequently detected. The benefit of this type of modeling is to determine the potential half-life of glyphosate in the Rincon Mountain District environment and provide information about periods of higher glyphosate concentrations that could potentially be in runoff after treatment applications. The modeled first half-life at the Box Canyon south ridge site was around 75 and 125 days for glyphosate and AMPA, respectively. The equation of the glyphosate decay follows the three-parameter equation:

$$C_t = C_0 e^{-kt} + a, \quad (3)$$

where

- t is the time that passed,
- C_t is the glyphosate concentration at time t,
- C_0 is the initial concentration of glyphosate and AMPA (4,930 and 6,766 µg/kg),
- k is the rate constant of glyphosate and AMPA (−0.00923 and −0.00559) in day^{-1},
- e is the exponential of 2.71828183, and
- a is the asymptote constant, which was 7.4 and 98 µg/kg for glyphosate and AMPA, respectively.

The decay curve is steeper for the first half-life and second order reactions level off more gradually and decay rates slow as time increases. It was estimated to take 330 and 595 days for glyphosate and AMPA concentrations, respectively, to approach a 95-percent reduction from the initially sprayed concentration. The estimated dissipation rates indicate a 2- to 3-month period in which the risk of high glyphosate concentrations transporting to downstream waters could occur. Such transport could be minimized if aerial spraying were timed with annual periods of low rainfall. This decay rate is somewhat consistent with what was observed in the Loma Verde canyon watershed 592 days after treatment although the amounts applied and the measured concentrations were greater in the Box Canyon watershed. The north ridge Box Canyon and the Lower Madrona Canyon east ridge terrestrial soil locations (USGS stations 320945110421001 and 320922110361301, respectively) also showed a similar pattern of decreasing glyphosate and AMPA between applications. The in situ decay was only modeled at the one location in the Box Canyon watershed using a small sample size. It should be noted, the second sample, taken approximately 250 days after treatment, had a large residual and actual concentrations were about twice as high as the modeled estimate indicating a lesser rate of decay in the first 200 days. Most notably, the GBH compounds in the treated terrestrial environments are persistent and last for at least a year or more. In addition, the repeat treatments are likely renewing GBH compound mass, increasing antecedent concentrations, and possibly compounding the AMPA metabolite concentrations as glyphosate degrades into AMPA. More sampling would be needed to understand soil and environmental variability to verify decay rate curves, but the results are consistent with the dissipation rates observed during other studies (Laitinen and others, 2006; Rodriguez-Gil and others, 2016; Yadav and others, 2017).

The prevailing consensus in the literature is that risk of groundwater pollution at depth is low and the most influential factors in glyphosate transport are rainfall intensity and subsequent erosion of particulates and glyphosate retained in upper 2 to 100 centimeters of the topsoil (Bowmer, 1982; Carlisle and Trevors, 1988; Feng and others, 1990; Laitinen and others, 2006; Borggaard and Gimsing, 2008; Battaglin and others, 2014; Yang and others, 2015; Napoli and others, 2015). The highest density of buffelgrass patches for all the watersheds studied was most often located on the soil type classified as the Lampshire-Romero-Rock outcrop complex (fig. 3). Dissipation rates of GBHs are affected by soil conditions and the properties of those soils. This soil type has few silts and clays, is of high permeability with low water capacity (Cochran and Richardson, 2003), has a shallow depth to bedrock, and is fragile with a high erosion factor that can promote mobilization of substrates sprayed with GBHs. In the Box Canyon watershed, these soils were treated for multiple years and the frequency of detections of glyphosate and AMPA increased when the spraying application (volume and area) increased and the annual rainfall was elevated, specifically during 2015 and 2017 when monsoon-related rainfall—typically intense with high runoff—was high (fig. 16*A*). The 2014 and 2016 years had greater winter precipitation—typically light to moderate intensity with low runoff—than 2015 and 2017. The driest of the 4 years analyzed was 2016 which coincided with the year that had the lowest number of detections in water and aquatic sediment samples within the Box Canyon watershed (fig. 16*B*).

The Madrona Canyon treatment area was also located on this soil type. The Madrona Canyon watershed was the least-sprayed watershed overall; in terms of volume and area, the treatment was an order of magnitude smaller than that of the Box Canyon watershed (fig. 17*A*) and the Madrona Canyon watershed had very few detections in the aquatic sediment and water (fig. 17*B*). The erodible sediments associated with the Lampshire-Romero-Rock outcrop complex were evident in an upstream tributary that drained the treatment area and it appeared to have flowed multiple times during the study. One aquatic sediment sample from Pool 02 in Madrona Canyon had glyphosate and AMPA present in the slightly drier year of 2016, although this might be explained by a September storm that had a 1-day total of greater than 1 inch of rain.

Results indicate that the soils in the Rincon Mountain District sprayed with GBHs most likely dissipated or transported with runoff. The few compounds that were detected in the Box Canyon and Madrona Canyon watershed pools were not detected on subsequent visits, indicating the compounds were from recent runoff and likely metabolized in the aquatic environment, and not from deeper groundwater sources that might renew concentrations. Snowmelt does infiltrate from higher elevations, mostly in untreated areas. This water sustains base flow in the pools the spring months and is unlikely transporting GBHs along deeper flow paths. At lower elevations there is potential for infiltration along short flow paths through shallow bedrock fractures associated with Cellar-rock and Lampshire-Romero-Rock outcrop complexes. Stable isotopic signatures of the groundwater can help to characterize water source and timing of infiltration. The groundwater collected at the sites will be marked with a time-averaged isotopic signature of precipitation in the areas where it fell as precipitation, unless evaporation or exchange with rock oxygen have taken place (Eastoe, 2012).

Groundwater stable isotope samples from previous sampling in the Rincon Mountain District and surrounding areas (Eastoe, 2012) were determined to plot along an elevation gradient (0.16 per mil per 100 meters for $\delta^{18}O$ and 1.1 per mil per 100 meters for $\delta^{2}H$). The stable isotopes were determined from volume-weighted precipitation samples from Tucson, Ariz. (2,444 ft), and the Santa Catalina Mountains at a higher elevation (7,946 ft) just north of Tucson. The stable isotope samples collected for the present study were from a small elevation range (2,948 to 3,815 ft) but span a large range of values, which supports the idea that the water in this study represents recent contributions to the groundwater from precipitation rather than from integrated groundwater sources (fig. 13). Pools thought to be affected by groundwater sources were sampled during base flow to generalize the age and source of the groundwater at such sites.

A range of stable isotope ratios were measured at Pool 00 in the Box Canyon watershed and differences in stable isotope ratios helped to distinguish waters influenced by recent rain and elevated GBH compounds from other pool sources. The 2015 treatment was followed by a wet September and this resulted in 0.17 µg/L of glyphosate and 0.63 µg/L of AMPA, and the stable-isotope ratios were low, at −121.7 and −15.16 per mil for $\delta^{2}H$ and $\delta^{18}O$, respectively. The low values are likely related to recent runoff, because the other two samples from Box Canyon Pool 00 from August, 2016, and April, 2017, had higher stable-isotope values (by an order of magnitude), which could be associated with other sources or evaporation. Glyphosate was not detected in these August and April samples and AMPA concentrations were much lower than those measured in September. The stable isotopes support runoff as the primary source of elevated GBH compounds. The timing of the GBH treatment along with rainfall likely contributed to the higher concentrations in the September 2015 sample.

Tritium isotopes were also measured at sites thought to have more groundwater contributions. Nuclear bomb tritium is still present in aquifers recharged with rainwater since about 1953 and therefore tritium can be used to distinguish between water containing tritium below detection limit, which must have recharged before about 1953, and water containing tritium above detection limit, which must contain some water that fell as rain since 1953. Values between 11.3 and 20.9 pCi/L are considered to represent water with residence time on the order of a few decades (Eastoe and others, 2012). The water samples ranged from 9.9 to 18.9 pCi/L, which represent groundwater with residence times of at the most a few decades and may represent more recently recharged waters on the order of years. Box Canyon watershed waters were all greater than 11 pCi/L. The two samples from Madrona Canyon (10.96 pCi/L) and Loma Verde canyon (9.87 pCi/L) were

