Smith River Plain Surface Water Monitoring Report 2021 – 2024

September 2025

Surface Water Ambient Monitoring Program (SWAMP)
North Coast Region

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1 EXECUTIVE SUMMARY

From 2021 through 2024, the North Coast Regional Water Quality Control Board (North Coast Water Board) implemented the Adaptive Management Monitoring Program (monitoring study) described in the 2021 Smith River Plain Water Quality Management Plan (Management Plan) to assess the water quality of coastal tributaries flowing through areas in the Smith River Plain used for cultivation of Easter lily bulbs, *Lilium longiflorum*. The monitoring study's main goals were to evaluate the effectiveness of current agricultural water quality control practices, determine the status and trends of pesticide concentrations in surface waters, and analyze associations between water quality and agricultural practices. The data collected are being used to inform the ongoing development of general Waste Discharge Requirements for regulating the potential water quality impacts of lily bulb cultivation activities (Lily Bulb Order).

The issuance of Waste Discharge Requirements is one of the regulatory mechanisms available to California's Regional Water Quality Control Boards¹ to address discharges of waste to waters of the State of California. North Coast Water Board staff intend to use the data collected from this study to inform the development of adaptive management requirements in the Lily Bulb Order for controlling waste discharges associated with synthetic and copper-based pesticides. The data collected in this study were also used to run the Biotic Ligand Model (BLM) to predict the bioavailability of copper in Smith River Plain receiving waters and its potential toxicity to aquatic life (see Section 4).

Surface water sampling was conducted between October 2021 and September 2024 across 25 events. Sampling was conducted during both wet (storm) and dry seasons and included events close to, or during precipitation events that generated stormwater runoff. Sampling was conducted primarily by North Coast Water Board staff, with additional sampling by Dr. Matthew Hurst of Cal Poly Humboldt and his graduate students under contract with the North Coast Water Board. Methods remained consistent throughout the study. Samples were analyzed by State Water Resources Control Board (State Water Board) contract laboratories, and results were uploaded to the California Environmental Data Exchange Network (CEDEN).

Over the study period, diuron and imidacloprid – both persistent and highly mobile current-use pesticides – were commonly detected downstream of lily bulb fields, generally below relevant water quality criteria (see Section 4). However, exceedances of water quality criteria were periodically observed at sampling locations in Lower Delilah Creek and Tillas Slough, primarily during storm events. Ethoprop, a less persistent current-use pesticide, was rarely detected, with only one water quality criteria exceedance. Dissolved copper concentrations were consistently elevated downstream of lily bulb fields relative to background, and occasionally the BLM predicted copper bioavailability at potentially toxic levels in samples collected during the storm season.

A comparison of the data set against rainfall records revealed sharp increases in diuron and imidacloprid concentrations during early overland flow from large storms (>2 inches in 3 days), followed by dilution as streamflow rose. After storms, moderate concentrations persisted, likely

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¹ Regional Water Quality Control Boards are the regional California regulatory agencies responsible for preserving, enhancing, and restoring the State's water resources through the implementation of both regulatory and non-regulatory programs.

from shallow groundwater contributions, suggesting both surface runoff and subsurface transport are pathways for pesticide delivery to streams. Outside the storm season, persistent low-level detections of diuron and imidacloprid indicate the possibility of ongoing transport through shallow groundwater baseflow. Dissolved copper followed a similar seasonal pattern, with predicted bioavailability and potential toxicity frequently elevated during storm events and reduced outside the storm season. Depressed pH levels in surfaces waters downstream of lily bulb fields during the wet (storm) season increased predicted copper bioavailability and potential toxicity. The decreasing pH observed in the Smith River Plain tributaries is consistent with long-term groundwater trends, which show a shift from alkaline conditions in the 1970s to slightly acidic conditions today.

Based on these findings, North Coast Water Board staff recommend reducing diuron, imidacloprid, and copper application rates in watersheds with exceedances of water quality criteria and predicted copper toxicity; identifying and implementing management practices that reduce pesticide and copper transport (e.g., increasing soil organic carbon content); and investigating mechanisms that contribute to depressed pH in receiving waters near lily bulb cultivation areas. Surface water monitoring should remain focused on storm-season sampling, with emphasis on capturing both initial overland flow and post-storm baseflow periods, particularly in tributaries with elevated application rates and exceedances of relevant water quality criteria. These recommendations are presented for potential consideration in the development and refinement of planned Waste Discharge Requirements for lily bulb operations.

2 INTRODUCTION

This report presents findings and analyses from the Adaptive Management Monitoring Program (monitoring study) described in the 2021 Smith River Plain Water Quality Management Plan (Management Plan) ². The monitoring study was designed to assess the water quality of coastal tributaries flowing through Easter lily bulb cultivation areas in the Smith River Plain and to evaluate the fate and transport of applied copper and synthetic pesticides used in lily bulb production. The data and analyses presented here are intended to improve understanding of surface water quality conditions in Smith River Plain tributaries and to inform the development of Waste Discharge Requirements for lily bulb discharges.

2.1 Background

The Smith River Plain is a coastal plain characterized by a network of small coastal tributaries located near the mouth of the Smith River in California's Del Norte County. The region experiences cool, dry summers and wet winters, with an average annual rainfall of approximately 75 inches and a storm season that typically spans from October through May. Predominant land uses in the Smith River Plain currently include lily bulb cultivation, cattle ranching, dairy production, and aggregate mining.

Lily bulb cultivation in the Smith River Plain, which is concentrated on roughly 1,200 acres along the north side of the Smith River, occurs on a rotation with pasture and forage crops, with no

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² <u>Smith River Plain Water Quality Management Plan - November 2021</u> <u>https://www.waterboards.ca.gov/northcoast/water_issues/programs/agricultural_lands/lily/pdf/20</u> <u>21/smithmgmttplan.pdf</u>

more than 200–250 acres planted each year. Cultivation occurs year-round, including during the storm season, when pesticide applications to manage nematodes, aphids, whiteflies, weeds, and botrytis have an elevated risk of being transported to surface waters via runoff and shallow groundwater.

