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DIURON FROM MAUI SUGARCANE FIELD RUNOFF IS POTENTIALLY HARMFUL TO LOCAL CORAL REEFS

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ABSTRACT

In a grassroots effort to identify stressors influencing the health of Maui's coral reefs, samples for the pre- and post-emergent herbicide, Diuron, were taken in July–August 2013, prior to, during, and after the passage of Tropical Storm Flossie on the south central coast of Maui, Hawaii. Diuron is routinely used on sugarcane fields adjacent to Hawaiian coastal waters and is a component of the anti-fouling paint used on small boats. It inhibits photosynthesis of terrestrial plants at concentrations as low as 0.1 parts per billion and can be lethal to endosymbiotic dinoflagellates in corals at concentrations less than 3 parts per billion, a concentration measured in runoff samples taken during this study. While Diuron was not detected in samples taken beyond the coastal outfall or in an adjacent boat basin, this effort provides evidence that a detectable influx of Diuron into Maui's coastal waters can result from a single rain event. Further, this study will inform efforts to support a ban on the use of Diuron in the wet season and guide monitoring efforts to better understand the effects of Diuron in coastal areas.

Keywords: Hawaii, endosymbiotic dinoflagellates, photosynthesis inhibitor, seasonal ban

INTRODUCTION

Diuron is registered by the U.S. Environmental Protection Agency (EPA) for pre- and post-emergent herbicide treatment of both crop and non-crop areas and is classified as a potential carcinogen. It is an effective herbicide used to control vegetation along rights of way areas adjacent roadways and canals and is also used on commercial crops like sugarcane to control weed growth. Diuron functions by directly inhibiting photosynthesis. It also kills a variety of aquatic organisms. Another source of Diuron in the marine environment is from the marine anti-fouling paint Duralux that is often used on small boats. This paint has, since the early 1990s, gradually replaced tributyltin as an anti-fouling agent.

Diuron is found in about 20% of U.S. rivers and streams according to the US Geological Survey and inhibits photosynthesis at concentrations as low as 0.1 parts per billion (ppb) (Cox, 2003). When introduced into aquatic environments via runoff, it also kills a variety of aquatic organisms. A recent study to connect upstream land use to water quality in Hawaii found Diuron in 14% of sites tested in surface water at concentrations up to 0.07 ppb, well below the strictest benchmark concentrations of concern (2 ppb) (State of Hawaii Department of Health, 2014). Only a trace amount of Diuron was found at Kaanapali on the western coast of Maui; however, the sampling protocol did not account for seasonal precipitation patterns that make the timing of sampling for contaminants extremely important (State of

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Hawaii Department of Health, 2014). Recent concerns over the excessive use of agricultural chemicals led Kaua'i County, Hawaii, to pass strict laws (Ordinance 960, October 2013) requiring buffer zones and full pesticide application disclosure (<http://qcode.us/codes/kauaiconity/revisions/960.pdf>).

A seminal article by Jones et al. (2003) on Diuron describes its potential lethal effects on corals that depend on photosynthetic zooxanthellae. They conducted laboratory studies in Australia, exposing corals to varying concentrations of Diuron. A 10-hour exposure to a 3 ppb Diuron concentration caused death to about 35% of the endosymbiotic dinoflagellates in *Acropora formosa*, *Montipora digitata*, *Porites cylindrical* and *Seriatopora hystrix*. This study and subsequent work eventually led to a ban in 2011 on the use of Diuron during the wet season on sugarcane fields that drain onto the Great Barrier Reef.

The coral coverage on Maui, Hawaii's Maalaea Reef has declined from 50–75% in 1993 to only 8% in 2009 (Maui Coral Reef Recovery Team, 2012) and there is concern that herbicides and pesticides are in part responsible for poor coral reef health. The similarity of the conditions in Australia to those on Maui prompted an investigation of the presence of Diuron in the waters of Maalaea Bay, Hawaii, that receive runoff from sugarcane fields.