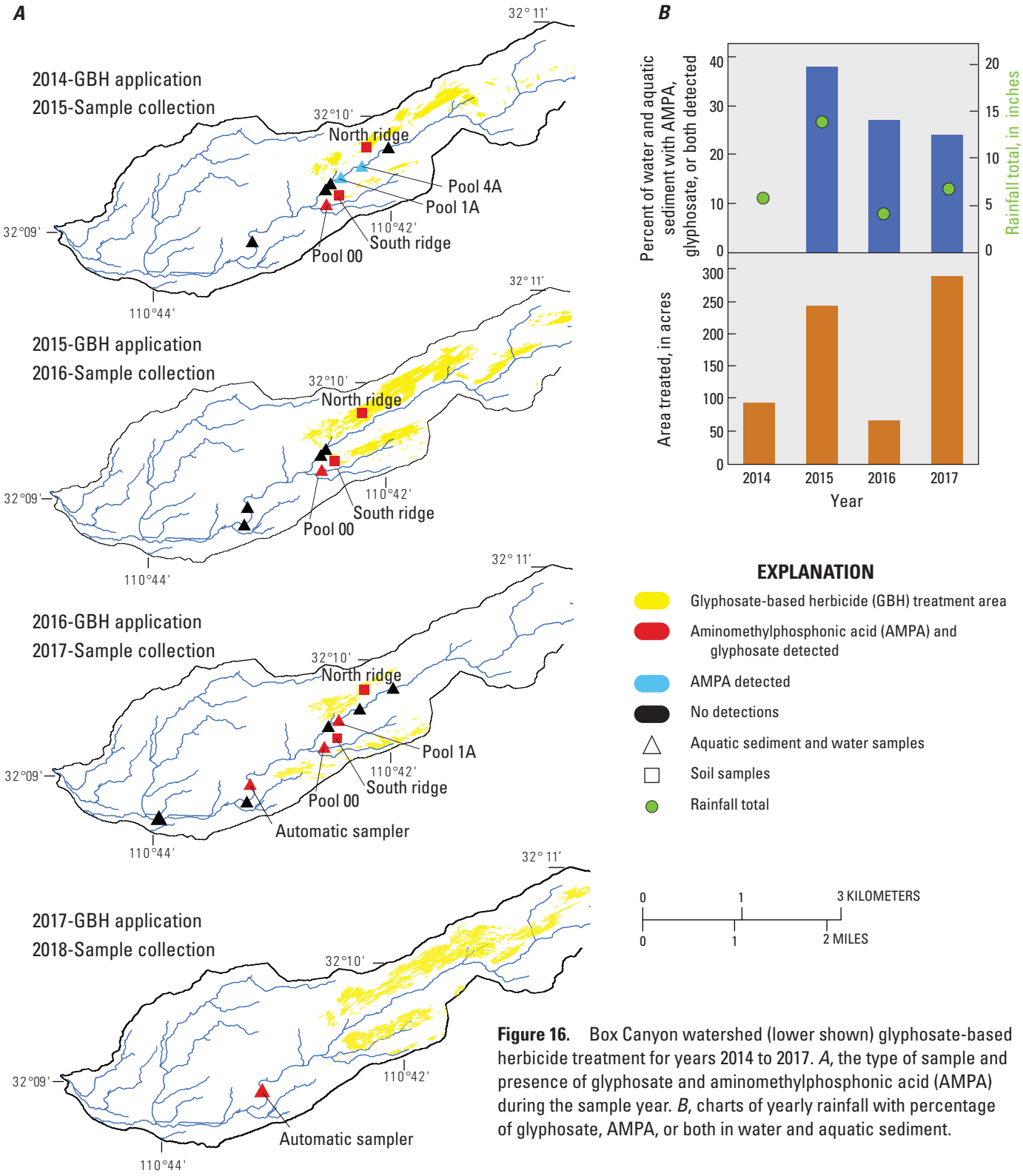

Figure 16. Box Canyon watershed (lower shown) glyphosate-based herbicide treatment for years 2014 to 2017. *A*, the type of sample and presence of glyphosate and aminomethylphosphonic acid (AMPA) during the sample year. *B*, charts of yearly rainfall with percentage of glyphosate, AMPA, or both in water and aquatic sediment.

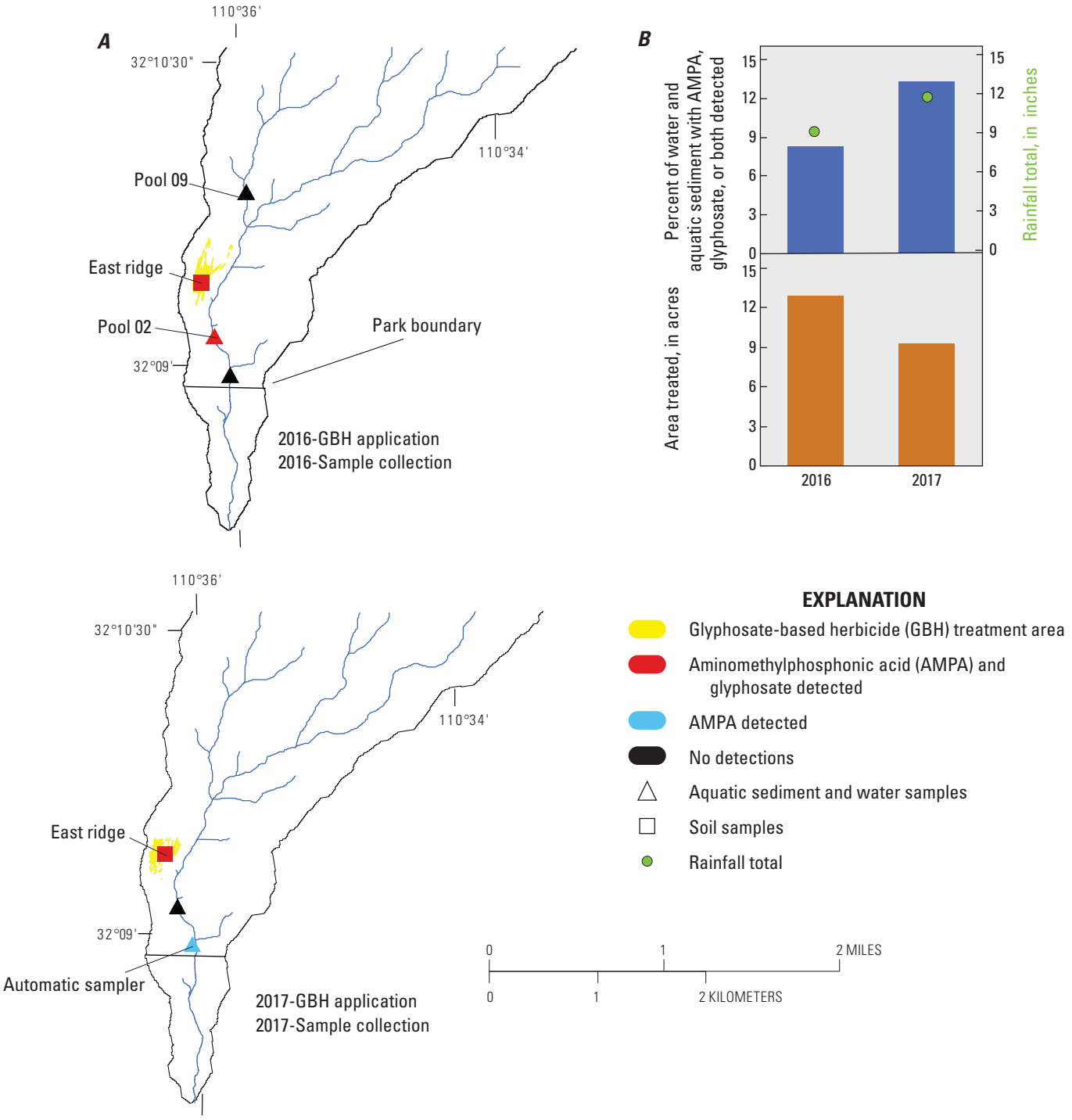

Figure 17. Madrona Canyon watershed glyphosate-based herbicide treatment for years 2016 to 2017. *A*, the type of sample and presence of glyphosate and aminomethylphosphonic acid (AMPA) during the sample year. *B*, charts of yearly rainfall with percentage of glyphosate, AMPA, or both in water and aquatic sediment.

slightly below the 11.3 pCi/L threshold and may represent water that has a small component of water recharged prior to the initiation of above ground nuclear testing starting in 1953. A sample collected from Loma Verde Pool 03 in June 2014 had a tritium value of 2.9 pCi/L with an associated $\delta^{18}O$ and $\delta^{2}H$ of −7.5 and −59 per mil respectively, indicating a minimal evaporative signature. The low tritium value from Loma Verde may suggest a component of older water in at least a portion of this watershed.

The tritium and stable isotope data provide supporting information about the waters sampled and help characterize the infiltration from recent runoff. Based on these data, the waters sampled for GBHs were young in age and most originated from recent runoff or nearby infiltration. Overall the tritium results were more like the tritium signature of rain in the region (Eastoe and others, 2012) and there was minimal evaporation based on most of the stable isotope samples, which indicates these waters are most commonly sourced from localized storm events rather than integrated during several storm seasons.