A Surface Water Ambient Monitoring Program (SWAMP) study conducted from 2013 to 2015 documented active ingredients from synthetic and copper-based pesticides in surface waters of the Smith River Plain at concentrations that exceeded U.S. EPA aquatic life benchmarks (Smith River Plain Surface Water and Sediment Monitoring Report 2013-2015, issued January 2018 [2018 SWAMP Report])³.

In response, the North Coast Regional Water Quality Control Board (North Coast Water Board) directed staff to develop a targeted, collaborative water quality management strategy. The resulting Management Plan (see footnote 2) was developed and finalized in 2021 by a Watershed Stewardship Team composed of the lily bulb growers, regulatory agencies (e.g., NOAA Fisheries, CA Department of Fish and Wildlife, CA Department of Pesticide Regulation), local stakeholders (e.g., Del Norte Resource Conservation District, Agricultural Commissioner, the Smith River Alliance), academic partners, and the Tolowa Dee-ni' Nation. The Management Plan established a voluntary framework for adaptive management and a planned monitoring study to evaluate water quality under ongoing lily bulb cultivation practices to inform future development of Waste Discharge Requirements for lily bulb operations.

2.2 Study Purpose

The objectives of the monitoring study as described in the 2021 Management Plan include, but are not limited to the following (paraphrased):

- Determine agricultural practice effectiveness in meeting water quality objectives.
- Determine water quality/pesticide status and trends in surface waters,
- Determine seasonal and agricultural associations/correlations (if any) within the water quality data set,
- Collect data necessary for running the Biotic Ligand Model (BLM), which is used to assess the bioavailability of dissolved copper to aquatic species and to develop sitespecific toxicity assessment endpoints consistent with the North Coast Water Board's Water Quality Control Plan (Basin Plan)4, and
- Inform development of the General Waste Discharge Requirements for Commercial Lily Bulb Operations in the Smith River Plain (Lily Bulb Order).

³ Smith River Plain Surface Water and Sediment Monitoring Report - January 2018 https://www.waterboards.ca.gov/northcoast/water_issues/programs/agricultural_lands/pdf/1801 16/180101-FINAL%20SWAMP%20REPORT_Smith%20River.pdf

⁴ <u>Water Quality Control Plan for the North Coast Region</u> <u>https://www.waterboards.ca.gov/northcoast/water_issues/programs/basin_plan/basin_plan_doc_uments/</u>

2.3 Monitoring Report Format

This report is organized into the following sections: The monitoring design and sampling methods in the monitoring study are presented in Section 3. Relevant water quality criteria for synthetic pesticides and dissolved copper are described in this Section 4 for the purpose of evaluating water quality monitoring results. The results of the data collection effort are presented in Section 5, including the results of BLM modeling. In addition to presenting analytical results, this report includes data analyses aimed at developing a preliminary understanding of fate and transport mechanisms. Section 6 presents two key analyses: the relationship between monitoring results and rainfall/storm events, and the relationship between monitoring results and pesticide and copper application rates. Section 7 presents conclusions that interpret monitoring data and analyses to characterize the fate and transport of agricultural chemicals from lily bulb cultivation in the Smith River Plain. Section 8 presents recommendations that focus on reducing pesticide and copper inputs from lily bulb fields, improving understanding of pH dynamics, and refining strategies to improve monitoring of storm-driven transport of copper and synthetic pesticides. Tabular summaries of laboratory results, field measurements, and additional information supporting the analysis and interpretation of the data set are included in Appendices A through G.

3 MONITORING STUDY METHODS

This section describes the study methods, including site selection, sample collection protocols, analytical testing, and timing of sampling events. The study was implemented by North Coast Water Board staff with support from Dr. Matthew Hurst of Cal Poly Humboldt and his graduate students. Funding was provided through the North Coast Water Board's Surface Water Ambient Monitoring Program (SWAMP). Samples were processed at State contract laboratories, including Moss Landing Marine Lab, Babcock Labs, and North Coast Labs.

3.1 Sampling Locations

The study was designed to characterize the range of synthetic pesticide and dissolved copper concentrations in surface waters potentially influenced by discharges from lily bulb fields, rather than to investigate discharges from individual lily bulb fields. Accordingly, sampling locations were selected at downstream portions of tributaries receiving drainage from areas of the Smith River Plain under lily bulb cultivation. Location selection focused on monitoring surface waters downstream of lily bulb fields and was further guided by the following factors:

- Locations accessible to staff
- Locations at the base of a watershed
- Locations with adequate stream flow
- Locations amenable to detecting changes in contaminant concentration and effects over time
- Locations most likely to characterize the accumulation of contaminants draining from agricultural lands
- Locations on waterbodies with potentially vulnerable aquatic species or habitat
- Locations with previous or companion water quality data available

North Coast Water Board staff collected samples at eleven locations described in Table 1, upstream and downstream of lily bulb cultivation areas. Most major drainage areas for

tributaries in the Smith River Plain that contain lily bulb operations were monitored (see Figure 1). Drainage areas outside blue line coastal tributaries were not monitored.

To reach sampling locations on private lands, lily bulb growers voluntarily granted exclusive access to their land to North Coast Water Board staff and Dr. Matthew Hurst. North Coast Water Board staff informed growers of sampling events and coordinated with them on timing to meet with staff in the field, open locked gates, or move livestock as needed. Monitoring study implementation would not have been possible without their cooperation and North Coast Water Board staff appreciate their willingness to facilitate this study.

Sampling locations are shown on Figure 1 and described in Table 1 below. Upstream locations are labeled with as 'Upper', and downstream locations are labeled with 'Lower' except for Tillas Slough, which is a downstream location. Sampling locations accessed through private property are indicated as such in Table 1.