The Hawaiian Commercial and Sugar Company's (HC&S) website acknowledges the application of Diuron to sugarcane fields in Maui at least once during each growing season (<http://mahaloindustriesllc.weebly.com/sugar-cane-operations.html>). Additionally, this website notes, "Also, noxious weeds are controlled by applications of Roundup® in specific problem areas." This is an ancillary weed control strategy using glyphosate (active ingredient in Roundup®), which binds to aquatic sediments for up to a year (EPA, 1993; Solomon and Thompson, 2003). According to a report by Santo et al. (2000), 0.54 kg of Diuron per acre are applied annually on sugarcane fields in Hawaii. Maalaea Bay is adjacent to the HC&S fields and those fields drain directly into it. This raised the question as to whether the presence of Diuron in Maalaea Bay could play a role in the reduction in corals there. This question was the focus of a 2013 study to test runoff from sugarcane fields into the near-shore waters of Maalaea Bay. The objective was to measure Diuron concentrations in runoff prior to, during, and after the passage of Tropical Storm Flossie in late July 2013.

METHODS

Study Area

Maalaea Bay is on the south central shore of a valley-like isthmus formed by erosional deposits from two overlapping volcanoes on Maui, Hawaii (20°44'36" N, 156°30'22" W) (Kyselka and Lanterman, 1980). The older, northwestern volcano is Puu Kukui (1,759 m). Haleakala is to the southeast, rising to 2,000 m (Figure 1). Maui's climate is characterized by annual wet and dry seasons, dominant trade winds from the north-northeast and marked geographic differences in rainfall related to topography. Maalaea Bay is on the leeward side of Maui and somewhat shielded from the trade winds. It is in the rain shadow of the mountains and experiences dry conditions except for sporadic showers associated with ephemeral frontal systems. Maalaea Harbor is at the northwestern-most part of the bay and separated from the coastal water flow from the south by a breakwater.



Figure 1. Maalaea Bay (square) and sampling site (oval), Maui, Hawaii, in relation to the local topography. The two rain gauges on Maui, Hawaii, are at Puu Kukui, Maui, Hawaii, in the north at 1,759 meters elevation and at Kepuni Gulch along the southwestern coast at 77.7 meters elevation (<http://hi.water.usgs.gov/recent/hawaii>). Data: LDEO-Columbia, NSF, NOAA, U.S. Navy, NGA, GEBCO. Image: Landsat. © 2014 Google.

Sampling

Water sampling took place before, during, and after the passage of Tropical Storm (TS) Flossie on July 29, 2013. It began on July 28 and ended six days later on August 3, 2013. Samples 1–2 and 4–7 were taken near the shore, from Island Sands Resort Condominium complex to Maalaea Harbor (Figure 2; Table 1) prior to TS Flossie. Sampling was repeated after TS Flossie (Samples 10–15). Samples 6, 7, 14 and 15 were taken on the northern side of the harbor. Samples 8 and 9 were drawn during TS Flossie from the runoff stream immediately east of Island Sands Resort Condominiums. Additional post-TS Flossie samples (16–17) were obtained on July 31 at Maalaea Harbor. Using a kayak on August 3, 2013, seven additional samples were gathered over the reef (Samples 18–24). One blank sample (Sample 3, distilled water) was added to the group as a control, making 24 samples in all.

Surface samples were taken directly into 750 ml amber glass bottles after each bottle was rinsed twice with ambient seawater. Subsurface samples were taken near bottom at depths from 1 to 4 meters using a Van Dorn bottle lowered on a calibrated line. Samples were stored at 4° C in the dark until they were shipped on cold packs to Mercury Science, Inc. (Raleigh, North Carolina) for analysis.



Figure 2. Sampling locations along Maalaea Bay, Maui, Hawaii. White squares indicate surface samples, white triangles indicate subsurface samples, and yellow squares mark stations that tested positive for Diuron in concentrations greater than 3 ppb (#8 and #9). © 2014 Google.