Ratios of concentrations of glyphosate to AMPA can provide a generalized interpretation of the GBH source and stage of dissipation in the watersheds. Because the soil half-life of AMPA (metabolite) is several times longer than glyphosate (parent compound), the increased accumulation of AMPA over time can provide information about the sources transported and the residence times of compounds. Larger ratios indicate soils were recently treated and transported, whereas smaller ratios indicate a longer period of transformation (dissipation) prior to transport from source to stream (Battaglin and others, 2005; Ramwell and others, 2014; Medalie and others, 2020). In the current study, ratios of one indicate neither glyphosate nor AMPA were detected. Few sample ratios were above one and these samples were water samples collected during runoff or soil collected shortly after GBH treatment. Ratios of 0.5 or less indicate AMPA concentrations are double or more than glyphosate concentrations. Using only ratios below one, the average ratio for soil samples (0.32) was very similar to the average ratio of aquatic sediment samples (0.36), which indicates the sediments found in pools were probably recently deposited from a terrestrial soil source where past GBH application has enough time for glyphosate to degrade to AMPA. Otherwise, aquatic sediments affected by persistent GBHs would likely manifest as smaller ratios than soil. The Box Canyon watershed had the most samples (all medium types) that were below a ratio of 0.5, which is consistent with most years of treatment (average ratio of 0.34). The one soil sample ratio from the 2014 treated Loma Verde canyon was very low at 0.072 whereas the most recent treatment area of Madrona Canyon had an average a ratio of 0.46.

Because glyphosate and AMPA often bind with soil particle surfaces, high intensity precipitation is needed to mobilize such particles and thus the GBHs. Studies have shown a peak in concentrations following heavy rain (Borggaard and Gimsing, 2008) and in one setting AMPA residues peaked as many as 3 weeks later in stream sediments after nearby application and then persisted for more than 1 year (Wan, 1986). Although no discharge was measured during runoff events, maximum flows can be estimated for the watershed from peak-flow recurrence interval regression equations to estimate instantaneous maximum loads (Paretti and others, 2014). The estimated peak discharges listed in table 2 for the Box Canyon watershed were used to compute an instantaneous load calculation. The 100-year recurrence interval flood for peak discharge is estimated between 1,800 and 6,950 cubic feet per second (95-percent confidence interval) (U.S. Geological Survey, 2018). The maximum glyphosate concentration observed in flood waters during the study was 0.20 µg/L in the Box Canyon watershed. Using these flow estimates and maximum glyphosate concentration in an instantaneous load calculation, the maximum peak load estimates range between 9.84×10^{-3} and 3.79×10^{-2} grams per second for the 95-percent lower and upper confidence interval, respectively.

To reframe these estimates using a daily load (total mass per day) calculation with a more common magnitude peak flow, like the 2-year to 5-year peak discharge, the daily loads would range between 132 and 335 grams per day for estimated flows between 278 and 709 cubic feet per second. To our knowledge, floods did not exceed a discharge of 300 cubic feet per second during the study. These observations were based on channel conditions (debris and water marks) during site visits while there was flooding. To put these daily load estimates in context, an over-the-counter common residential-use gallon of Roundup ready-to-use contains 45.4 grams (0.1 pound) a.e. of glyphosate and Roundup super concentration contains 1,633 grams (3.6 pounds) a.e. of glyphosate.

Studies of the household application measured maximum concentrations between 4.00 and 8.99 µg/L of glyphosate and 1.00 and 5.8 µg/L of AMPA in runoff waters collected in the downstream urban drainage (Ramwell and others, 2014; Tang and others, 2015). Rain total and intensity along with user application (frequency and amount applied) affected the runoff concentrations and caused high variability in the measured concentrations (Ramwell and others, 2014; Tang and others, 2015; Hanke and others, 2010). These findings indicate that only a small percentage of the applied GBHs was transported as glyphosate by rainfall runoff and flooding during this study. Relative to what has been reported with household usage, the concentrations transporting from the Rincon Mountain District are lower. It is also assumed that most of the applied GBH was retained in the watershed and (or) degraded. It should be noted that these daily load estimates make several assumptions and do not account for sources of variability. This calculation scenario uses a high-flow maximum discharge to demonstrate what a representative maximum load estimate might be during a high-flow event in the Rincon Mountain District. It should be noted that during the study many of the runoff events had no detections of glyphosate or AMPA.

National Comparison of Different Studies and Applications

Glyphosate-based pesticides are the most widely used in the United States for agricultural and non-agricultural use and have become the largest-selling pesticides in the world (Franz and others, 1997; Baylis, 2000; Veiga and others, 2001; Kolpin and others, 2006). As of 2014, non-agriculture glyphosate use was 26.5 million pounds (Aspelin, 1997; Kiely and others, 2004; Grube and others, 2011; Battaglin and others, 2014; Benbrook, 2016). Several studies have broadly summarized glyphosate and AMPA occurrence and concentration in surface water, groundwater, atmosphere, and sediment samples from diverse hydrologic settings and a wide geographic range of locations in the United States (Battaglin and others, 2005, 2014; Scribner and others, 2007; Struger and others, 2008; Medalie and others, 2020). The studies have also used the data to identify in which hydrologic settings, land-use activities, and medium (water, air, sediment) glyphosate and AMPA are likely to be present, and to a limited degree the temporal patterns of their occurrence or concentrations.

As a comparison to the Rincon Mountain District's use of the GBH, the urban residential, commercial, and municipal uses of GBHs are far more common and frequent. Among other organic and inorganic compounds, stormwater runoff often contains glyphosate, AMPA, and related surfactants at concentrations far exceeding concentrations observed during the Rincon Mountain District study (Ramwell and others, 2002, 2014; Struger and others, 2008, 2015; Byer and others, 2008; Botta and others, 2009; Hanke and others, 2010; Tang and others, 2015). Nonetheless, the extent, type of GBHs used, and contribution to surface-water contamination in an urbanized setting have not been well quantified. Ramwell and others (2014) reported finding maximum concentrations of 8.99 µg/L of glyphosate and 1.15 µg/L of AMPA in runoff waters from localized applications but also noted a marked decrease with subsequent runoff events. Rain total and intensity along with the frequency and amount of GBHs applied affected the magnitude and variability of concentrations measured in runoff (Ramwell and others, 2002, 2014; Hanke and others, 2010; Tang and others, 2015). Differences between what was applied and what was measured as a load were large. Runoff from larger impervious surfaces, such as applications to weeds near sidewalks and roads, resulted in the highest concentrations in the urban setting (Ramwell and others, 2002; Botta and others, 2009; Struger and others, 2015). Concentrations from runoff of these surfaces were as high as 650 µg/L for glyphosate, but glyphosate measurements from subsequent events were 50 and 3.2 µg/L, 2 and 25 days later, respectively (Ramwell and others, 2014). The maximum glyphosate concentrations observed in the Rincon Mountain District runoff were 0.2 and 0.63 µg/L for standing base-flow samples. These measurements were an order to several orders of magnitude lower than concentrations observed in the urban environment where these herbicides are generally applied more frequently (multiple seasons) and where runoff may affect surface and groundwater resources (rivers and shallow wells).

During this study, water concentrations of glyphosate and AMPA were mostly below the laboratory reporting limit and the only samples with detections were collected during runoff and from Pool 00. The Rincon Mountain District median and maximum glyphosate and AMPA water concentrations were lower than median and maximum reported in two U.S. Geological Survey national assessments that compiled samples collected from various land-use settings and watershed sizes within the United States (Battaglin and others, 2014; Medalie and others, 2020; fig. 18*A*). Two of the runoff samples collected in the Box Canyon watershed had concentrations higher than many of the concentrations measured in the national studies, which is a compiled range of concentrations from rivers, streams, wetlands, ponds, and lakes. Medalie and others (2020) observed greater concentrations of glyphosate and AMPA in smaller watersheds or streams compared with larger watersheds and rivers, which is relevant to the small, steeply sloped watersheds commonly present in the Rincon Mountain District.

Similar to the water, median and maximum aquatic sediment glyphosate and AMPA concentrations were lower than the median and maximum soil and sediment sample concentrations compiled from the Midwest region in Battaglin and others (2014; data from 7 sites in Indiana and Mississippi; fig. 18*B*). The highest aquatic sediment concentrations measured in the Box Canyon Pool 00 were higher than a portion of those Midwest concentrations, but these concentrations were statistical outliers in the current study (22 and 76 µg/kg of glyphosate and AMPA, respectively). Aquatic sediments with elevated GBH compounds were mostly found in Pool 00. Pool 00 is below a small catchment—roughly 5 percent of the total watershed area—that had less sustained flow compared to the greater Box Canyon watershed; however, a relatively large percentage of the area of this small catchment was sprayed between 2014 and 2016 (fig. 17*A*). The infrequently flowing drainage feeding Pool 00 likely retains depositional materials sourced from upstream runoff, such as sediments and organic material, as well as potential for wind-blown materials owing to the near proximity of the treatment area. Most aquatic sediment samples had no glyphosate or AMPA, and the few samples from other pools with GBH detections were associated with specific runoff events. Outside of areas like Pool 00, aquatic sediments with GBHs present a low risk for the long-term exposure to aquatic organisms because fine sediments are so limited in the three watersheds.