Table 1. Monitoring Study Station Names (with CEDEN Station Codes) and Descriptions

Upstream	Upstream	Downstream	Downstream
Monitoring	Location	Monitoring	Location
Station Name	Description	Station Name	Description
Upper Ritmer (103RI2000)	Ritmer Creek @ Ocean View Dr.	Lower Ritmer (103RI1000)	Ritmer Creek (private property)
Upper Delilah	Delilah Creek	Lower Delilah	Delilah Creek
(103DE7500)	(private property)	(103DE5776)	@ Sarina Road
Upper Rowdy	Rowdy Creek	Lower Rowdy	Rowdy Creek
(103RW2000)	@ Highway 101	(103RW0319)	(private property)
Upper Morrison	Morrison Creek	Lower Morrison	Morrison Creek
(103MO3500)	@ Highway 101	(103MO2500)	@ Fred Haight Dr.
Upper Mello	Mello Creek	Lower Mello	Mello Creek
(103ME2000)	(private property)	(103ME1000)	@ Fred Haight Dr.
n/a	n/a	Tillas Slough (103TL1789)	Tillas Slough at Tide Gate

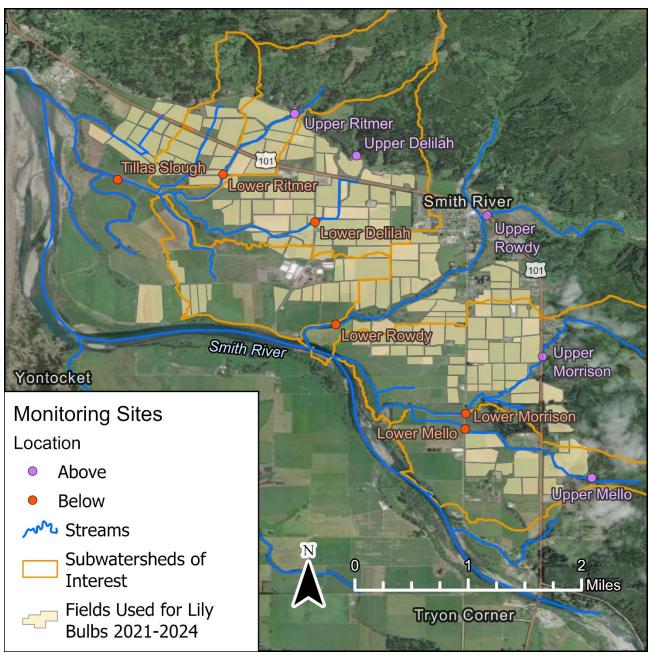


Figure 1. Surface Water Sampling Locations, October 2021 to September 2024

3.2 Sample Collection Protocols

Monitoring study protocols for sample collection and analysis followed the California Surface Water Ambient Monitoring Program Standard Operating Procedures and Quality Assurance Program Plan. After sampling, analysis, and completion of all quality control checks, State Water Board staff entered the data into the California Environmental Data Exchange Network (CEDEN) for incorporation into the statewide database, which may be accessed by the public anytime via online query⁵.

North Coast Water Board staff measured standard field parameters using a YSI Datasonde during all site visits and collected surface water grab samples for the analysis of conventional water quality constituents, dissolved copper, and pesticides using the approved methods described above.

3.3 Selection of Analytes

Pesticides selected for laboratory analysis were identified through a risk assessment conducted as part of the 2021 Management Plan. The assessment considered multiple factors, including pesticide physiochemical properties, results from the 2013-2015 SWAMP surface water and sediment monitoring documented in the 2018 SWAMP Report, Pesticide Use Reports from 2014-2018, and prioritization protocols developed by the CA Department of Pesticide Regulation (DPR). DPR's prioritization process incorporates both pesticide use and aquatic toxicity, with toxicity values derived from U.S. EPA Aquatic Life Benchmarks⁶. A probability-based use ranking and toxicity ranking were combined into a final prioritization score, which was evaluated for fish and invertebrates. Final selection of pesticides was based on final prioritization score, pesticide properties and prior SWAMP monitoring results.

Additional parameters measured during the study included standard water quality indicators (e.g., temperature, dissolved oxygen, specific conductivity, salinity, pH) and parameters required for the Biotic Ligand Model (BLM), including major cations (magnesium, sodium, potassium, calcium), anions (chloride, sulfide, sulfate), and dissolved organic carbon.

The analytes included in the study are listed in the following tables. There are three categories of analytes: pesticides, BLM constituents, and ancillary parameters. The lab method used for each analyte is referenced in the table.

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⁵ <u>CEDEN - California Environmental Data Exchange Network</u> https://ceden.org/index.shtml

⁶ Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk.

Table 2. Pesticide Analytes

Chlorpyrifos (EPA 525.3)	Imidacloprid (NCL ME 321)	Tebuconazole (EPA 525.3, EPA 8270C)
Dimethipin (EPA 525.3)	Oxyfluorfen (EPA 525.3)	Tribufos (EPA 525.3)
Diuron (NCL ME 321, EPA 632M)	Permethrin (EPA 525.3, EPA 8081BM)	Hexachlorocyclohexane (EPA 8081BM)
Ethoprop (EPA 8141A)	Profenofos (EPA 525.3)	

Table 3. Biotic Ligand Model (BLM) Constituent Analytes

Alkalinity (SM 2320 B)	Dissolved Organic Carbon (SM 5310 B)	Sodium (EPA 200.7, EPA 1638M)
Calcium (EPA 200.7, EPA 1638M)	Magnesium (EPA 200.7, EPA 1638M)	Sulfate (EPA 300.0)
Chloride, Total (EPA300.0)	pH (Field Measure)	Sulfide (SM 4500-S2)
Copper, Dissolved (EPA 200.8, EPA 1638M)	Potassium (EPA 200.7, EPA 1638M)	Temperature (Field Measure)

Table 4. Ancillary Analytes

Bicarbonate (SM 2320 B)	Nitrate as Nitrogen (EPA 300.0, SM 4500-NO3 I v21)	Suspended Sediment Conc. (MPSL-108v2, ASTM D3977)
Dissolved Oxygen (Field Measure)	Oxygen, Saturation (Field Measure)	Carbonate, Total (SM 2320 B)
Hardness (SM 2340 B, EPA 130.1)	Salinity, Total (Field Measure)	Hydroxide (SM 2320 B)
Specific Conductivity (Field Measure)		

3.4 Timing of Sampling Events

Table 5 summarizes the month of sample collection, the categories of data collected, and whether sampling occurred during the wet or dry season. Several wet-season events were specifically triggered by forecasted storms of at least 0.5 inches of rainfall to capture runoff conditions. Section 6.1 provides additional detail on storm events and rainfall amounts during the study period and discusses their potential influence on pesticide concentrations in surface waters.