Analytical Methods

Samples were analyzed by immunoassay using the Diuron Plate Assay Kit manufactured by Abraxis (<http://www.abraxiskits.com/productByCat.php?catId=47>) (Celgene, Summit, NJ). Briefly, 50 μ l aliquots of whole water samples and Diuron standard solutions were analyzed according to kit instructions. Samples were not concentrated or extracted. Samples were read using a Wallac Victor2 1420 Multilabel Counter (Perkin Elmer, Waltham, MA), at 450 nm wave length. Diuron concentrations were calculated using the calibration curve generated by a serial dilution of the standard included in the kit (Table 1) (Schneider et al., 1994). The detection limit of the test kit was 0.03 ppb Diuron. Samples containing less than 0.03 ppb Diuron were categorized as non-detectable or below detection (BD).

Precipitation

Because of the importance of seasonal precipitation on the delivery and concentration of pollutants in runoff on Maui, the US Geological Survey's stream gauge database was examined. There are nine stream gauges on Maui but none on the western side of the island (<http://waterwatch.usgs.gov/?m=real&r=hi>). However, there are two rain gauges, one located at the summit of Puu Kukui (20°37'10.2" N, 156°15'06.8" W) at 1,759 m elevation and the other at Kepuni Gulch (20°37'10.2" N, 156°15'06.8" W) on the southwestern coast at 77.7 m elevation (<http://hi.water.usgs.gov/recent/hawaii/puukukui.html>) (see Figure 1). Of these two locations, the Kepuni Gulch rain gauge, at a lower altitude and on the coast, more closely reflects the precipitation pattern expected at the sampling site in Maalaea Bay. However, because of the importance of topography and the direction of approach of frontal systems, the Kepuni Gulch rain gauge is only an approximation of the conditions at Maalaea Bay.

Table 1. Conditions and Diuron concentrations of water samples taken in Maalaea Bay, summer 2013. Samples 8 and 9 were positive for Diuron.

| Sample No. | Date of Sampling (2013) | Time of Sampling (HST ^a) | Location of Sample Site | Sampling Depth | Diuron Concentration (ppb) |
|--|-------------------------|--------------------------------------|--|----------------|----------------------------|
| 3 (Distilled Water) | 28 Jul | 1522 | n/a | n/a | BD ^b |
| <i>Taken before Tropical Storm Flossie</i> | | | | | |
| 1 | 28 Jul | 1550 | East of Island Sands outflow, 20°47.690' N, 156°30.395' W | Surface | BD |
| 2 | 28 Jul | 1555 | West of Island Sands outflow, 20°47.688' N, 156°30.399' W | Surface | BD |
| 4 | 28 Jul | 1610 | Lauloa steps, 20°47.639' N, 156°30.463' W | Surface | BD |
| 5 | 28 Jul | 1625 | Glass Beach, 20°47.537' N, 156°30.596' W | Surface | BD |
| 6 | 28 Jul | 1640 | Slip 65, Maalaea Harbor, 20°47.492' N, 156°30.735' W | Surface | BD |
| 7 | 28 Jul | 1645 | Slip 65, Maalaea Harbor, 20°47.492' N, 156°30.735' W | 1.75 m | BD |
| <i>Taken during Tropical Storm Flossie, 2 hours after rain started</i> | | | | | |
| 8 | 29 Jul | 1855 | Island Sands stream at water line, 20°47.696' N, 156°30.404' W | n/a | 3.4 |
| 9 | 29 Jul | 1857 | Island Sands stream at water line, 20°47.696' N, 156°30.404' W | n/a | 3.3 |
| <i>Taken after Tropical Storm Flossie</i> | | | | | |
| 10 | 30 Jul | 1600 | East of Island Sands outflow, 20°47.690' N, 156°30.395' W | Surface | BD |
| 11 | 30 Jul | 1605 | West of Island Sands outflow, 20°47.688' N, 156°30.399' W | Surface | BD |
| 12 | 30 Jul | 1610 | Lauloa steps, 20°47.639' N, 156°30.463' W | Surface | BD |
| 13 | 30 Jul | 1628 | Glass Beach, 20°47.537' N, 156°30.596' W | Surface | BD |
| 14 | 30 Jul | 1640 | Slip 65, Maalaea Harbor, 20°47.492' N, 156°30.735' W | Surface | BD |
| 15 | 30 Jul | 1645 | Slip 65, Maalaea Harbor, 20°47.492' N, 156°30.735' W | 1.75 m | BD |
| 16 | 31 Jul | 1614 | Slip 72, Maalaea Harbor ^c , 20°47.434' N, 156°30.703' W | Surface | BD |
| 17 | 31 Jul | 1618 | Slip 72, Maalaea Harbor ^c , 20°47.434' N, 156°30.703' W | 4 m | BD |
| 18 | 3 Aug | 0945 | Lauloa steps line, outside station, 20°47.626' N, 156°30.444' W | Surface | BD |
| 19 | 3 Aug | 0951 | Lauloa steps line, outside station, 20°47.626' N, 156°30.444' W | 1 m | BD |
| 20 | 3 Aug | 1004 | Lauloa steps line, inner station, 20°47.634' N, 156°30.457' W | Surface | BD |
| 21 | 3 Aug | 1011 | Lauloa steps line, inner station, 20°47.634' N, 156°30.457' W | 1.5 m | BD |
| 22 | 3 Aug | 1035 | East line of stream, 20°47.692' N, 156°30.359' W | Surface | BD |
| 23 | 3 Aug | 1041 | East line of stream, 20°47.692' N, 156°30.359' W | 2 m | BD |
| 24 | 3 Aug | 1053 | Off stream, 20°47.666' N, 156°30.380' W | 2 m | BD |