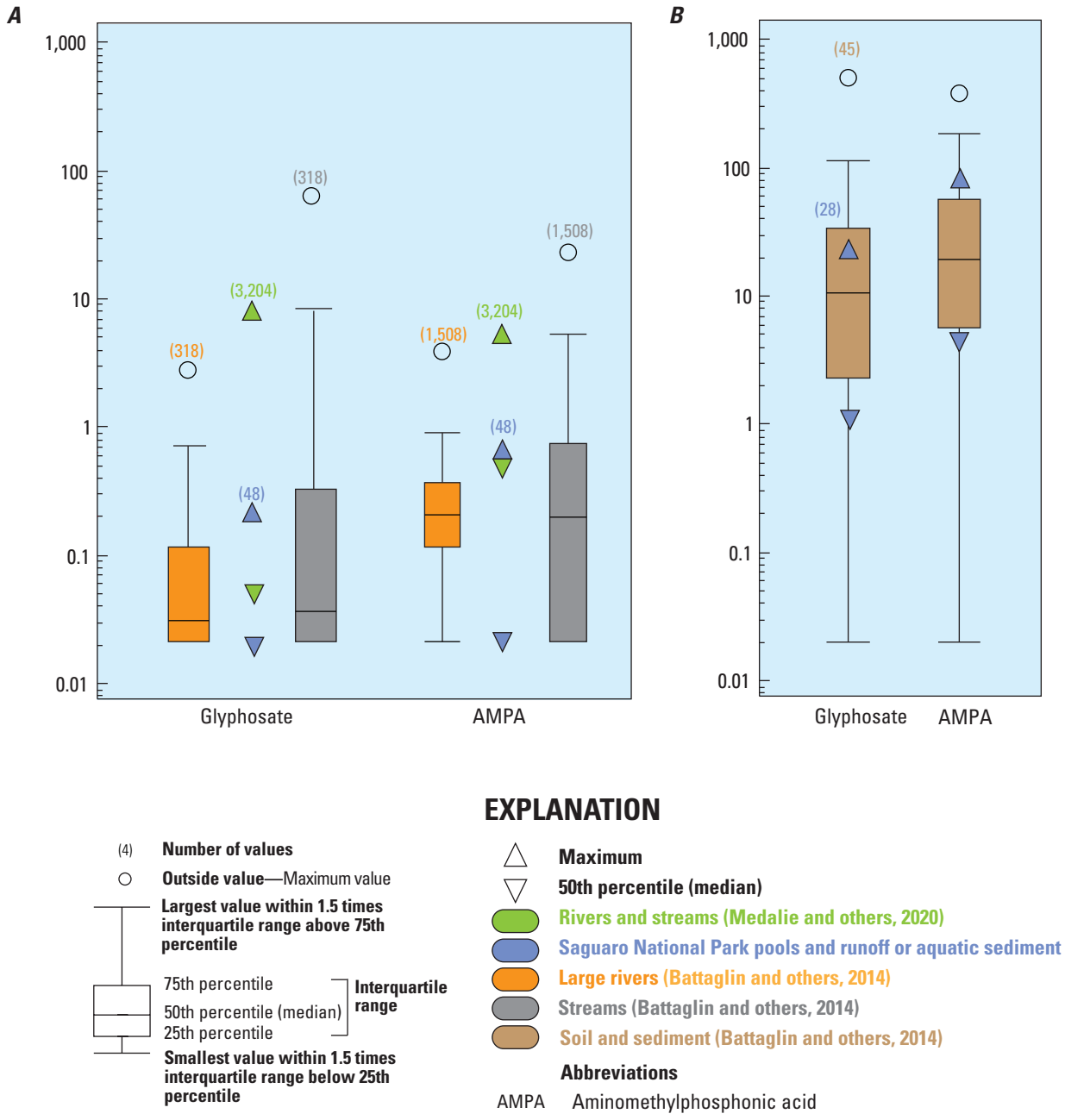

Figure 18. A compilation of glyphosate and aminomethylphosphonic acid (AMPA) concentrations from different U.S. Geological Survey studies and the Rincon Mountain District. Glyphosate and AMPA concentrations observed in *A*, water and *B*, in sediment and compared between this study and other national USGS studies.

Toxicological Review

Glyphosate is a weak acid (alone referred to as "technical grade glyphosate") and the active ingredient in all glyphosate formulation products. The glyphosate in different products carry many chemical forms, such as isopropylamine, dimethylamine, trimesium, and potassium salts (Hanson and others, 2013). Each salt has a different molecular weight affecting the ratio of acid to salt and changing the acid equivalent and chemical properties of many of these formulations. The salts, as well as surfactants and other adjuvants, enhance the adsorption into the plant or change the delivery of the glyphosate into the plant membrane. Although most added surfactants or other adjuvants are not considered active ingredients, they nonetheless have known biological effects (Giesy, and others, 2000; Tsui and Chu, 2003; Edginton and others, 2004; Howe and others, 2004; Fuentes and others, 2011; Papoulias and others, 2013; Vincent and Davidson, 2015). Specifically, surfactants have the greatest negative effect on organisms of all formulation components. The various formulations will

affect the physical and chemical properties, efficacy, and toxicity of the herbicide in different ways. Furthermore, these differences complicate comparisons between formulations and limit studies designed to understand the biological effects and biochemical pathways affecting plant and animal species. As a result, the primary studies of GBH toxicity focus on the active ingredient (glyphosate) or the most common salt (isopropylamine) rather than on the surfactants (which have the greatest negative effect on non-target organisms).

As previously described, when comparing glyphosate concentrations in the different forms (whether it be the technical grade, salts, or other formulations) the a.i. should be converted to the a.e. Glyphosate is an acid but generally comes in different types of salts mixed in solution. Labels contain percentage information as a weight of a.i. per weight of dry or liquid product. This percentage or concentration of glyphosate in a specific salt does not allow researchers to compare percent of glyphosate active ingredient among products. Using an a.e. measure (glyphosate acid per unit volume of product) instead standardizes the percent glyphosate regardless of salt formulation (Hanson and others, 2013).

All pesticides sold or distributed in the United States must be registered by the U.S. Environmental Protection Agency and this registration must be based on scientific studies showing the pesticides can be used without posing unreasonable risks to people or the environment (U.S. Environmental Protection Agency, 1993). Several studies and reviews have investigated various formulations for a wide range of concentrations under different conditions and for different species (Giesy, and others, 2000; Hurley and others, 2008; Székács and Darvas, 2012; Durkin, 2011; Relyea, 2011; Annett and others, 2014). Durkin (2011) provides an extensive literature review and comprehensive human health and ecological risk assessment of glyphosate and glyphosate formulations for the U.S. Department of Agriculture, Forest Service. From this risk analysis, tools were developed to perform many of the calculations used in the human health risk assessments and ecological risk assessments prepared for the different glyphosate applications used by the U.S. Forest Service. Annett and others (2014) also provide an extensive review of the chronic and acute effects.

The U.S. Environmental Protection Agency's drinking water standards (2018) list maximum contaminant levels at 700 µg/L for glyphosate. The child health advisory of the 1- and 10-day dose that is not expected to cause any adverse noncarcinogenic effects during the given 1- or 10-day period is 20 mg/L. The daily oral exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime is 2 milligrams per kilogram per day and the drinking water lifetime exposure level is 70,000 µg/L (U.S. Environmental Protection Agency, 2018). The aquatic life benchmarks for glyphosate and AMPA were all several orders of magnitude greater than any surface-water concentration observed during the study.

Acute toxicity testing determines the concentration of effluent or ambient waters that causes an adverse effect (usually death) on a group of test organisms during a short-term exposure (for example, 24, 48, or 96 hours; U.S. Environmental Protection Agency, 2019). Acute concentrations for fish are 21,500; 249,500; and 34,700 µg/L for glyphosate (technical grade weak acid), AMPA, and the glyphosate isopropylamine salt, respectively (table 8). The invertebrate acute benchmarks are 26,600 and 341,500 µg/L for glyphosate and AMPA, respectively. Chronic toxicity test is a short-term test, usually 96 hours or longer in duration, in which sublethal effects (for example, significantly reduced growth or reproduction) are usually measured in addition to lethality. Chronic levels of glyphosate for fish and invertebrates are 25,700 and 49,900 µg/L, respectively (U.S. Environmental Protection Agency, 2004). The Canadian freshwater-quality guideline is 800 µg/L (Canadian Council of Ministers of the Environment, 2012).

The U.S. Environmental Protection Agency Reregistration Eligibility Decision for glyphosate (U.S Environmental Protection Agency, 1993) states that glyphosate is slightly toxic to birds and is practically non-toxic to fish, aquatic invertebrates, and honeybees, but the inert ingredient—mostly surfactants—in some products must be labeled "toxic to fish" if used in aquatic environments. Although most of the available data indicate that the mammalian toxicity of glyphosate is low, and very few specific hazards can be identified, there are concerns about unknown, less obvious effects to biochemical parameters in blood as well as tissues, and inhibition of some enzymes (Jiraungkoorskul and others, 2003; Cavalcante and others, 2008; Modesto and Martinez, 2010; de Castilhos Ghisi and Cestari, 2013; Webster and others, 2014; Smith and others, 2019).

