COMMENTARY

Investigating Sources of Toxicity in Stormwater: Algae Mortality in Runoff Upstream of the Lawrence Livermore National Laboratory

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A source evaluation case study is presented for observations of algae toxicity in an intermittent stream passing through the Lawrence Livermore National Laboratory near Livermore, California. A five-step procedure is discussed to determine the cause of water toxicity problems and to determine appropriate environmental management practices. With this approach, an upstream electrical transfer station was identified as the probable source of herbicides causing the toxicity. In addition, an analytical solution for solute transport in overland flow was used to estimate the application level of 40 kg/ha. Finally, this source investigation demonstrates that pesticides can affect stream water quality, regardless of application within levels suggested on manufacturer labels. Environmental managers need to ensure that pesticides that could harm aquatic organisms (including algae) not be used near streams or storm drainage areas, and that application timing should be considered for environmental protection.

Introduction

Stormwater quality monitoring at industrial facilities is required by the United States Environmental Protection Agency (USEPA) in accordance with the Federal Water Pollution Control Act (the Clean Water Act of 1972, 33 USC 1251, Section 402). In California, this requirement is enforced by the State Water Resources Control Board and Regional Water Quality Control Boards with permits issued under the National Pollutant Discharge and Elimination System (NPDES). The specific programs for stormwater runoff are most often operated under the statewide general permit for the Waste Discharge Requirements for Discharges of Storm Water Associated with Industrial Activities (Water Quality Order No. 02-01-DWQ, CAS000001).

Although stormwater monitoring under these programs began in the 1980s, many factors, including cost, monitoring designs, and sampling procedures, have limited the overall effectiveness of stormwater monitoring programs (Charbeneau and Barrett, 1998; Leecaster, Schiff, and Tiefenthaler, 2002). In response, toxicity testing provides an alternative method to examine whether survival or health of an indicator species is affected by the stormwater quality. Unfortunately, although toxicity tests are a direct method for determining if water quality negatively affects aquatic organisms, it is often difficult to determine what constituent actually causes toxicity (Schiff, Bay, and Diehl, 2003).

Moreover, determining sources of toxins in stormwater is complicated by dynamic runoff processes that transport toxins downstream during a short period. Stormwater runoff occurs in pulses, whereby water, sediments, and solutes get flushed through a stream on time scales related to storm duration (minutes to hours). The flush of water, or the hydrograph (total runoff volume per unit time), may be characterized for each storm by using flumes or staging wells (McCuen, 1989). Therefore, if an environmental manager needs to estimate the total loading of a pollutant, the hydrograph shows the volume per unit time, and concentration measurements (mass/water volume) can be used to calculate mass (Charbeneau and Barrett, 1998). Unfortunately, the concentration of dissolved constituents in stormwater runoff often does

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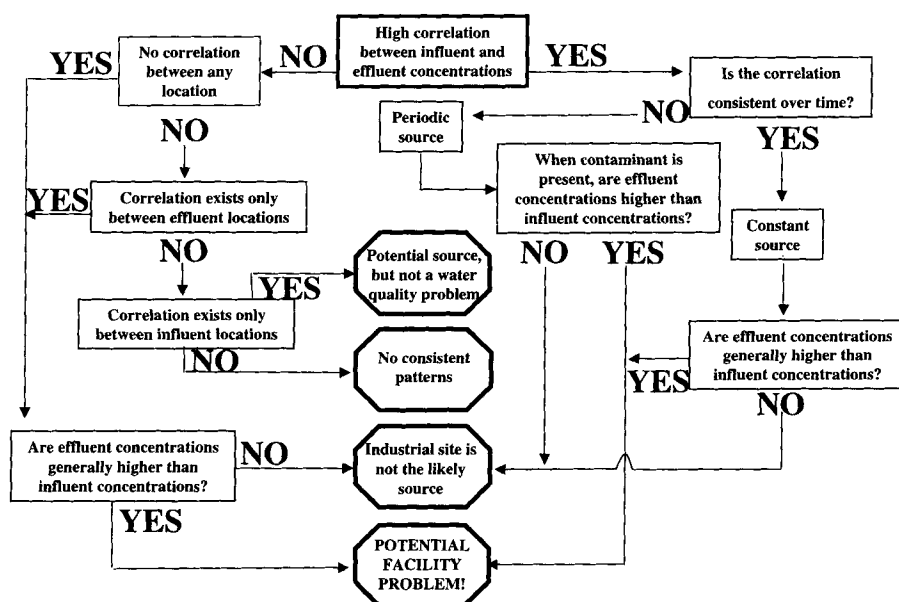
Figure 1. Industrial site decision tree for stormwater chemistry, Lawrence Livermore National Laboratory.

not rise and fall with the runoff hydrograph. Most of the salts and other material are flushed into storm runoff before the hydrograph peak (Bertrand-Krajewski, Chebbo, and Saget, 1998). This early arrival of solutes, called the first flush, is the portion of the runoff most likely to contain soluble toxins (Sansalone and Buchberger, 1997). When this flush is observed to contain dissolved contaminants, it has been called a "pollutograph" (Black, 1997).

When stormwater samples are found to be toxic to test organisms, a source investigation usually follows, as a first step toward preventing toxicity. Once the pollutograph is gone, however, it is not possible to resample the stream water to find out exactly what was causing the observed toxic response to test organisms. Resampling stream water during the next storm can identify a continuous source; however, if the toxicity relates to independent isolated events, a more detailed analysis may be necessary. One alternative is to combine monitoring of the chemical constituents most likely to cause water quality problems with whole effluent toxicity testing. Then, when toxicity occurs, the chemical data may be reexamined to help identify possible causes.

Source Investigation

This article documents algae toxicity in surface water samples collected from a government industrial research facility, Lawrence Livermore National Laboratory (LLNL), in the greater San Francisco Bay area in California, USA.