Table 5. Sampling Events for the 2021-2024 Monitoring Study Period

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
2021												
2022												
2023												
2024												

Wet Season Sampling Event (October – May)

Dry Season Sampling Event (June – September)

Not all monitoring stations were sampled during every event, either because flows were too low to collect samples or because conditions made the stations unsafe to access. Samples for BLM constituents and ancillary analytes were collected at each sampling event, but pesticide samples were limited to select events due to cost constraints. In some cases, analytical results were unavailable because sample bottles were lost or damaged in transit, laboratory quality control issues arose, or holding times for certain parameters were exceeded. In the data tables presented in Appendix A to this report, unsampled locations are indicated as "NS" (not sampled), and lost or damaged samples are indicated as "LOST."

4 RELEVANT WATER QUALITY CRITERIA

Relevant water quality criteria for synthetic pesticides and copper are described in this section for the purposes of evaluating water quality monitoring results. These criteria were selected from a variety of sources and are generally consistent with the State Water Board's guidelines for listing impaired waters under Section 303(d) of the Clean Water Act. North Coast Water Board staff worked closely with State Water Board staff to ensure consistency, whenever possible, between evaluations using the water quality criteria listed below and current 303(d) listing guidelines.

As a general approach, North Coast Water Board staff reviewed all available pesticide water quality criteria and selected the most protective (i.e., lowest) values for relevant beneficial uses. Table 6 presents the relevant water quality criteria for both ecological beneficial uses and drinking water. Throughout this report, water quality monitoring results are evaluated against water quality criteria. Unless otherwise noted, references to "water quality criteria" in the report mean the lowest applicable value shown in Table 6.

4.1 Beneficial Uses of Water in the Smith River Plain

The North Coast Water Board's mission is (in part) to protect the beneficial uses of waters of the state by maintaining water quality and/or enhancing it to a level supportive of those uses. The beneficial uses of the Smith River Plain Hydrologic Subarea are designated in the Basin Plan (see footnote 4) and are listed below:

- Municipal and Domestic Supply
- Agricultural Supply
- Industrial Service Supply
- Industrial Process Supply
- Freshwater Replenishment
- Navigation
- Water Contact Recreation
- Non-Contact Water Recreation
- Commercial and Sport Fishing
- Cold Freshwater Fishery
- Wildlife Habitat
- Rare, Threatened, or Endangered Species
- Marine Habitat
- Spawning, Reproduction, and/or Early Development
- Migration of Aquatic Organisms
- Estuarine Habitat
- Aquaculture
- Tribal Subsistence Fishing, Tribal Tradition and Culture

Table 6. Relevant Water Quality Criteria for Pesticides and Beneficial Uses Protected

Pesticide	Water Quality Criterion (ug/L)	Use Protected	Source or Reference ⁷
Diuron	1.3	Cold Freshwater Habitat	UC Davis Water Quality Criteria for Diuron
Diuron	2.0	Municipal Drinking Water	USGS Health Based Screening Level (HBSL) for one-in-a-million cancer risk estimate
Ethoprop	0.8	Cold Freshwater Habitat	EPA Chronic Aquatic Life Benchmarks for Pesticides - Freshwater Invertebrates
Ethoprop	0.37	Municipal Drinking Water	EPA Chronic Noncancer Human Health Benchmarks for Pesticides
Imidacloprid	0.016	Cold Freshwater Habitat	UC Davis Water Quality Criteria for Imidacloprid
Imidacloprid	283	Municipal Drinking Water	DPR Human Health Reference Levels for Pesticides
Permethrin	0.002	Cold Freshwater Habitat	UC Davis Water Quality Criteria for Pyrethroids
Permethrin	2900	Municipal Drinking Water	EPA Chronic Noncancer Human Health Benchmarks for Pesticides
Dissolved Copper in Freshwater	Varies w/ hardness (See data tables in Appendix A)	Cold Freshwater Habitat	California Toxics Rule (chronic and acute criteria)
Dissolved Copper in Saltwater (acute)	4.8	Estuarine Habitat	California Toxics Rule
Dissolved Copper in Saltwater (chronic)	3.1	Estuarine Habitat	California Toxics Rule
Dissolved Copper (chronic and acute)	Toxicity Unit ⁸ <1	Cold Freshwater and Estuarine Habitats	Biotic Ligand Model

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⁷ See Section 9 for references to the Water Quality Criteria listed in this section and in Table 6.

⁸ The toxicity unit (TU) is a simple ratio of the measured concentration of dissolved copper to the BLM-generated criteria and is calculated by dividing the measured value by the modelled criteria. See the 'Dissolved Copper Results' section below for more information on how the 'TU' is calculated and used.

4.2 EPA Aquatic Life Benchmarks

The U.S. EPA developed Aquatic Life Benchmarks for freshwater species that are based on toxicity values reviewed by the EPA and used in EPA risk assessments developed as part of the decision-making process for pesticide registration. The toxicity data used to develop Aquatic Life Benchmarks are extracted from the most recent publicly available EPA Office of Pesticide Programs risk assessment for the individual pesticide and are typically based on the most sensitive value for each taxon. The benchmarks are reviewed and updated annually and may be revised when new risk assessments become available.

EPA Aquatic Life Benchmarks are intended to protect aquatic organisms – such as fish, invertebrates, and plants – from harmful effects. Aquatic Life Benchmarks are estimates of the concentrations below which pesticides are not expected to represent a risk to aquatic life. These benchmarks are not regulatory criteria or standards, rather benchmarks for use in ecological risk assessment in the pesticide registration process.

4.3 EPA Chronic Noncancer Human Health Benchmarks

The EPA Chronic Noncancer Human Health Benchmarks (HHBPs) are concentrations of pesticide residues in drinking water that are not expected to cause adverse health effects from long-term exposure (typically over a lifetime), excluding cancer risks. These benchmarks help evaluate potential human health risks from chronic exposure to pesticides in drinking water and can be used to interpret water monitoring data. The criteria are based on EPA human health risk assessments conducted during pesticide registration. If a pesticide concentration exceeds the benchmark, it does not automatically indicate a health risk, but it could warrant further investigation.