Acute toxicity testing determines what constitutes a lethal concentration of a substance for 50 percent (LC50) of a given animal population. Chronic toxicity studies generally feed different oral doses of the substance to determine a toxic dose for a specific animal. Chronic limits commonly use the no-observed-adverse-effect concentration (NOAEC) and the lowest-observed-adverse-effect concentration (LOAEC). The NOAEC is a concentration where there is no biologically or statistically significant increase in the frequency or severity of any adverse effects of the tested protocol. The LOAEC is the concentration or amount of a substance determined by experiment or observation that causes an adverse alteration of morphology, function, capacity, growth, development, or lifespan of a target organism distinguished from normal organisms of the same species under defined conditions of exposure. Studies that evaluate acute toxicity and chronic toxicity for glyphosate may not be realistically representative of environmental conditions or routes of exposure, especially for cases where herbicides will be applied in natural resource management settings. However, the LC50 does define an upper limit for organisms, which provides a means to compare various organisms' sensitivities to a given glyphosate formulation, and the effect on a given organism of various glyphosate formulations. The 96-hour LC50 estimates are commonly used to compare this upper toxicity level (U.S. Environmental Protection Agency, 1993).

Table 8. A review summary of the toxicity of glyphosate-based herbicides and aminomethylphosphonic acid (AMPA) on fish, invertebrates and amphibians.

[AMPA, aminomethylphosphonic acid; IPA, isopropylamine salt; h, hour; <, less than; >, greater than; %, percent; a.e., acid equivalent; AST, aspartate transaminase; ALT, alanine transaminase; ALP, alkaline phosphatase; mRNA, messenger ribonucleic acid; TRb, T-cell receptor beta chain; POEA, polyoxyethylene tallow amine; GS, Gosner stage; LC50, lethal concentration of 50 percent of the population tested; LC10, lethal concentration of 10 percent of the population tested; NOAEC, no observed adverse effect concentration; LOAEC, lowest observed adverse effect concentration; --, not applicable]

Reference	Species or general group	Chemical	Exposure type, organism stage, and information	LC50, in micrograms per liter	NOAEC, in micrograms per liter	LOAEC, in micrograms per liter	Exposure duration or endpoint	Effect information
U.S. Environmental Protection Agency, 2019	Fish	Glyphosate	Acute	21,500	--	--	Lethal	--
	Fish	Glyphosate metabolite AMPA	Acute	249,500	--	--	Lethal	--
	Fish	Glyphosate IPA	Acute	34,700	--	--	Lethal	--
	Invertebrates	Glyphosate	Acute	26,600	--	--	Lethal	--
	Invertebrates	Glyphosate metabolite AMPA	Acute	341,500	--	--	Lethal	--
	Fish	Glyphosate	Chronic	25,700	--	--	Lethal	--
	Invertebrates	Glyphosate	Chronic	49,900	--	--	Lethal	--
U.S. Environmental Protection Agency, 2008	Fathead minnow	Glyphosate acid, technical grade	Chronic	--	25,700	--	Life-cycle	--
	Rainbow trout	Vision (356 grams per liter glyphosate acid with surfactant)	Chronic	--	8	4.25–45.75	2 months	Behavior
Webster and others, 2014	Zebra fish	Glyphosate and Roundup	Chronic	--	--	10,000	21 days	Reproductive effects
Smith and others, 2019	Japanese medaka	Roundup	Chronic	--	--	500 and 5,000	15 days	Reproductive and epigenetic effects.
Cavalcante and others, 2008	Streaked prochilod	Roundup	Acute	--	--	10,000	6, 24, 96 h	Genotoxic effects
Modesto and Martinez, 2010	Streaked prochilod	Roundup	Acute	--	--	10,000	6, 24, 96 h	Oxidative stress in liver and inhibited acetylcholinesterase production.
de Castilhos Ghisi and Cestari, 2013	Mottled corydoras	Roundup	Chronic	--	--	6.67 (3.20 glyphosate)	3, 6, 9 days	Genotoxic effects
Jiraungkoorskul and others, 2003	Nile tilapia	Roundup (IPA, 48% a.e.)	Chronic	--	--	7,200	3 months	Decrease in plasma AST, ALT, and ALP enzyme activities; changes in gill, liver, and kidney consistent with tissue degeneration.
	Nile tilapia	Roundup (IPA, 48% a.e.)	Chronic	--	500	1,500	3 months	Organs exhibited varying degrees of histopathological change.
Cauble and Wagner, 2005	Cascades frog larvae	Roundup, 50.2% IPA	Chronic	--	--	1,000 to 2,000	43 days	Decrease in survival times and earlier metamorphosis in 1,000 micrograms per liter.

Table 8. A review summary of the toxicity of glyphosate-based herbicides and aminomethylphosphonic acid (AMPA) on fish, invertebrates and amphibians. —Continued

[AMPA, aminomethylphosphonic acid; IPA, isopropylamine salt; h, hour; <, less than; >, greater than; %, percent; a.e., acid equivalent; AST, aspartate transaminase; ALT, alanine transaminase; ALP, alkaline phosphatase; mRNA, messenger ribonucleic acid; TRb, T-cell receptor beta chain; POEA, polyoxyethylene tallow amine; GS, Gosner stage; LC50, lethal concentration of 50 percent of the population tested; LC10, lethal concentration of 10 percent of the population tested; NOAEC, no observed adverse effect concentration; LOAEC, lowest observed adverse effect concentration; --, not applicable]

Reference	Species or general group	Chemical	Exposure type, organism stage, and information	LC50, in micrograms per liter	NOAEC, in micrograms per liter	LOAEC, in micrograms per liter	Exposure duration or endpoint	Effect information
Howe and others, 2004	Green frog, northern leopard frog, wood frog, and the American toad	Roundup Original, Roundup Transorb-15% POEA, and Roundup Bioctive, Touchdown, and Glyfos Autand, Glyfos BIO, the active ingredient, glyphosate IPA, and POEA (larvae treated with Roundup Original at 1,800 micrograms a.e per liter or with Roundup Transorb at 0.6 and 1.8 milligrams a.e. per liter)	Acute: GS 25; Concentrations were renewed only once each week over the 6 week duration of exposure.	--	--	600 to 1,800	42 days	Changes in TRb mRNA, sex ratio, tail length, tail damage, histology, and morphometrics.
	Leopard frog	Roundup Original	Acute: GS 25	2,900	--	--	--	Lethal
	Leopard frog		Acute: GS20	6,500	--	--	--	Lethal
	Wood frog		Acute: GS 25	5,100	--	--	--	Lethal
	Wood frog		Acute: GS 20	>8,000	--	--	--	Lethal
	American toad		Acute: GS 25	<4,000	--	--	--	Lethal
	American toad		Acute: GS 20	8,000	--	--	--	Lethal
	Green frog		Acute: GS 25	2,000	--	--	--	Lethal
	Green frog		Acute: GS 20	7,100	--	--	--	Lethal
	Green frog	Glyphosate technical	Acute: GS 25	>17,900	--	--	--	Lethal
	Green frog	POEA	Acute: GS 25	2,200	--	--	--	Lethal
	Green frog	Roundup Biactive	Acute: GS 25	>17,900	--	--	--	Lethal
	Green frog	Touchdown	Acute: GS 25	>17,900	--	--	--	Lethal
	Green frog	Glyfos BIO (glyphosate IPA, and POEA)	Acute: GS 25	>17,900	--	--	--	Lethal
	Green frog	Glyfos AU (glyphosate IPA, and POEA)	Acute: GS 25	8,900	--	--	--	Lethal
	Green frog	Roundup Transorb (15 percent POEA)	Acute: GS 25	2,200	--	--	--	Lethal

Table 8. A review summary of the toxicity of glyphosate-based herbicides and aminomethylphosphonic acid (AMPA) on fish, invertebrates and amphibians. —Continued

[AMPA, aminomethylphosphonic acid; IPA, isopropylamine salt; h, hour; <, less than; >, greater than; %, percent; a.e., acid equivalent; AST, aspartate transaminase; ALT, alanine transaminase; ALP, alkaline phosphatase; mRNA, messenger ribonucleic acid; TRb, T-cell receptor beta chain; POEA, polyoxyethylene tallow amine; GS, Gosner stage; LC50, lethal concentration of 50 percent of the population tested; LC10, lethal concentration of 10 percent of the population tested; NOAEC, no observed adverse effect concentration; LOAEC, lowest observed adverse effect concentration; --, not applicable]

Reference	Species or general group	Chemical	Exposure type, organism stage, and information	LC50, in micrograms per liter	NOAEC, in micrograms per liter	LOAEC, in micrograms per liter	Exposure duration or endpoint	Effect information
Edge and others, 2014	Wood frog larvae	Roundup Weed and Grass Control1 and Roundup WeatherMax	Acute	--	--	140–1,100 and 4,940 to 8,260	--	Lethal
	Wood frog larvae	Roundup WeatherMax	Acute	--	--	210low, 2,880high	--	Lethal
Jones and others, 2010	Two families: woodfrogs and American toads	Roundup Original Max	Acute	--	--	1,000–3,000	--	Lethal
Relyea and Jones, 2009	Wood frog, Leopard frog, Cascades frog, Green frog, American bullfrog, American toad, Western toad, Gray tree frog	Roundup Original Max	Acute	--	--	1,000–5,000, lethal 800 to 2,000 for larval anurans	--	Lethal, at 1,000 micrograms per liter for most leopard frogs
	Wood frog		Acute	1,900	--	1,300 (LC10)	--	--
	Leopard frog		Acute	1,500	--	1,200 (LC10)	--	--
	Cascades frog		Acute	1,700	--	1,200 (LC10)	--	--
	Green frog		Acute	1,400	--	1,000 (LC10)	--	--
	American bullfrog		Acute	800	--	500 (LC10)	--	--
	American toad		Acute	1,600	--	1,200 (LC10)	--	--
	Western toad		Acute	2,000	--	1,700 (LC10)	--	--
	Gray tree frog		Acute	1,700	--	1,400 (LC10)	--	--
	Spring peeper		Acute	800	--	100 (LC10)	--	--
	Northwestern salamander		Acute	2,800	--	2,400 (LC10)	--	--
	Spotted salamander		Acute	2,800	--	2,400 (LC10)	--	--
	Blue-spotted salamander		Acute	3,200	--	2,700 (LC10)	--	--
	Red-spotted newt		Acute	2,700	--	2,300 (LC10)	--	--