^aHawaii Standard Time

^bBelow detection (<0.03 ppb)

^cWinds at 25–30 knots

RESULTS

Diuron Analysis

Twenty-two of the 24 samples (Table 1) had no detectable Diuron concentrations (< 0.03 ppb). Twenty-one samples were obtained adjacent to and over the reef. One sample (Sample 3) was a distilled water blank. Two of the 24 samples had concentrations of >3 ppb (3.4 ppb, Sample 8; 3.3 ppb, Sample 9) (Table 1). Those samples were obtained from the stream on the eastern side of the Island Sands Resort Condominium complex on 29 July 2013 (Figure 2). The stream, which contained runoff from TS Flossie, was sampled approximately 2 hours (1855 Hawaiian Standard Time [HST]) after the rains began while the stream was flowing. Three hours later (2200 HST) the stream was no longer flowing. No elevated Diuron concentrations were recorded for the samples taken in the Maalaea Harbor boat basin before or after the passage of TS Flossie.

Precipitation

Rainfall averages more than 980 cm per year at the higher elevations of Puu Kukui (Figure 3) while during the same period Kepuni Gulch has an average of only 30–31 cm of precipitation (Figure 4) (http://www.prh.noaa.gov/hnl/hydro/pages/maui_05.gif; <http://waterdata.usgs.gov/hi/nwis/>). We note the relatively few rainfall occurrences of 5 cm or greater at Kepuni Gulch throughout the eight-year record (Figure 4), and observe there were no rainfall events with precipitation totals of 5 cm during the period between 2010 and 2012, a time of extremely dry conditions. Tropical Storm Flossie's rainfall measured 10 cm on 29 July 2013 and about 7 cm the following day, making this a major runoff event for Maalaea Bay. In contrast, rainfall events at Puu Kukui seem to average 12–13 cm and commonly exceed 25 cm (Figure 3). Unfortunately, the rain gauge at Puu Kukui was not operational during the passage of TS Flossie in late July 2013 for comparative measurements between the two rain gauges.