For the purposes of this discussion, *algae toxicity* refers to the increase in mortality and decrease in mass growth (relative to a control sample) resulting from exposure to a given water sample. A source investigation, as it is used here, is the follow-on investigation, which includes laboratory experiments, additional measurements, modeling, and analysis performed to systematically identify the cause(s), or source(s), of an observed algae toxicity event. As a National Research Laboratory for the Department of Energy, LLNL has both the responsibility and the opportunity to critically examine water quality issues in a manner that may not be as common for other industrial discharge permit holders. At this facility, the five steps of a source investigation include:

1. Recognizing a water quality problem,
2. Identifying a number of potential causes for the problem,
3. Investigating in order to focus on primary causative agents,
4. Finding and confirming the sources of the agents identified in #3, and
5. Determining the conditions under which the causative agents were released.

The first of these five steps may be obvious, as in the case of toxicity testing, or less obvious where an increasing trend in a water quality parameter exists. In the second case, available background data are valuable in identifying unusual changes in water quality. Figure 1 shows a novel decision tree that is used at LLNL to determine if a water quality problem has originated on or upstream of the facility. Once a source has

been identified, then solutions may be developed to stop toxicity problems and avoid future occurrences.

Identifying direct causes for toxicity in stormwater is a complicated task. Algae mortality may be caused by elevated metals concentrations (e.g., zinc), increased turbidity for an extended time, various pesticides, extreme changes in pH, a decrease in the availability of a limiting nutrient, or extreme changes in water temperature (Admiraal et al., 1999; Anderson et al., 2003; Fahl et al., 1995; Gledhill et al., 1997; Ma and Liang, 2001; Paulsson, Nystrom, and Blanck, 2000; Radix et al., 2000; Schiff, Bay, and Diehl, 2003). Given that most compliance monitoring performed at industrial facilities requires only a single sample per storm collected for a limited number of storms, information to help focus on the cause of the toxicity is often unavailable. As a result, environmental managers need established approaches to identify causes of toxicity in stormwater samples. Such methods include identifying the most likely causes and eliminating them one by one. As part of step 3, a source investigation should determine the possible causes of toxicity that could be the reason for the magnitude of the response observed.

After causative agents have been identified, the final two steps deal with finding how those agents were mobilized in stormwater so that corrective actions can be identified, evaluated, and implemented. The source area must have been exposed to the causative agents and also have had contact with stormwater. Issues to be evaluated include how and when the source got there, if it is possible to identify the toxic agent and prevent contact between the source stormwater, how much of the source was released, and if it is still there. All these issues will be examined within this case study of algae toxicity.

Methods and Materials

The Livermore Site

Lawrence Livermore National Laboratory is one of three national research laboratories operated for the Department of Energy by the University of California. The 3.28-km^2 facility is located just east of the City of Livermore, California, approximately 30 km due east of the San Francisco Bay. The historic mission of the LLNL of nuclear weapons research and national security has broadened to include research on strategic defense, energy, environmental sciences, biomedical studies, economics, and education. The site experiences a Mediterranean climate, with hot dry summers and cool mild winters. Annual rainfall averages

36 cm, ranging from 54 cm in wet years to 21 cm in dryer years.

The Livermore site is crossed by two intermittent streams, Arroyo Las Positas and Arroyo Seco. This investigation involves water samples from Arroyo Las Positas, a tributary of Alameda Creek that flows into the San Francisco Bay (Figure 2). Four monitoring locations have been established on the Arroyo Las Positas, three influent locations (GRNE, ALPE, and ALPO), and one effluent location (WPDC) (Figure 2).

Toxicity Testing at LLNL

Toxicity monitoring is performed at LLNL at the discharge point along the Arroyo Las Positas, usually once a year during the first storm that produces significant runoff, in order to characterize the first flush of solutes (or the first pollutograph) of the wet season. Grab samples are collected by automatic water samplers, and acute and chronic toxicity tests are performed on the water, using different indicator species for various links in the aquatic food chain. Water samples from the Arroyo Las Positas are sent to a contract laboratory (BC Laboratories Inc., Bakersfield, California) for chemical analysis and toxicity testing. In some cases, follow-up analyses are performed on site by an LLNL laboratory.

Lawrence Livermore National Laboratory uses the algae species *Selenastrum capricornutu* to represent primary producers; a daphnid species, *Ceriodaphnia dubia*, to represent primary consumers; and fathead minnows (*Pimephales promelas*) to represent secondary consumers. Water dilutions of 0 (Lab Control), 6.25, 12.5, 25, 50, and 100% (undiluted sample water) are used to determine whether a dose-response relationship exists for both survival and growth of the test species. From these data, No Observed Effect Concentrations (NOECs), a toxicity index, and Lowest Observed Effect Concentrations (LOECs) are calculated according to methods established by the USEPA (US Environmental Protection Agency, 2002).