Table 8. A review summary of the toxicity of glyphosate-based herbicides and aminomethylphosphonic acid (AMPA) on fish, invertebrates and amphibians. —Continued

[AMPA, aminomethylphosphonic acid; IPA, isopropylamine salt; h, hour; <, less than; >, greater than; %, percent; a.e., acid equivalent; AST, aspartate transaminase; ALT, alanine transaminase; ALP, alkaline phosphatase; mRNA, messenger ribonucleic acid; TRb, T-cell receptor beta chain; POEA, polyoxyethylene tallow amine; GS, Gosner stage; LC50, lethal concentration of 50 percent of the population tested; LC10, lethal concentration of 10 percent of the population tested; NOAEC, no observed adverse effect concentration; LOAEC, lowest observed adverse effect concentration; --, not applicable]

Reference	Species or general group	Chemical	Exposure type, organism stage, and information	LC50, in micrograms per liter	NOAEC, in micrograms per liter	LOAEC, in micrograms per liter	Exposure duration or endpoint	Effect information
Relyea, 2005	Wood frog	Roundup	Acute	600–2,500	--	--	--	Lethal
	Leopard frog		Acute	600–2,500	--	--	--	Lethal
	Green frog		Acute	600–2,500	--	--	--	Lethal
	American bullfrog		Acute	600–2,500	--	--	--	Lethal
	American toad		Acute	600–2,500	--	--	--	Lethal
	Gray tree frog		Acute	600–2,500	--	--	--	Lethal
Navarro-Martín and others, 2014	Wood frog tadpoles	Four different concentrations of VisionMax®	Chronic	--	--	21 to 2,900 effects observed	--	Changes in sex ratios, gonadal morphology, histology. Gene expression alteration in brain and tail tissues.
	Wood frog tadpoles	Roundup WeatherMax®, Vision® herbicides as well as the active ingredient (IPA) and the POEA surfactant of Vision®	Chronic: GS 37–42	--	--	--	--	Treatment reduced the genes controlling development in tadpoles. Affected hormone receptors for the liver, brain, and tail.
	Wood frog tadpoles	Roundup WeatherMax®	Acute	2,890	--	--	--	100% mortality after first pulse
	Wood frog tadpoles	Roundup WeatherMax®	Chronic: GS 36–38	--	--	210	--	Increased condition factor
	Wood frog tadpoles	Vision®	Chronic: GS 36–38	--	--	2,890	--	Increased condition factor
	Wood frog tadpoles	IPA and the POEA	Chronic: GS 42	--	--	--	--	Decreased condition factor
Papoulias and others, 2013	Plains leopard	Glyphosate	Acute	--	--	1,150–1,170	--	Ovarian dysgenesis, high rates of testicular oocytes, and female-biased sex ratios.
Giesy and others, 2000	Most sensitive species, centric diatom, genus *Skeletonema*	Roundup, glyphosate	Chronic	--	280–3,360	--	--	--
	Invertebrate, Water flea Fish,		Chronic	--	500–3200	--	--	--
	Rainbow trout		Chronic	--	740	--	21 days	--

Table 8. A review summary of the toxicity of glyphosate-based herbicides and aminomethylphosphonic acid (AMPA) on fish, invertebrates and amphibians. —Continued

[AMPA, aminomethylphosphonic acid; IPA, isopropylamine salt; h, hour; <, less than; >, greater than; %, percent; a.e., acid equivalent; AST, aspartate transaminase; ALT, alanine transaminase; ALP, alkaline phosphatase; mRNA, messenger ribonucleic acid; TRb, T-cell receptor beta chain; POEA, polyoxyethylene tallow amine; GS, Gosner stage; LC50, lethal concentration of 50 percent of the population tested; LC10, lethal concentration of 10 percent of the population tested; NOAEC, no observed adverse effect concentration; LOAEC, lowest observed adverse effect concentration; --, not applicable]

Reference	Species or general group	Chemical	Exposure type, organism stage, and information	LC50, in micrograms per liter	NOAEC, in micrograms per liter	LOAEC, in micrograms per liter	Exposure duration or endpoint	Effect information
Fuentes and others, 2011	Leopard frog	Roundup Original [IPA of glyphosate (29.7% a.e.) with MON 0818 (15%)]	Acute/chronic:96 h, GS 25	1,800	1,290	1,320	--	--
	Southern leopard frog		Acute/chronic:96 h, GS 25	2,050	1,520	1,810	--	--
	Cope's gray tree frog		Acute/chronic:96 h, GS 25	2,500	1,740	2,100	--	--
	American bullfrog		Acute/chronic:96 h, GS 25	2,770	2,020	2,520	--	--
	Fowler's toad		Acute/chronic:96 h, GS 25	4,210	3,400	3,950	--	--
	Green frog		Acute/chronic:96 h, GS 25	4,220	3,270	3,680	--	--
	Southern leopard frog	Roundup WeatherMAX [potassium salt of glyphosate (39.9% a.e.) with a proprietary surfactant]	Acute/chronic:96 h, GS 25	1,330	680	980	--	--
	Fowler's toad		Acute/chronic:96 h, GS 25	1,960	1,540	1,560	--	--
	American bullfrog		Acute/chronic:96 h, GS 25	1,970	1,330	1,370	--	--
	Leopard frog		Acute/chronic:96 h, GS 25	2,270	1,650	1,680	--	--
	Green frog		Acute/chronic:96 h, GS 25	2,770	1,910	2,370	--	--
	Cope's gray tree frog		Acute/chronic:96 h, GS 25	3,260	2,480	2,870	--	--
Moore and others, 2012	Leopard frog	MON 0818 (POEA)	Acute: 96 h, GS 25	680	380	--	--	--
	Cope's gray tree frog		Acute: 96 h, GS 25	830	590	--	--	--
	American bullfrog		Acute: 96 h, GS 25	830	590	--	--	--
	Fowler's toad		Acute: 96 h, GS 25	800	590	--	--	--
	Green frog		Acute: 96 h, GS 25	1,320	920	--	--	--

Table 8. A review summary of the toxicity of glyphosate-based herbicides and aminomethylphosphonic acid (AMPA) on fish, invertebrates and amphibians. —Continued

[AMPA, aminomethylphosphonic acid; IPA, isopropylamine salt; h, hour; <, less than; >, greater than; %, percent; a.e., acid equivalent; AST, aspartate transaminase; ALT, alanine transaminase; ALP, alkaline phosphatase; mRNA, messenger ribonucleic acid; TRb, T-cell receptor beta chain; POEA, polyoxyethylene tallow amine; GS, Gosner stage; LC50, lethal concentration of 50 percent of the population tested; LC10, lethal concentration of 10 percent of the population tested; NOAEC, no observed adverse effect concentration; LOAEC, lowest observed adverse effect concentration; --, not applicable]

Reference	Species or general group	Chemical	Exposure type, organism stage, and information	LC50, in micrograms per liter	NOAEC, in micrograms per liter	LOAEC, in micrograms per liter	Exposure duration or endpoint	Effect information
Edginton and others, 2004	African clawed frog	Vision (356 grams per liter glyphosate acid with surfactant, MON 0818)	Acute: Embryo pH 6; GS 8–25	15,000	--	6,200 (LC10)	--	--
	African clawed frog		Acute: Embryo pH 7.5; GS 8–25	7,900	--	4,000 (LC10)	--	--
	African clawed frog		Acute: Larvae pH 6; GS 25	2,100	--	1,900 (LC10)	--	--
	African clawed frog		Acute: Larvae pH 7.5; GS 25	800	--	800 (LC10)	--	--
	American toad		Acute: Embryo pH 6; GS 8–25	4,800	--	2,200 (LC10)	--	--
	American toad		Acute: Embryo pH 7.5; GS 8–25	6,400	--	4,300 (LC10)	--	--
	American toad		Acute: Larvae pH 6; Gosner stage 25	2,900	--	2,100 (LC10)	--	--
	American toad		Acute: Larvae pH 7.5; GS 25	1,700	--	1,200 (LC10)	--	--
	Green frog		Acute: Embryo pH 6; GS 8–25	5,300	--	2,600 (LC10)	--	--
	Green frog		Acute: Embryo pH 7.5; GS 8–25	4,100	--	2,800 (LC10)	--	--
	Green frog		Acute: Larvae pH 6; GS 25	3,500	--	2,100 (LC10)	--	--
	Green frog		Acute: Larvae pH 7.5; GS 25	1,400	--	800 (LC10)	--	--
	Leopard frog		Acute: Embryo pH 6; GS 8–25	15,000	--	13,000 (LC10)	--	--
	Leopard frog		Acute: Embryo pH 7.5; GS 8–25	7,500	--	6,700 (LC10)	--	--
	Leopard frog		Acute: Larvae pH 6; GS 25	1,800	--	1,100 (LC10)	--	--
	Leopard frog		Acute: Larvae pH 7.5; GS 25	1,100	--	800 (LC10)	--	--