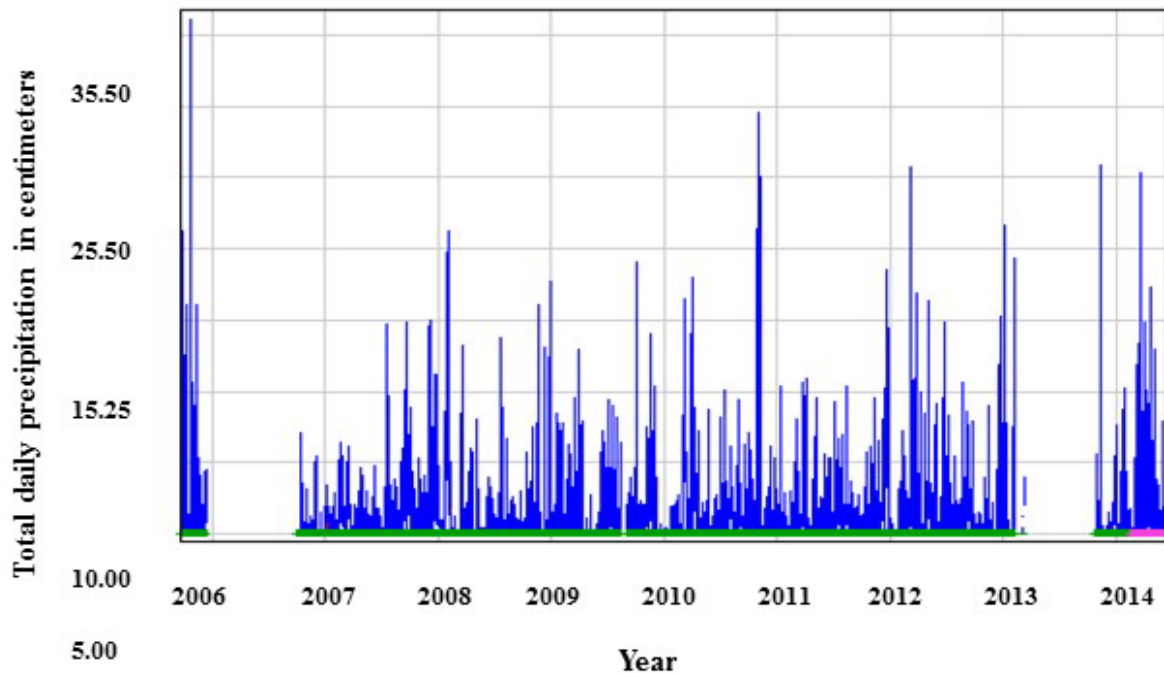


Figure 3. Daily precipitation total in centimeters at the US Geological Service rain gauge at Puu Kukui, Maui, Hawaii, from 2006 to April 2014. USGS rain gauge 205327156351102 380.0 is located 1,759 meters above sea level in north-central Maui, Hawaii (<http://waterdata.usgs.gov/hi/nwis/>).