Chemical Water Quality Monitoring at LLNL

Stormwater runoff from LLNL is monitored for a variety of water quality parameters in addition to the annual toxicity bioassays. Parameters monitored at the site include radionuclides, total organic carbon, total suspended solids, specific conductivity, pH, chemical oxygen demand, total dissolved solids, oil and grease, metals, minerals, anions,
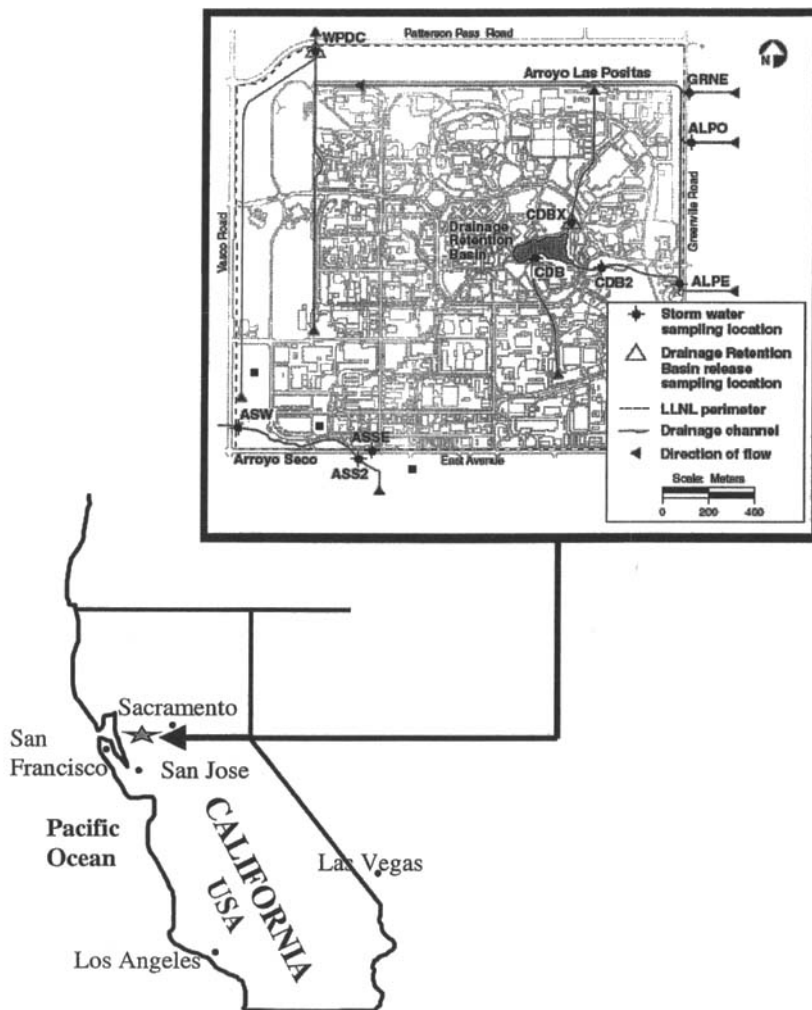
Lawrence Livermore National Laboratory

Figure 2. Map of the stormwater sampling locations at the Lawrence Livermore National Laboratory.

temperature, nutrients, and a wide range of organic compounds. Therefore, when a toxicity test reveals a toxic response, the various water quality parameters measured may be used to identify potential causes.

All water samples from LLNL are collected by grab sampling from storm runoff flowing in the stream channels. Standard sample bottle requirements, special sampling techniques, and preservation requirements for each analyte are specified in the LLNL *Environmental Monitoring Plan* (Tate et al., 1999) and are correctly implemented throughout sampling and analysis. Sampling is conducted away from the edge of the water to minimize the collection of sediment with the sample matrix. Because these data are collected as part of the compliance network for the industrial stormwater permit, stringent quality assurance and quality control measures are applied to all

chemical analysis and data. These include the use of duplicate samples, blanks, spikes, and matrix spikes in the chemical analysis and quality assurance checks on the data in the database system. Details on the quality assurance program at LLNL may be found in chapter 14 of the annual Environmental Report (Biermann et al., 2000).

The Source Evaluation

1. Problem Recognition

Algae toxicity monitoring has been performed in water samples from storm runoff since 1999 at LLNL. Before that date, however, algae toxicity tests had been performed since 1993 in water from the Drainage Retention Basin (see Figure 2) in the center of the site, along with invertebrate and fish toxicity tests. Beginning in 1995/1996, chloro-

Table 1. *Herbicide Concentrations. Bromacil was analyzed using USEPA Standard Analysis method 507.4. Diuron was analyzed using USEPA Standard Analysis method 632.3. Samples were coded and sent to an off-site laboratory for analysis*

Treatment group	Calculated herbicide concentration (mg/L)
Control	*
Bromacil	36
Diuron	24
Bark leachate	*
Bromacil and diuron	36 and 24, respectively
Bromacil and bark leachate	36
Diuron and bark leachate	24
Bromacil, diuron, and bark leachate	36 and 24, respectively

* Not analyzed for herbicides.

Table 2. *Mean $\pm$ standard deviation (SD) (n = 5) percent growth (cells per mL) data for water treatment groups*

Treatment group	Mean $\pm$ SD growth (cells/mL)	Percent growth
Control	$7.8 \times 10^5 \pm 2.0 \times 10^4$	295
Bromacil	$1.4 \times 10^5 \pm 1.5 \times 10^4$	−30
Diuron	$1.3 \times 10^5 \pm 7.7 \times 10^3$	−34
Bark leachate	$3.5 \times 10^5 \pm 1.3 \times 10^4$	77
Bromacil and diuron	$1.6 \times 10^5 \pm 1.2 \times 10^4$	−20
Bromacil and bark leachate	$1.5 \times 10^5 \pm 1.4 \times 10^4$	−26
Diuron and bark leachate	$1.5 \times 10^5 \pm 1.5 \times 10^4$	−25
Bromacil, diuron, and bark leachate	$1.1 \times 10^5 \pm 1.1 \times 10^4$	−44

phyll-a measurements suggested that the basin had experienced a decrease in planktonic algae. Algae toxicity tests revealed growth inhibition (Brandstetter et al., 1997). In response to this observation, studies were initiated to determine the cause of algae toxicity. The potential causes of toxicity problems in the drainage retention basin were identified as: the leachate from landscaping bark placed around the drainage basin, the herbicide bromacil, and the herbicide diuron. Toxicity tests were performed using treatments of these three potential causes, both individually and all together, in order to examine compounding toxicity (see Table 1).

The percent algae cells/mL growth data are summarized in Table 2, and pH data from the cultures on day 1 and day 5 are summarized in Table 3. It is clear from Table 2 that all three potential toxic compounds included in the examination negatively affected algal growth. The two herbicides, diuron and bromacil, had the greatest impact, with total growth of −34% and −30%, respectively. The bark leachate also affected the algae, however, suggesting that either tannins in the bark have a chemical impact or that the discoloration of the water had a physical effect on photosynthesis.