Table 8. A review summary of the toxicity of glyphosate-based herbicides and aminomethylphosphonic acid (AMPA) on fish, invertebrates and amphibians. —Continued

[AMPA, aminomethylphosphonic acid; IPA, isopropylamine salt; h, hour; <, less than; >, greater than; %, percent; a.e., acid equivalent; AST, aspartate transaminase; ALT, alanine transaminase; ALP, alkaline phosphatase; mRNA, messenger ribonucleic acid; TRb, T-cell receptor beta chain; POEA, polyoxyethylene tallow amine; GS, Gosner stage; LC50, lethal concentration of 50 percent of the population tested; LC10, lethal concentration of 10 percent of the population tested; NOAEC, no observed adverse effect concentration; LOAEC, lowest observed adverse effect concentration; --, not applicable]

Reference	Species or general group	Chemical	Exposure type, organism stage, and information	LC50, in micrograms per liter	NOAEC, in micrograms per liter	LOAEC, in micrograms per liter	Exposure duration or endpoint	Effect information
Vincent and Davidson, 2015	Western toad tadpoles	Glyphosate IPA alone	Acute: 48 h	6,392,000	--	--	--	--
	Western toad tadpoles	Glyphosate IPA with Agri-dex	Acute: 48 h	4,254,000	--	--	--	--
	Western toad tadpoles	Glyphosate IPA with Competitor	Acute: 48 h	711,000	--	--	--	--

Durkin's (2011) literature review and ecological risk assessment of glyphosate and glyphosate formulations presents a wide range of LC50 studies and toxicity testing performed by the U.S. Environmental Protection Agency and other researchers that includes data from the research studies mentioned earlier in the section (Giesy and others, 2000; Hurley and others, 2008; Relyea, 2011; Székács and Darvas, 2012). As a way to summarize Durkin's (2011) data review in the context of the Rincon Mountain District study, LC50 a.e. concentrations were compiled for fish, aquatic-phase amphibians (tadpoles and frogs only), and aquatic invertebrates (appendixes 6–8 in Durkin, 2011), and broadly grouped by glyphosate formulation type as a means to generalize acute toxicity testing in the aquatic environment. This approach compiles single LC50 concentrations reported from multiple studies without consideration of uncertainty or study design and presented as a statistical distribution or boxplot. Because these LC50 distributions are presented for a broad group of organisms exposed to a range of glyphosate products, the values presented should by no means be used to define ecological criteria for aquatic resources in the Rincon Mountain District. The purpose of placing the Rincon Mountain District results within the context of the LC50 distributions is to provide a broader value range that could be considered the upper bounds of detrimental effects to aquatic organisms in the park. General comparisons among fish, amphibians, and aquatic invertebrates LC50 results were made for the technical grade glyphosate and glyphosate formulations presented by Durkin (2011). A higher LC50 response indicates a less toxic substance; therefore, a low LC50 response is related to a more toxic chemical response.

The technical grade form of glyphosate overall had a higher LC50 dose or required more chemical to get the LC50 response for all three groups of organisms (fish, amphibians, and invertebrates) when compared to other formulations. Median concentrations for fish and amphibians were near 100 mg/L a.e., whereas aquatic invertebrates were slightly higher at around 130 mg/L a.e. Aquatic macroinvertebrates overall appeared to be more tolerant of glyphosate than the other two groups. This tolerance was more obvious in the glyphosate formulation LC50 toxicity testing where LC50 responses for aquatic invertebrates were 5 to 10 times greater than for fish and amphibians, respectively. Median LC50 concentrations for the glyphosate formulations were around 8 mg/L a.e. for fish, 4 mg/L a.e. for frogs, and 44 mg/L a.e. for aquatic macroinvertebrates (Durkin, 2011). For reference these concentrations are 4 to 5 orders of magnitude greater than the highest concentration detected in water at the Rincon Mountain District (0.0002 mg/L a.e.).

The most common fish family tested was the salmonids (rainbow trout and other salmon species). Although no fish currently reside in the three the Rincon Mountain District watersheds studied, future introduction of native fish is a possibility. However, the glyphosate formulation LC50 species summarized here have little species relation to the possible options for native fish reintroduction and the LC50 response for native fish may be quite different (fig. 19*A*). The amphibian testing focused primarily on four species, but none appeared to have major differences in the glyphosate formulation LC50 testing. Life stage appeared to be an important tolerance factor; tadpoles and embryos overall had greater LC50 concentrations. There were species from the genus *Lithobates,* the same genus as the lowland leopard frog, used in many of the toxicity tests, but comparing this directly to native species response would require further testing (Durkin, 2011).

Distinguishing between the different formulations presented in Durkin (2011) would be difficult and would require individual analysis of each study, which was outside the scope of this review. Some general groupings were applied to the different glyphosate formulations (fig. 19*B*). Primarily, these were distinguished as the inclusion or non-inclusion of the surfactant POEA, or the inclusion of another unknown surfactant such as those in Roundup brand name formulations. General patterns indicated that lower LC50 (greater toxicity) concentrations were associated with the POEA surfactant formulations (median concentration of 7 mg/L a.e.) as well as the various unspecific Roundup formulations with surfactants (median concentration of 11 mg/L a.e.). Overall, the non-surfactant formulations had much higher LC50 (lower toxicity) concentrations. Although associated pH data were limited, there did appear to be a trend in the response to concentrations at different pHs (6 to 9.5) for technical grade glyphosate which increased 2 orders of magnitude with increased pH (less harmful) and decreased 1 order of magnitude with decreasing pH for glyphosate formulations (more harmful).

Research on more environmentally relevant concentrations, such as chronic toxicity, genotoxic effects, and endocrine disrupting effects were reviewed for this report. There is no literature specifically on the lowland leopard frog, but studies have been conducted on many aquatic invertebrate and vertebrate species. Physiological and neurological pathways can be affected by low-level concentrations of glyphosate and glyphosate formulations (Jiraungkoorskul and others, 2003; Cauble and Wagner, 2005; Cavalcante and others, 2008; Modesto and Martinez, 2010; de Castilhos Ghisi and Cestari, 2013; Webster and others, 2014). Published NOAECs and LOAECs are generally multiple orders of magnitude above the highest glyphosate concentrations measured in water resources during this study. More important considerations are the potential interactions among disease, pesticides, and water quality in amphibian habitats. It is possible low-level concentrations might not always have immediate or obvious effects, but the combination of exposure, timing, and emerging diseases will have the greatest effect on aquatic organisms. Sediments may also play a larger role in the potential effects to amphibians (Fuentes and others, 2011). Aquatic sediment detections in the Rincon Mountain District were infrequent, but they were observed in sensitive habitats used by lowland leopard frogs. Unfortunately, no studies provide sediment effect levels that could be compared to sediment levels in the Rincon Mountain District pools.