4.4 US Geologic Survey (USGS) Health Based Screening Levels

Health-Based Screening Levels (HBSLs) are federal, non-enforceable (by the EPA or other federal agency) water-quality benchmarks developed by the USGS. They were developed to supplement EPA Maximum Contaminant Levels and HHBPs, for purposes of determining whether contaminants found in surface-water or groundwater sources of drinking water may indicate a potential human-health concern, and for prioritizing monitoring efforts. They provide a basis for a more comprehensive evaluation of contaminant-occurrence data in the context of human health. The cancer based HBSLs represent a concentration in water that corresponds to a specified cancer risk (not a no-effect concentration), in this case a one-in-a-million cancer risk. The human-health toxicity values used to calculate HBSLs are published by EPA, peer reviewed, and are the most recently available. HBSLs are calculated assuming an adult's lifetime of exposure to drinking water. As a result, contaminant concentrations indicative of long-term exposure are most appropriate to compare to these benchmarks.

4.5 UC Davis Water Quality Criteria

University of California at Davis (UC Davis) developed a methodology for deriving freshwater water quality criteria for the protection of aquatic life in coordination with the California Central Valley Regional Water Quality Control Board. UC Davis developed a statistical methodology for deriving the criteria, which involves calculating the 5th or 1st percentile of a species sensitivity distribution to protect aquatic life using available toxicity studies. The UC Davis methodology has been used to derive aquatic life criteria for several pesticides of particular concern in the Sacramento River and San Joaquin River watersheds. However, the UC Davis reports

describing the criteria development note that use of the criteria would be appropriate for any freshwater ecosystem in North America, unless more sensitive species are likely to occur. These criteria are intended to help assess monitoring data and provide information on whether pesticides should be prioritized for developing water quality control programs.

4.6 DPR Human Health Reference Levels for Pesticides

DPR Human Health Reference Levels (HHRLs) are identified by DPR's Human Health Assessment Branch. Pesticide concentrations measured in water exceeding these reference levels indicate a health concern. They are not legally enforceable standards but can be used to identify pesticide levels that could pose a human health risk, requiring further assessment. DPR calculates HHRLs based on toxicity data and exposure scenarios, often considering the summation of related compounds like metabolites. They are intended to be used as screening tool, a means to assess monitoring data, and/or as a trigger for further investigations and potential regulatory action to address the health concern.

4.7 California Toxics Rule Criteria

One set of water quality criteria for dissolved copper are based on the California Toxics Rule (CTR). These copper criteria are consistent with the guidelines used for developing the State's list of impaired waterbodies, pursuant to Section 303(d) of the federal Clean Water Act. Rows appearing at the bottom of the BLM Constituent data tables presented in Appendix A to this report contain calculated values for water hardness and for CTR dissolved copper criteria. The CTR criteria serve as potential reference thresholds for the dissolved copper sampling results that appear directly above them in the tables. There are two types of criteria presented for each dissolved copper sampling result; an acute concentration criterion labeled as 'CTR 1-hour', and a chronic concentration criterion labeled as 'CTR 4-day.' The CTR criteria are included in this report for reference. However, analyses and discussions in Sections 5 and 6 will focus on evaluating the dissolved copper data set using the BLM model outputs.

4.8 Biotic Ligand Model

A second set of water quality criteria for dissolved copper is based on the model outputs of the Biotic Ligand Model (BLM). As mentioned in the Introduction Section above, the BLM represents a refinement of the hardness-based CTR criteria. The BLM is the current EPA recommended method for determining copper concentrations protective of aquatic life on a site-specific basis and has been adopted by the State of Idaho Department of Environmental Quality and the State of Oregon Department of Environmental Quality to develop state-wide, site-specific water quality criteria for copper. Several other states have used the BLM for site-specific monitoring efforts but have yet to adopt statewide BLM-based criteria. In California, the State Water Board is developing a proposed water quality control policy to establish methods, protocols, and procedures for Regional Water Quality Control Boards to develop, adopt, and implement site-specific water quality objectives for copper and zinc based on the BLM.

The BLM uses a set of ten parameters to account for complex chemical reactions associated with copper in the environment: pH, Dissolved Organic Carbon (DOC), Calcium (Ca), Magnesium (Mg), Sodium (Na), Sulfate (SO4), Potassium (K), Chlorine (Cl), Alkalinity, and Temperature. Using these ten parameters, the BLM generates an Instantaneous Water Quality Criterion (IWQC). The IWQC is used in the context of this study as a water quality threshold for dissolved copper for that specific site and sampling event only. The model's output also includes a toxicity unit (numerical value) to represent the relative risk of copper toxicity in the waterbody

at the time of sample collection. Exceedances of the IWQC mean that dissolved copper bioavailability was predicted to occur at a potentially toxic level for the sample in question. In this report, the term "predicted copper toxicity" is used when dissolved copper bioavailability is evaluated using BLM model outputs. Dissolved copper bioavailability predictions using the BLM are presented in Section 5.2 of this report.

5 MONITORING STUDY RESULTS

North Coast Water Board staff previously shared the Smith River Plain Surface Water Monitoring Provisional Data Summary 2021-2024, which summarized the provisional monitoring study sampling results, with the Lily Bulb Order Technical Advisory Group, a group of stakeholders working with staff on Order development. Except for results from Tillas Slough with high salinity (see Section 5.2), the provisional results featured in the data summary have now been verified as final by the State Water Board's quality control staff and have been uploaded to the State's CEDEN database. The verified results of the monitoring study are presented below. A tabular summary of laboratory results and field measurements is presented in Appendix A.

5.1 Synthetic Pesticide Results

Synthetic pesticide detections, the range of concentrations detected, and the number of exceedances of water quality criteria are summarized in Tables 7-9. Diuron, ethoprop, and imidacloprid were the three pesticides associated with lily bulb cultivation in the study that were detected at monitoring stations downstream of lily bulb cultivation areas. Each pesticide is described below with tables following that summarize the monitoring results. These data have met the required quality control checks. All samples were analyzed by certified laboratories and can be relied upon to inform development of the Lily Bulb Order. The data have been uploaded to the CEDEN database consistent with statewide policy and can be publicly accessed via online query from the CEDEN website (see footnote 5).