Therefore, the issue of algae growth inhibition in the drainage retention basin was considered to have been resolved. The herbicides diuron and bromacil (ingredients of the brand name Karmex®), along with the bark mulching near shore, were the most likely causes, and applications of these materials were therefore suspended or modified. For the herbicides, LLNL established a policy that applications would not occur within 15 m of storm drains and would not be applied when rain was predicted

for the next day. New bark applications were also restricted to dry months, in order to allow the bark to weather enough to produce no water quality problems in the following wet season.

The issue did not appear to be resolved in stormwater runoff flowing off site in the Arroyo Las Positas, however. In January of 2000 and again in January 2001, algae toxicity was observed in water samples from stormwater in the Arroyo Las Positas (Table 4). In fact, the algae test on January 8, 2001, indicated toxicity in stormwater with a NOEC of less than 6.25% and a LOEC of 6.25%. If algae toxicity in the stormwater runoff was not caused by water quality problems in the drainage retention basin, then there had to be another source causing toxicity.

2. Potential Causes of Toxicity in Stormwater

The past problems in the drainage retention basin focused attention on bark leachate, diuron, and bromacil as potential causes of the toxicity observed in the stormwater runoff. There were no large variations in pH, temperature, or other nutrients like nitrate and orthophosphate observed on theses sampling dates (Campbell et al., 2001). There were other possible causes worthy of consideration, however, such as metals and other herbicides. There are normal background metals concentrations (e.g., copper and zinc) in the stormwater that, when water hardness is low, could be toxic to plant life. This possibility was examined; however, it appears unlikely, as metal toxicity is directly related to water hardness (Marshack, 2000), and the hardness was generally high in stormwater and the metals concentrations were also too low to cause the observed algae toxicity. This is in part due to groundwater discharges into the storm drains beginning in 1997 when LLNL began to operate groundwater

Table 3. Days 1 and 5 mean ± standard deviation (SD) (n = 3) pH data for water treatment groups

Treatment group	Mean Day 1 pH	Mean Day 5 pH
Control	8.80	6.79
Bromacil	8.80	6.93
Diuron	8.80	6.82
Bark leachate	8.80	6.82
Bromacil and diuron	8.79	6.82
Bromacil and bark leachate	8.80	6.99
Diuron and bark leachate	8.81	7.17
Bromacil, diuron, and bark leachate	8.81	6.93

remediation units that were permitted to discharge cleaned groundwater. These discharges significantly increase the total hardness in the Arroyo Las Positas to levels usually greater than 100 mg/L. The hardness on January 10, 2000, and January 8, 2001, ranged from 78 mg/L to 412 mg/L at sampling locations along the Arroyo Las Positas, while the maximum copper and zinc concentrations on those dates were 0.01 mg/L and 0.1 mg/L, respectively. Therefore, metal toxicity was ruled out as a potential cause of the algae growth inhibition.

There is another herbicide applied on the LLNL site and also by local utilities in roadside maintenance. Glyphosate is an ingredient in the common pesticide Roundup®, and was measured in stormwater at concentrations ranging from <9 to 47 µg/L. These concentrations are not high enough to cause the toxicity observed, however; but to confirm that this herbicide was not involved in the problem it was included in the source investigation.

Table 4. Chronic algae toxicity test results from stormwater collected from Arroyo Las Positas, January 11, 2000, and January 8, 2001

Sample concentration (%)	96-h growth Count (10^6 cells/mL)	Variance (%)
January 11, 2000		
Control	1.19	10.2
6.25	1.16	9.0
12.5	1.25	6.4
25	1.01	9.9
50	0.60	8.3
100	0.50	7.7
January 8, 2001		
Control	1.76	10.3
6.25	0.94	6.5
12.5	0.75	5.4
25	0.38	14.9
50	0.10	4.0
100	0.04	7.6

3. Primary Causative Agents

There was evidence that diuron was present in the stormwater on January 10, 2000, and January 8, 2001, at concentrations high enough to be toxic to algae. On January 8, diuron concentrations at the effluent WPDC were 14 µg/L, whereas at influent sample locations GRNE, ALPO, and ALPE the values were 1600, 4.6, and 4.5 µg/L, respectively. Diuron has been reported to be toxic to algae at 9 to 14 µg/L, to invertebrates at 1400 µg/L, and to fish at 500 µg/L (Cornell University, 1983). The very high concentration at location GRNE was greater than all these thresholds. Bromacil concentrations followed a similar pattern for that sampling event, with values of <1, 2500,
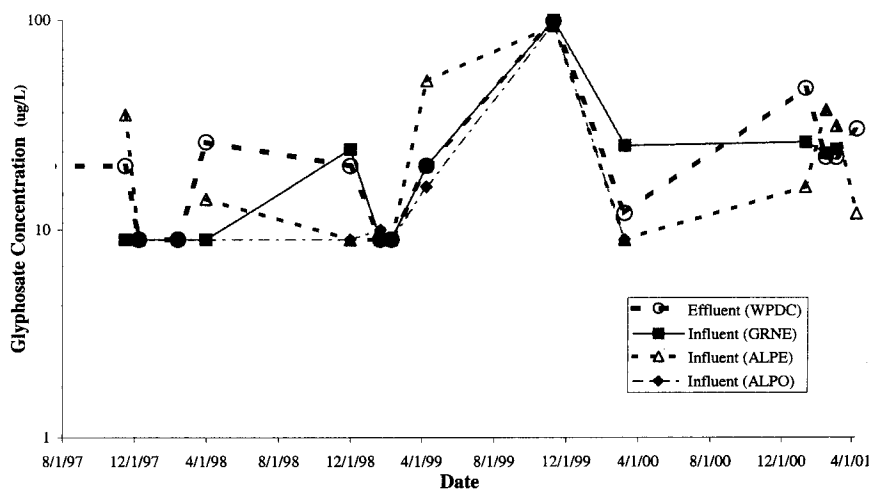