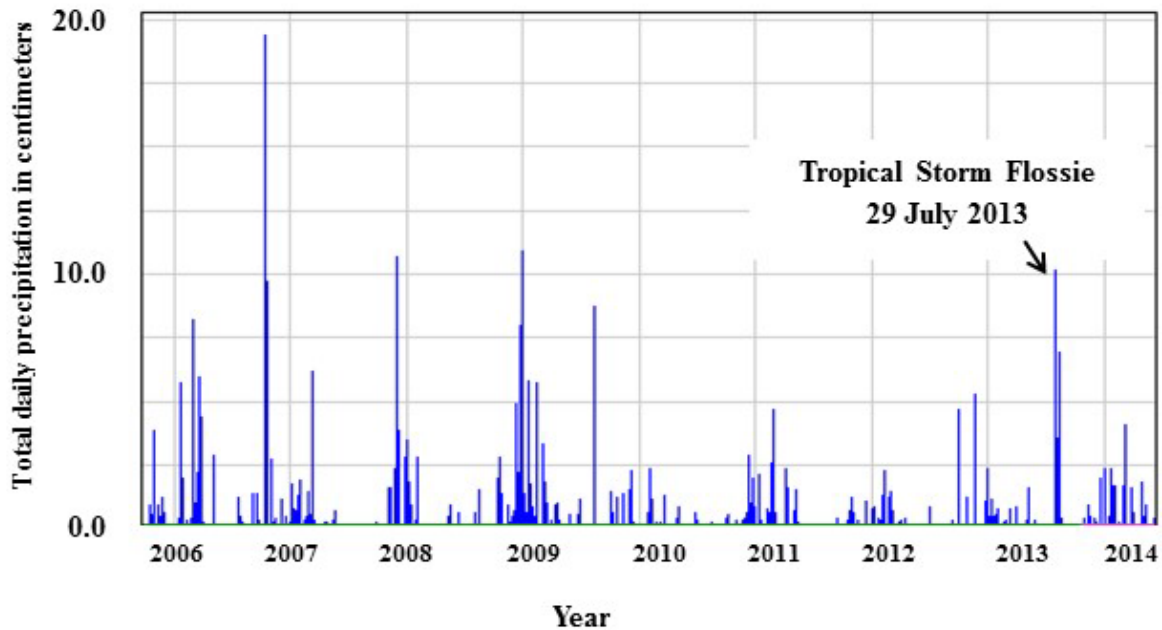


Figure 4. Daily precipitation total in centimeters at the US Geological Service rain gauge at Kepuni Gulch, Maui, Hawaii from 2006 to April 2014. USGS rain gauge 203721156151601 is located 77.7 meters above sea level on the southwestern coast of Maui (<http://waterdata.usgs.gov/hi/nwis/>).

DISCUSSION

Runoff from the 1.39 km² HC&S sugarcane field in Maalaea, Maui, contained concentrations of Diuron (>3 ppb). This concentration of Diuron is significant in that it has the potential to be lethal to corals. Laboratory studies completed in Australia by Jones et al. (2003) show that concentrations of Diuron similar to those found in the Maalaea runoff killed about 35% of the corals within 10 hours. The relatively minor runoff from TS Flossie was diluted as it entered the ocean and Diuron was not detectable away from the outfall. During TS Flossie, only a trace of rain was recorded at Kahului Airport (<http://cdo.ncdc.noaa.gov/qclcd/QCLCD>), about 15 km north of Maalaea Bay. Summer is generally the dry season on Maui, with higher precipitation in winter. An extreme example of seasonal rainfall occurred on 13–14 January, 2011, when 7.0 cm of rainfall was recorded (<http://cdo.ncdc.noaa.gov/qclcd/QCLCD>) at the Kahului Airport, although this event was not recorded by the Kepuni Gulch rain gage 60 km to the south. For the July 2013 rain event, the stream flow lasted only several hours; after the January 2011 storm, the outfall stream continued to flow for several days (personal observation, T. Royer). Thus, extreme rain events have the potential to inject high volumes of runoff with potentially high concentrations of Diuron or other herbicides and pesticides directly onto the reef. Further, the accumulation of Diuron in sediments associated with runoff events and subsequent release into the food web is a consideration as well. Its half-life is reported to be on the order of hundreds of days (Australian Pesticides and Veterinary Medicines Authority, 2011).

The State of Hawaii has no ongoing stream monitoring program for pesticides, and there is little information for evaluation of current pesticide use practices resulting in off-site movement into state waters. Data from the State of Hawaii Department of Health draft report (2014) provide preliminary information on the presence /absence of pesticide residue levels in surface waters and support one of the Maui Coral Reef Recovery Team's (2012) highest priorities for direct restoration of Maui's reef ecosystems, reduction sedimentation and runoff. Because of the recent awareness heightened by the Maui

Coral Reef Recovery Team's report (2012) and the State of Hawaii Department of Health's draft report (2014) on pesticides and water quality, plans are underway to develop a catchment basin for the runoff from the stream draining the sugarcane field adjacent to Maalaea Bay. This is a step in the right direction and in concert with the Coral Reef Recovery Team's goal of identifying key stressors to Maui's coral reefs. Another step toward this goal would be the Hawaiian Commercial and Sugar Company (HC&S) agreement to halt the use of Diuron on its sugarcane fields until more extensive studies of the effects of Diuron on Maui's corals can be carried out. Further, HC&S should not replace Diuron with other herbicides, such as Roundup[®], until they have been proven safe for use in areas adjacent to coral reef ecosystems.

It is not known if Maui's coral population of *Montipora* spp. or *Pocillopora* spp. (Brown, 2008) is more or less sensitive to Diuron than the corals found on the Great Barrier Reef in Australia; however, the fragile condition of the reef dictates immediate relief from any factors that might be affecting its health. Future studies should include routine monitoring for Diuron, as well as other herbicides and pesticides, in the runoff and over the reef, and the responses of local corals. This sampling should take into account the seasonal rainfall pattern along the southern Maui coast and the sporadic nature of the runoff.

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