5.1.1 Diuron

Diuron is a pre-emergent long-lasting herbicide used to control both annual and perennial weeds. It has relatively low water solubility (approximately 42 mg/L at 25°C) and a moderate to low soil adsorption coefficient, meaning that it is mobile in the environment and has the potential to leach into groundwater under certain environmental conditions (EPA, 2003). Diuron is also environmentally persistent, with a soil half-life between 146-229 days (Management Plan, 2021), depending on soil properties and climate. These combined properties – moderate to low adsorption, persistence, and limited solubility – make diuron a threat to water quality. Diuron has been detected in monitoring wells in agricultural regions of California and is listed as having the potential to pollute groundwater on the California Code of Regulations Section 6800 Groundwater Protection List.⁹ The following table summarizes the detections, range of concentrations, and the number of water quality criterion exceedances.

⁹ <u>California Code of Regulations, Title 3, Division 6, Chapter 4. Environmental Protection</u> <u>https://www.cdpr.ca.gov/laws-and-regulations/california-code-of-regulations-title-3-food-and-agriculture-division-6-pesticides-and-pest-control-operations/chapter-4-environmental-protection/#6800-groundwater-protection-list</u>

Table 7. Detections, Exceedances, and Range of Concentrations for Diuron. (Water Quality Criterion: 1.3 ug/L)

Station	Number of Samples	Number of Detections	Number of Exceedances	Range of Concentrations (ug/L)
Upper Delilah	19	1 (5%)	0 (0%)	0.0015
Lower Delilah	19	18 (95%)	1 (5%)	0.023 - 5.9
Upper Morrison	19	1 (5%)	0 (0%)	0.0022
Lower Morrison	15	14 (93%)	0 (0%)	0.002 - 0.28
Lower Ritmer	19	14 (74%)	0 (0%)	0.0021 - 0.028
Lower Rowdy	20	3 (15%)	0 (0%)	0.0009 - 0.0054
Tillas Slough	18	18 (100%)	0 (0%)	0.0053 - 1.0

Diuron was the most commonly detected pesticide (not counting dissolved copper) during the study. Diuron was detected 67 times at the lower monitoring stations and two times at the upper monitoring stations. At Lower Delilah and Tillas Slough it was detected in every sample except one – 36 out of 37 samples. Diuron exceeded the water quality criterion once out of the 67 detections, during a storm event in March 2023.

5.1.2 Ethoprop

Ethoprop is an organophosphate nematicide and insecticide. In lily bulb cultivation, ethoprop is primarily used to control plant-parasitic nematodes. Ethoprop has moderate water solubility (~750 mg/L at 25°C) and a low soil organic carbon partition coefficient (Koc values generally range from 40 to 150 mL/g), indicating a high potential for mobility in soils (EPA, 2006; PPDB, 2023). Ethoprop is also moderately volatile and can volatilize from moist soils shortly after application. It degrades primarily via microbial activity and hydrolysis, with a relatively short soil half-life ranging from 1.3 – 13.6 days (Management Plan, 2021). Ethoprop has been detected in monitoring wells in agricultural regions of California and is listed as having the potential to pollute groundwater on the California Code of Regulations Section 6800 Groundwater Protection List. The following table summarizes the detections, range of concentrations, and the number water quality criterion exceedances.

Ethoprop was detected six times during the study with a single exceedance of the water quality criterion. Ethoprop is applied during the fall around the time of planting from September – November.

Table 8. Detections, Exceedances, and Range of Concentrations for Ethoprop. (Water Quality Criterion: 0.37 ug/L)

Station	Number of Samples	Number of Detections	Number of Exceedances	Range of Concentrations (ug/L)
Lower Delilah	14	3 (21%)	1 (7%)	0.02 - 2.0
Lower Morrison	10	2 (20%)	0 (0%)	0.018 - 0.027
Lower Ritmer	13	0 (0%)	0 (0%)	Non-detect
Lower Rowdy	14	0 (0%)	0 (0%)	Non-detect
Tillas Slough	13	1 (8%)	0 (0%)	0.0044

5.1.3 <u>Imidacloprid</u>

Imidacloprid is a systemic neonicotinoid insecticide widely used to control insect pests, such as aphids, whiteflies, and leafhoppers. It is absorbed by plant roots and distributed throughout plant tissues to provide pest resistance. It has moderate water solubility (~610 mg/L at 20°C) and low volatility (PPDB, 2023). Its soil organic carbon partition coefficient (Koc) ranges from 159 to 960 mL/g (Hardin, 2018), indicating moderate mobility in soils, though it can leach more readily in sandy or low-organic matter soils with a reported Koc of 157 mL/g in low-humus sandy soil (CDPR, 2006). Imidacloprid is persistent in the environment, with a soil half-life between 174-191 days (Management Plan, 2021). It degrades primarily through microbial activity and photolysis, but the degradation process is relatively slow in low-light or anaerobic conditions. Imidacloprid has been frequently detected in California's surface waters – often at concentrations exceeding ecological thresholds for aquatic invertebrates (DPR, 2020; USGS, 2019). Due to its high water solubility and persistence, imidacloprid has a strong potential to migrate into surface waters and groundwater. The following table summarizes the detections, range of concentrations, and the number of water quality criterion exceedances.

Imidacloprid was detected in 35 samples taken at the downstream monitoring stations, with one detection at an upstream site in Upper Delilah Creek (very low concentration).

Imidacloprid was detected 15 out of 18 times at the Lower Delilah sampling site and at the same frequency in Tillas Slough. In Lower Delilah, the water quality criterion was exceeded 6 times out of the 15 times detected, at a 40% rate. The highest detection of imidacloprid was 0.065 ug/L, which occurred during the same sampling event as the highest diuron concentration – during a March 2023 storm event.