Figure 3. Historical glyphosate concentrations in samples collected from the stormwater monitoring locations, Lawrence Livermore National Laboratory, 1997 to 2001.
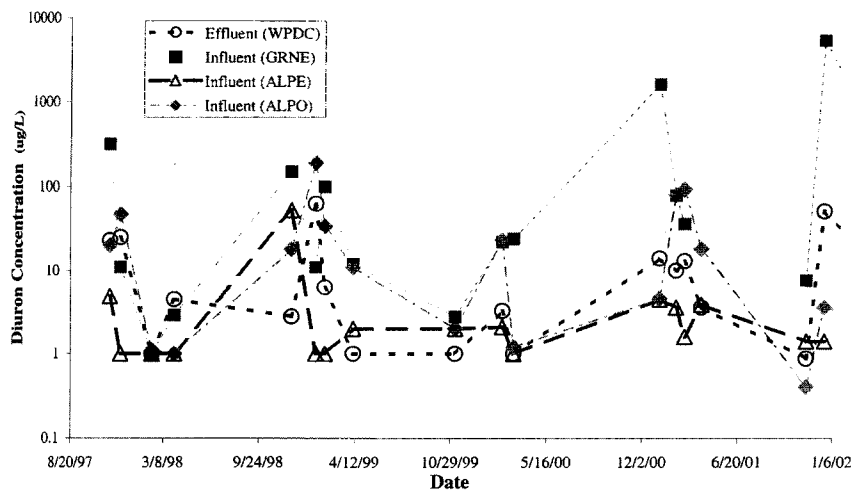
Figure 4. Historical diuron concentrations in samples collected from the stormwater monitoring locations, Lawrence Livermore National Laboratory, 1997 to 2001.

1.1, and 7 µg/L for sites WPDC, GRNE, ALPE, and ALPO, respectively. Bromacil is reported to be less toxic than diuron, so while these concentrations are elevated, the diuron is likely the most responsible for the toxicity.

All three herbicides (diuron, bromacil, and glyphosate) have been measured at elevated concentrations in waters entering the Livermore site. The historical values for these herbicides entering and leaving the Arroyo Las Positas at LLNL are shown in Figures 3, 4, and 5. Glyphosate concentrations consistently range from 9 to 100 µg/L (Figure 3). The California EPA Primary Maximum Contaminant Level for glyphosate in drinking water is 700 µg/L (Mathews et al., 1999). The other two herbicides show greater variability in measured concentrations. Diuron concentrations vary from 1 to 1600 µg/L, the highest value being that measured at influent location GRNE on January 8, 2001. Measured diuron concentrations leaving the Livermore site at WPDC are almost

always lower than the influent concentrations (GRNE, ALPE, and ALPO), suggesting that the source is upstream (Figure 4). The same pattern is repeated for bromacil, where measurements at influent location GRNE are most often the highest values (Figure 5).

4. Confirming the Source

Because this test was conducted at only a single sampling location, it was difficult to determine if the effects should be attributed to LLNL or to upstream water quality. Therefore, additional samples were collected for chronic algae toxicity tests at both the effluent (WPDC) and influent (GRNE, ALPO, and ALPE) locations during the next significant storm event on February 12, 2001. Diuron concentrations on this date were 10.0, 79.0, 3.6, and 80.0 µg/L for WPDC, GRNE, ALPE, and ALPO, respectively. The toxicity results
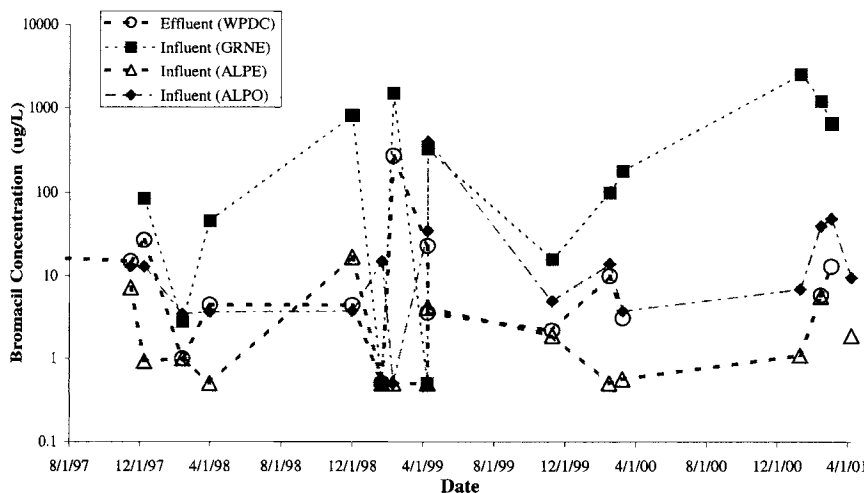

Figure 5. Historical bromacil concentrations in samples collected from the stormwater monitoring locations, Lawrence Livermore National Laboratory, 1997 to 2001.

Table 5. Chronic algae toxicity test results in Arroyo Las Positas stormwater on February 12, 2001

Sample concentration (%)	96-h growth	
	Count (10^6 cells/mL)	Variance (%)
WPDC location		
Control	1.349	8.7
6.25	1.683	5.8
12.5	1.399	7.9
25	0.991	6.7
50	0.623	9.5
100	0.174	9.7
GRNE location		
Control	1.456	6.9
6.25	0.067	9.3
12.5	0.026	5.1
25	0.017	9.3
50	0.014	10.6
100	0.013	13.9
ALPO location		
Control	1.355	6.3
6.25	1.221	11.9
12.5	0.534	4.3
25	0.205	9.4
50	0.048	19.8
100	0.024	9.5
ALPE location		
Control	1.414	10.3
6.25	1.510	6.5
12.5	1.597	5.4
25	1.028	14.9
50	0.684	4.0
100	0.178	7.6

were consistent with these measurements (Table 5), confirming an upstream source for algae toxicity.