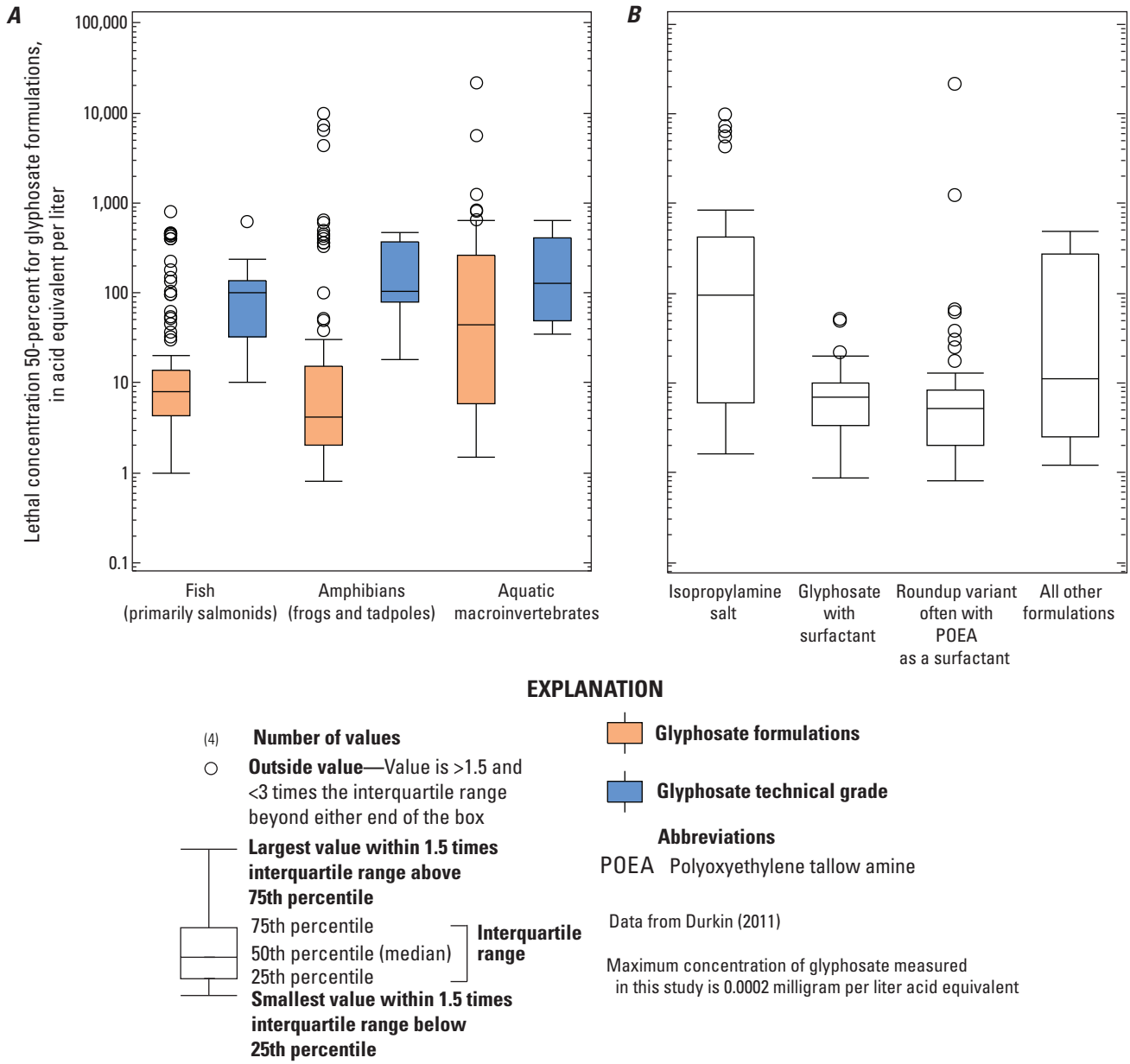

Figure 19. Glyphosate-based herbicide lethal concentration 50 percent (LC50). *A*, General groups classified as fish, amphibians, and macroinvertebrates and *B,* LC50 concentrations grouped by glyphosate-based herbicide formulations.

All measured glyphosate concentrations in the study were well below the Federal water-quality criteria and benchmarks for drinking water, chronic, and acute levels for surface-water and freshwater organisms (U.S. Environmental Protection Agency, 2018). Glyphosate from the application area is thus likely to have low ecotoxicological significance. Concentrations observed in the aquatic resources in the Rincon Mountain District were low relative to other published NOAEC and LOAEC criteria (U.S. Environmental Protection Agency, 1993). Additional studies could focus on relevant concentrations using environmental conditions consistent with the Rincon Mountain District, but in a laboratory setting. This would help control the variability of the levels observed in water and sediment and understand the exposure timing and potential effects this may have on the metamorphosis of lowland leopard frogs.

Summary

The National Park Service staff has been tasked to protect the Rincon Mountain District desert ecosystems from an unprecedented threat from buffelgrass (*Cenchrus ciliaris* L.). The dense monoculture buffelgrass infestations greatly increase the connectivity of dry fuels that carry intense wildfires, which native species are not adapted to withstand. The Rincon Mountain District initiated a helicopter aerial restoration plan to control dense buffelgrass patches in remote areas and in 2014, more than 250 acres of buffelgrass in the Rincon Mountain District were treated with glyphosate-based herbicides (GBHs). This widespread aerial application of GBHs continued through 2018, but the potential transport and effects to aquatic ecosystems were unknown.

In 2015–18, the U.S. Geological Survey, in cooperation with the National Park Service, studied the occurrence, distribution, fate, and transport of glyphosate in surface water and sediments derived from areas that were treated during past and current aerial herbicide applications. Three watersheds, treated with different regimens of GBHs, were sampled for glyphosate and the primary metabolite of glyphosate, aminomethylphosphonic acid (AMPA), during various hydrologic flow conditions. Water and aquatic sediment were collected from three watersheds, each in a different stage of application during the U.S. Geological Survey study. Loma Verde canyon had received no aerial treatment since 2014, whereas the Box Canyon watershed was aerially treated every year beginning in 2014. The Madrona Canyon watershed was first sprayed in 2016 and aerial application continued once a year though the entirety of the study. In addition, terrestrial soil samples were sampled from areas sprayed to understand dissipation rates and herbicide transport via sediments washing away during rainfall runoff. The concentrations present in water and sediment samples were compared to ecological benchmarks and characterized within the context of the environmental conditions of the park setting.

Of the 48 water samples collected and analyzed for glyphosate and AMPA, 10.4 percent and 14.6 percent were detected above the laboratory minimum detection limit, respectively. Mean water concentrations, calculated using specific statistical methods for non-detects, were equal to the laboratory minimum detection limit of 0.02 microgram per liter for samples collected in all the watersheds. In aquatic sediments, glyphosate and AMPA were detected in 10.7 and 25.0 percent of the samples, whereas 89.5 and 100 percent of the terrestrial soil samples had detections for glyphosate and AMPA, respectively. Mean aquatic sediment concentrations were 1.13 and 4.42 micrograms per kilogram (µg/kg) for glyphosate and AMPA, respectively. Mean terrestrial soil concentrations were orders of magnitude greater than water and aquatic sediment with concentrations of 678 µg/kg for AMPA and 1,240 µg/kg for glyphosate. Hours after glyphosate-based herbicide was applied, the concentrations of glyphosate and AMPA were present in terrestrial soil samples near or above the laboratory maximum detection limit of 5,000 µg/kg. The Box Canyon watershed was the most intensively treated watershed in terms of total land area treated, total amount of GBH applied, and number of years treated. The frequent and large volume of treatment resulted in the highest number of detections of glyphosate and AMPA in water (3 and 7 detections, respectively) and in aquatic sediment (2 and 6 detections, respectively) samples. In comparison, the other two watersheds had two or fewer detections for glyphosate and AMPA in water and aquatic sediment.

Glyphosate detected in pools was associated with increased rainfall closer in time to the last herbicide treatment. Glyphosate and AMPA concentration ratios above one, along with stable-isotope and tritium results, indicated that runoff processes were the primary transport mechanism for the two compounds when found in streams and pools rather than subsurface recharge or deeper flow paths. Pool 00 (USGS station 320915110423101) located in a small tributary of the larger Box Canyon watershed consistently had detections of glyphosate and AMPA in aquatic sediments, but these frequent concentrations were likely related to the intensive application upstream, near the steep terrain above the head of the channel that supplies the downstream pool. Intense flows during summer rainfall events move treated sediments into this channel where vegetation and the incised bedrock banks of the pool retained those sediments and ultimately led to frequent detections of both compounds. Isotope results in most of the pools and tinajas indicated that the water source had residence time representative of recently recharged waters, on the order of years.

No water concentrations exceeded published criteria for human health or aquatic life. Median and maximum glyphosate and AMPA water concentrations were lower than those reported in other national assessments, but concentrations observed in individual runoff samples were higher than a proportion of the concentrations measured in national U.S. Geological Survey studies. A similar finding was observed with aquatic sediment concentrations measured in the Rincon Mountain District. Results from the study were compared and assessed in the context of other studies examining GBHs and their effects on amphibians, fish, and macroinvertebrates. This comparison was used to generalize the potential risk to aquatic species similar to those species in the Rincon Mountain District. Concentrations of published effect levels were several orders magnitude greater than the highest concentration detected in water at the Rincon Mountain District. Most published studies evaluate acute and chronic toxicity for glyphosate and GBHs, and these criteria may not be representative of environmental conditions in the Rincon Mountain District. The classic lethal dose studies conducted in a controlled laboratory setting may not be suitable for comparison to the longer, variable, low-dose exposure conditions in the pools and tinajas in the Rincon Mountain District. However, this study determined that the fate of GBHs transported from treated areas to potential aquatic habitat was highly variable in occurrence, timing, and concentrations. This variability in glyphosate concentrations was too high, and the potential exposure was determined to be far too complex to directly compare with the results from controlled studies. No testing has been conducted on the lowland leopard frog and additional studies would need to be completed to understand the potential effects of these levels in relation to environmental conditions consistent with those in the Rincon Mountain District.

Very little information exists about the fate of GBHs in the semiarid desert using aerial treatment methods. This study provides the first information collected on GBHs used to control invasive buffelgrass in a remote, mountainous, and semiarid setting. The information about the transport and fate of herbicide application near aquatic habitat will help to inform managers about the broader ecosystem implications and provide useful information to other agencies implementing buffelgrass remediation strategies near aquatic habitat.

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