Table 9. Detections, Exceedances, and Range of Concentrations for Imidacloprid. (Water Quality Criterion: 0.016 ug/L)

Station	Number of Samples	Number of Detections	Number of Exceedances	Range of Concentrations (ug/L)
Upper Delilah	19	1 (5%)	0 (0%)	0.0007
Lower Delilah	18	15 (83%)	6 (33%)	0.002 - 0.064
Lower Morrison	15	2 (13%)	0 (0%)	0.0008
Lower Ritmer	19	3 (16%)	0 (0%)	0.001 - 0.0021
Lower Rowdy	20	0 (0%)	0 (0%)	Non-detect
Tillas Slough	18	15 (83%)	2 (11%)	0.003 - 0.065

5.1.4 <u>Date and Precipitation for Synthetic Pesticide Samples Exceeding Thresholds</u>

The following tables provide the date of sampling, the recorded precipitation for the day of sampling and the previous day, the precipitation total for the 4 days preceding the sampling event, and the observed precipitation at the time of sampling taken from the field sheets filled out by the sampling crew at the time of sampling. Lower Delilah and Tillas Slough were the only monitoring stations with pesticide sample results that exceeded the water quality criteria. The relevant water quality criterion is provided next to the chemical name in parentheses. Analysis of the relationship between pesticide concentrations in samples and precipitation before and during the sampling event is presented in Section 6.1.

Table 10. Lower Delilah Pesticide Sample Results that Exceeded Thresholds

Pesticide Threshold and Sample Concentrations	Date	24-hour Precipitation Prior to Sampling	96-Hour Precipitation Prior to Day of Sampling	Precipitation at Sampling as Recorded on Field Sheets
Imidacloprid (0.016 ug/L)				
0.064 ug/L	10/25/21	1.49"	7.48"	drizzle
0.054 ug/L	3/5/23	2.44"	2.18"	drizzle
0.023 ug/L	6/20/23	0.02"	0.11"	none
0.028 ug/L	11/5/23	3.01"	3.09"	rain
0.062 ug/L	6/19/24	0.0"	0.0"	none
0.033 ug/L	9/26/24	0.0"	0.01"	none
Diuron (1.3 ug/L)				
5.9 ug/L	3/5/23	2.05"	2.18"	drizzle
Ethoprop (0.37 ug/L)				
2.0 ug/L	11/5/23	3.01"	3.09"	rain

Table 11. Tillas Slough Pesticide Sample Results that Exceeded Thresholds

Pesticide Threshold and Sample Concentrations	Date	24-hour Precipitation Prior to Sampling	96-Hour Precipitation Prior to Day of Sampling	Precipitation at Sampling as Recorded on Field Sheets
Imidacloprid (0.016 ug/L)				
0.065 ug/L	3/5/23	2.44"	2.18"	none
0.043 ug/L	5/15/23	0.0"	0.0"	none

5.2 Dissolved Copper Results

Surface water samples were analyzed for dissolved copper. Copper is a naturally occurring element which is present in all California soils. Dissolved copper concentrations in upstream samples demonstrate the background condition. This is relevant to this study since pesticide compounds that include copper are also applied to the agricultural fields of the Smith River Plain at various times throughout the year. Copper was analyzed for the dissolved fraction because the dissolved fraction is more bioavailable and therefore more likely to affect aquatic organisms. However, metals that are not dissolved can also become bioavailable under lower pH and lower dissolved oxygen conditions.

Uniquely, from early summer to fall during the study period, salinity at the Tillas Slough monitoring station consistently exceeded the freshwater limit (>1 part per thousand). Dissolved copper concentrations reported for surface water samples collected under this condition were anomalously high; therefore, so were levels of predicted copper toxicity. During these saline conditions, dissolved copper concentrations were strongly and positively related to salinity levels. Due to their anomalous nature, dissolved copper concentrations associated with high salinity are in the process of being re-verified by staff.

5.2.5 Biotic Ligand Model Criteria

This section presents the results of BLM modeling using input parameters collected over the study period. The BLM is used to assess the sublethal effects of dissolved copper, such as impairments of sensory function and behaviors in aquatic species by accounting for factors affecting the bioavailability of dissolved copper in the water column (see Section 4.8). The monitoring study results include 20-24 sets of input parameters depending on the sample location. The variation is due to some sample results being lost, quality control issues, or insufficient flow to collect a sample. Where data were missing, the BLM guidance allows for estimation of the additional data points subject to certain conditions. In some cases, data points were estimated to complete the data sets. The BLM is a model that provides additional refinement of the water quality criteria for dissolved copper contained in CTR. Where CTR considers water hardness as a factor in determining risk of toxicity from dissolved copper, the BLM adds several more parameters to provide more accurate and supportive criteria for the water quality conditions when and where the sample was collected.

As part of the analysis, BLM model results for each sampling event were used to establish instantaneous water quality criteria (IWQC) to compare to the dissolved copper concentration in the sample. The model's output includes calculated criteria and a toxicity unit to represent the relative risk of copper toxicity in the waterbody at the time of sample collection. The toxicity unit is a simple ratio of the measured concentration of dissolved copper to the BLM-generated criteria and is calculated by dividing the measured value by the modeled criteria. So, if the measured copper concentration equals the BLM generated instantaneous criterion, then the toxicity unit (TU) is equal to 1.0 – corresponding to a 1:1 ratio. If the measured concentration is above the BLM-generated value, the TU is greater than 1.0. If the measured concentration is below the BLM value, the TU is less than 1.0. The BLM toxicity units are one way of assessing water quality conditions in comparison to the Basin Plan narrative toxicity standard, which requires waters to contain no toxic substances in toxic amounts.