To examine the tendency for the influent locations to degrade the water quality in the Arroyo Las Positas, a correlation analysis was performed. Standardized correlation coefficients were calculated for concentrations of each pesticide at each location in relation to the other locations on the stream (Daniel, 1995). The goal was to determine if high concentrations at one of the influent locations could be correlated to the effluent location (WPDC) or if high concentrations at that influent did not affect total water quality at WPDC. The latter would be possible if the proportion of the flow relative to the total is small or if the water (from ALPE, for example) is first mixed in the drainage retention basin before release to the effluent location.

The correlation analysis demonstrated that, in general, a high diuron concentration at ALPO correlated with a high diuron measurement at WPDC, with a standardized correlation coefficient of 0.8473 (Table 6). The tributary sampled at location ALPO receives storm runoff from some of the same land surface areas as location GRNE, however, usually with a one to two storm lag. This means that if herbicides were applied near water source areas flowing to location GRNE, they would likely appear in stormwater samples from location ALPO during the subsequent storm. This explains why the results of the correlation analysis contrast with the case of January 8, 2001, where diuron was elevated at WPDC and only 4.5 at ALPO. In addition, flow does not always occur at the location GRNE, and when it does the volume of water is small. This must explain the low correlations between this location and others on the arroyo. The correlations between other sampling locations for diuron concentrations were generally low. Although these results do not exactly implicate a historical relationship between diuron concentrations at influent location GRNE and effluent location WPDC, we believe the high correlation between ALPO and WPDC at least demonstrates a historical upstream source for the pesticide.

The results of the correlation analysis for bromacil are also not in agreement with observations made on January 8, but there is a good correlation between WPDC and GRNE (Table 6). In contrast to the other two pesticides, the correlation coefficients for glyphosate are high for all comparisons. The correlations between values at WPDC and influent locations estimated for diuron and bromacil suggest that these herbicides are most often from off-site sources, whereas the high correlation in glyphosate concentrations between all sampling locations demonstrates that all these values fluctuate together. This suggests that the source of glyphosate is uniform spraying of the pesticide, possibly from roadway spraying around the periphery of the Livermore site.

The historically high diuron and bromacil concentrations at GRNE and ALPO, along with the correlation between the concentrations of these herbicides at these locations, demonstrate that upstream activities are the most likely source for the observed toxicity. An electrical transfer station exists upstream of the Livermore site on Greenville Road. It is the main source of stormwater runoff to the GRNE sampling location, and it also contributes runoff to the sampling location ALPO (Figure 6). It appears that herbicide applications at that site were the source of the algae toxicity observed in the arroyo water samples from the LLNL site.

Table 6. Correlation coefficients between herbicide concentrations in samples from the influent (GRNE, ALPE, ALPO) and effluent (WPDC) locations on Arroyo Los Positas; see text for discussion of high correlations (bold)

	WPDC	GRNE	ALPE
Diuron			
WPDC			
GRNE	0.0634		
ALPE	−0.1515	0.0506	
ALPO	**0.8473**	−0.1824	−0.1169
Bromacil			
WPDC			
GRNE	**0.3176**		
ALPE	−0.1476	0.1098	
ALPO	−0.1112	−0.0617	0.0721
Glyphosate			
WPDC			
GRNE	**0.9317**		
ALPE	**0.7862**	**0.8301**	
ALPO	**0.8254**	**0.9075**	**0.7996**

5. Conditions of Release and Management

As the upstream electrical transfer station is the likely source for algae toxicity, and not LLNL, no information was available for the final step in the source evaluation identifying the amount and timing of the pesticide application. As a result, a simple analytical solution for solute transport in surface runoff was employed to estimate the initial mass of the herbicides applied and examine transport. The following model calculations are only our best estimates based on the information available. Although the model results are consistent with the limited number of observations, there is no information on the accuracy of the model prediction. Therefore, the model application and results are presented to illustrate the logical progression of the source evaluation. The model proposed by Havis, Smith, and Adrian (1992) was selected. This model is an analytical solution for mass transport in surface overland runoff, where the concentration of the solute [$C(t)$] is:

$$C(t) = \left[\frac{KC_{mo}}{h} + \frac{(K+f)}{Z_1}C_o\right] \bullet \frac{[\exp(yt) - \exp(xt)]}{y - x}$$
$$+ C_o\frac{[y \bullet \exp(yt) - x \bullet \exp(xt)]}{y - x} + C_\infty, \quad (1)$$

where solute retardation (Z_1) is given by:

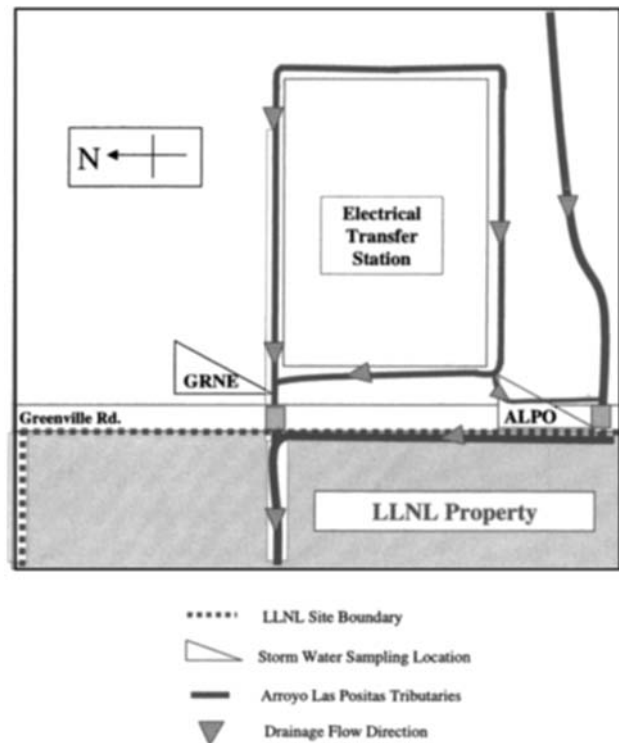$$Z_1 = [\rho_b K_d(1 - n) + n]\varepsilon \quad (2)$$

and where:

Figure 6. Map of the electrical transfer station upstream of Lawrence Livermore National Laboratory on the Arroyo Las Positas.

$$x = \frac{R(f + K)}{hZ_1 y}$$
$$y = \left\{\left[\frac{(K+f)}{2Z_1} + \frac{(K+R)}{2h}\right]^2 - \frac{R(f+K)}{hZ_1}\right\}^{1/2}$$
$$- \frac{K+f}{2Z_1} - \frac{K+R}{2h} \quad (3)$$

and

K = film transport coefficient, cm/s;

C_{mo} = initial concentration of the solute in the soil in μg/cm³;

h = depth of overland flow, cm;

f = infiltration rate, cm/s;

C_o = initial concentration of the solute in rainfall, μg/cm³;

R = rainfall rate, cm/s;

t = time, s;

ρ_b = soil bulk density, g/cm³;

K_d = solute partitioning coefficient;

n = soil porosity; and

ε = depth of the mixing zone between surface runoff and soil water in soil, cm.

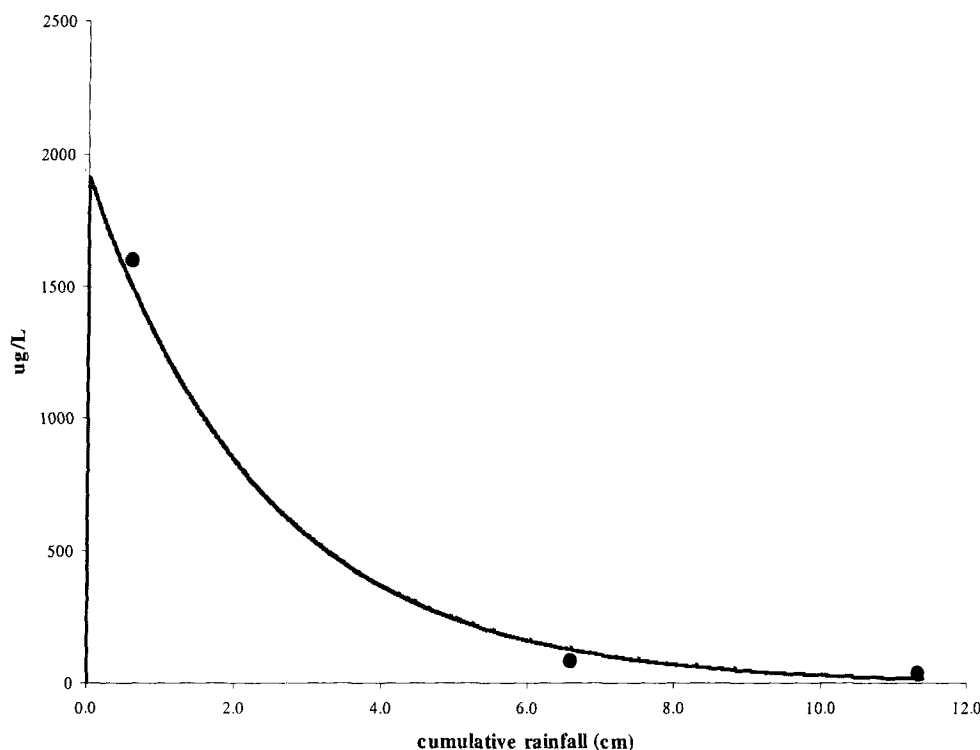Investigating Sources of Toxicity in Stormwater   31

Figure 7. The Havis model (solid line) compared with data from Lawrence Livermore National Laboratory sampling location GRNE (points), plotted against cumulative rainfall.

Bromacil and diuron are pre-emergent herbicides and therefore are generally applied near the beginning of the wet season in California. In addition, it is understood that they work better if application is followed by rain or irrigation to allow for incorporation of the herbicide into growing plants and seeds. Notice in Figure 4 that the peaks in diuron concentrations most often occur around December, when the first significant rains occurred during the monitoring period. This substantiates that the herbicides tend to be applied at the beginning of each growth season.

Assuming a single annual application of the herbicides, the Havis model was used to estimate the initial mass that would have been applied to produce concentrations observed at sampling location GRNE. To do this, the model was calculated assuming a solute partitioning coefficient (K_d) of 2.54 (Louchart, Voltz, and Andrieux, 2000) and using the 2001 rainfall totals. Reasonable values for infiltration rate (1.4×10^{-6} cm/s), soil bulk density (2.0 g/cm^3), soil porosity (0.2), and depth of the mixing zone (0.6 cm) were selected based on experience with other studies at LLNL. Using these values essentially assumes that most of the water reaching the ground as precipitation becomes surface runoff. The model was then fit to the observed diuron concentrations on January 8, January 10,

and February 12 of 2001 (Figure 7) to estimate initial concentration of the solute in the soil.

This exercise revealed that the application must have been approximately 2000 µg/cm^3, or a total of 98.7 kg (258 lb), of diuron over the entire surface area (approximately 3 ha) of the electrical transfer station (Figure 6). This application level equates to about 40 kg/ha (36 lb/acre). Manufacturers suggest application levels of 9 to 11 kg/ha, whereas normal application levels have been found to range from 0.7 to 9 kg/ha around cropped areas and 17 to 54 kg/ha on non-agricultural areas (Cornell University, 1983).

Therefore, although this application level is higher than the manufacturer's suggested application level, it is not larger than the reported normal range for non-agricultural land use areas. Similarly, a study by Scanlin and Feng (1997) on the pesticide diazinon in a northern California creek suggested that even when the pesticide was applied by residential users according to label directions, water quality problems persisted. According to the Havis model developed in this case, even an application level of 10 kg/ha (in the manufacturer's suggested range), the concentration of diuron at sampling location GRNE on January 8, 2001, would be approximately 373 µg/L, placing it at toxic levels for algae
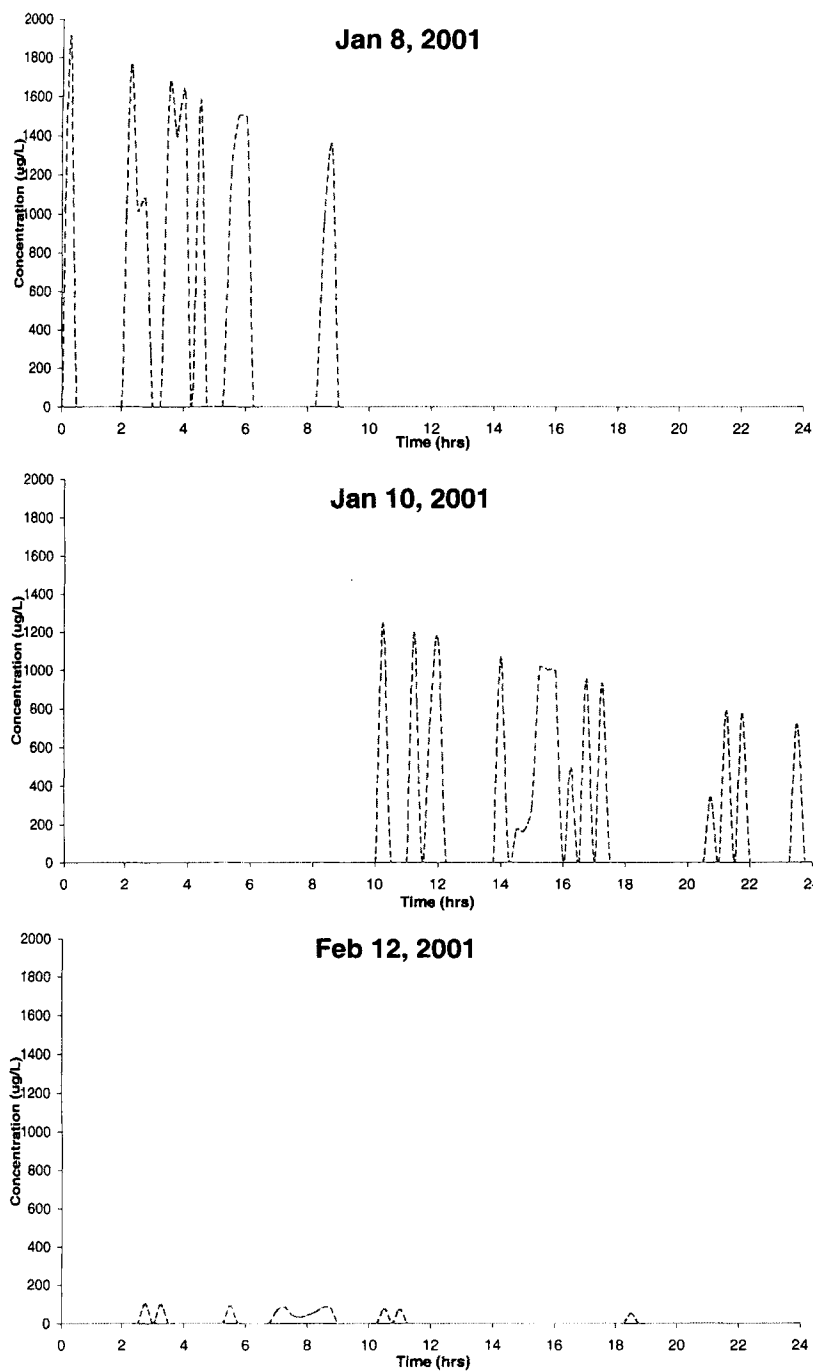
Figure 8. Havis model output for January 8, January 10, and February 12, 2001, predicting diuron concentrations in stormwater at Lawrence Livermore National Laboratory sampling location GRNE.

(Cornell University, 1983). The 40 kg/ha application level estimate and high stormwater concentration (1600 µg/L) in January 2001 at location GRNE identify the need to consider more than the recommended application quantity suggested on pesticide labels. If an area where pesticides are applied drains directly into a stream, even a small amount of mobilized pesticide can exceed toxic levels and significantly affect aquatic life.

Figure 8 shows the concentrations estimated by the model to have been mobilized and moved into the Arroyo Las Positas near the GRNE sampling location in each of the first three storms sampled in 2001. The concentrations are very high on January 8, when the first algae toxicity sample was collected in 2001. By February 12, the concentrations are much lower, but still higher than the concentrations needed to produce a toxic response in algae of 9 to 14 µg/L.

Summary and Conclusions

A source evaluation for observations of algae toxicity in an intermittent stream near Livermore, California, is presented. A five-step procedure is proposed to determine the source of a failed toxicity test and to determine appropriate environmental management practices. Potential sources for the toxicity identified were metals toxicity and three different herbicides. Two herbicides were determined to be the most likely sources of toxicity—bromacil and diuron. Historical data, correlation analysis, and follow-up toxicity tests were used to confirm that the source of these herbicides was upstream of LLNL. An electrical transfer station was identified as the probable source, and an analytical solution for solute transport in overland flow was used to estimate the application level of 40 kg/ha (36 lb/acre).

This examination demonstrates the value of a well-designed monitoring program that combines chemical measurements and toxicity testing. The importance of the five-step approach is also illustrated as each step increased our understanding of the problem, improving our ability to develop solutions.

Finally, it is clear that even small quantities of a pesticide applied without considerations of its impact can result in degradation of environmental quality. The conclusion of this study supports the findings of Scanlin and Feng (1997), in which a legally applied insecticide was found to cause in-stream toxicity when the insecticide was carried to a local creek by stormwater runoff. This finding presents a problem for environmental managers who rely on US Environmental Protection Agency and state approval of a pesticide as an indication that the material will not cause water quality degradation when used in accordance with its labeled requirements. Regardless of labeling, environmental managers need to ensure that pesticides that could harm aquatic organisms, including algae, not be used in close proximity to streams or storm drainage pathways, and that the least toxic alternative to abate the pest species is used.

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