The BLM provides a better prediction of toxicity and the potential sensory and behavioral impairment in the aquatic environment than the hardness-based CTR criterion because it takes into account copper speciation and complexation, and competitive binding by other cations to

the biotic ligand (gill surface) of an aquatic organism. Copper tends to form organic and inorganic complexes with other charged ions and molecules that can make it biologically unavailable to the ligand – effectively neutralizing the toxic effect it may have had as a free copper ion (Cu²⁺). In 2018, Meyer and DeForest performed a meta-analysis of 107 cases where the hardness-based CTR criterion was compared with the BLM-based criterion to determine both models' ability to protect fish, amphibians, and aquatic invertebrates from behavioral and sensory effects. Both models' outputs were compared to the 20% impairment concentration (IC₂₀), the concentration of copper which produces a 20% inhibition of a given behavior or sensory effect. The study showed that the hardness-based criteria were not protective for chronic effects in 26.2% of cases. In contrast, the BLM-based criteria were not protective for chronic effects in only 4.7% of cases, indicating a greater degree of certainty that aquatic species would be protected from chronic effects if copper concentrations remained below the BLM-based criteria. (Meyer and DeForest, 2018)

The BLM-derived IWQC and modeled toxicity unit values are presented in the data tables in Appendix A for each dissolved copper measurement and can be compared to the CTR criteria. While the BLM provides more accurate predictions of toxic and behavioral effects for a given copper concentration compared to the CTR criteria, it should be noted that the BLM does not always produce criteria with lower, more stringent values. For example, waters with high dissolved organic carbon concentrations, such as those downstream from a wastewater treatment facility, will produce less-stringent criteria using the BLM than those derived from the hardness-based model. On the other hand, in areas with very few organic inputs, or those with more acidic conditions, such as in the Smith River Plain tributaries, BLM-derived criteria may be more stringent than CTR-based criteria.

5.2.6 Comparison of Dissolved Copper Results to Biotic Ligand Model Criteria

The following table summarizes the range of dissolved copper concentrations and the number water quality criterion exceedances observed during the monitoring study.

Table 12. Exceedances and Range of Concentrations for Dissolved Copper (BLM Water Quality Criteria

Station	Station Code	Range of Cu Values (ug/L)	Total Samples	Acute BLM Exceedances	Chronic BLM Exceedances
Upper Station Totals	103DE7500 103ME2000 103MO2500 103RI2000 103RW2000	Non-detect – 1.13	116	2 (2%)	6 (5%)
Lower Delilah	103DE5776	0.77 – 14.8	23	8 (35%)	13 (56%)
Lower Mello	103ME1000	0.98 – 2.15	3	2 (67%)	3 (100%)
Lower Morrison	103MO2500	0.36 – 1.03	19	1 (5%)	4 (21%)
Lower Ritmer	103RI1000	0.45 – 2.14	24	4 (17%)	8 (33%)
Lower Rowdy	103RW0319	0.16 – 0.79	24	0 (0%)	1 (4%)
Tillas Slough	103TL1789	2.03 – 6.81	12	2 (17%)	4 (33%)
Lower Station Totals		0.16 – 14.8	106	17 (16%)	33 (31%)

Dissolved copper was measured at concentrations between non-detect and 1.13 ug/L at the monitoring stations above lily bulb fields and between 0.16 and 14.8 ug/L at stations below lily bulb fields. The results clearly demonstrate an increase in dissolved copper concentrations at the monitoring stations downstream of the lily bulb cultivation areas compared to the upstream stations.

6 DISCUSSION

North Coast Water Board staff performed several analyses in support of developing a conceptual model of copper and synthetic pesticide fate and transport from application in lily bulb fields to detection in surface water samples. Precipitation, background/ambient water quality, and rates of copper and pesticide applications were evaluated and compared with the location, frequency, and magnitude of pesticide detections. Daily precipitation records were downloaded from the Community Collaborative Rain, Hail, and Snow Network website for Station CA-DN-6: Smith River 1.1 SSE located near the Morrison Creek crossing at Highway 101 (Figure 2). Pesticide Use Reports obtained from the Del Norte County Agricultural Commissioner were used to calculate monthly application mass by tributary area to the Tillas Slough and the lower monitoring stations (Appendices C and D). Tributary areas to each sampling location were delineated using digital elevation models (DEMs) from the California Coastal Commission and the US Geologic Survey (USGS). While more recent, the California Coastal Commission DEM did not cover the entire lily bulb growing region, therefore, USGS DEMs were used to cover the missing area. Due to the difficulty of delineation in the low gradient estuary region with relatively coarse DEM resolution, streamlines from CDFW and the USGS National Hydrography Dataset were utilized to further modify the final DEM. Final tributary catchment areas were developed using the standard watershed delineation procedure (i.e., flow direction, flow accumulation, etc.) with the downstream sampling locations as pour points, or outlets.

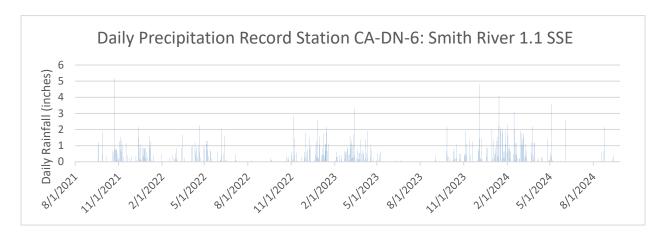


Figure 2. Daily Precipitation Station CA-DN-6: Smith River 1.1 SSE

6.1 Rainfall and Storm Events

Cool summers and mild winters characterize the climate of the study area – a classic North Coast Mediterranean precipitation regime with distinct storm event clustering. Normal annual precipitation is about 75 inches with up to 20 major storms per season. Early season storms in October-November are often associated with first major Pacific storm systems delivering up to 2 inches per day. Winter season storms in December through early March are associated with high-intensity atmospheric river events. In extreme cases, atmospheric river events can deliver up to 3.5 inches in a day and can last up to 10 days. Spring tapering begins in mid-March, transitioning to a dry summer pattern by end of June with late season storms still delivering up to 3 inches of rain. Precipitation totals during the study period ranged from below normal (71.77 inches in Water Year¹⁰ [WY] 2022) to slightly above normal (78.65 inches in WY 2023) to 140 percent of normal (105.88 inches in WY 2024). Extreme events (>3 inches per day) were rare during the study period, with a third of storms lasting between 3-5 days delivering up to 8 inches. Most rainfall was delivered in short (1-2 day) storms with an intensity of less than 1 inch per day.

Analysis of storm event patterns and diuron/imidacloprid detections focused on rainfall events which were expected to produce overland flow and the potential to deliver residual pesticides to tributary streams. For purpose of analysis, staff selected storms which exceeded 2 inches of rain within a 72-hour period and defined the end of a storm to coincide with the end of a 48-hour period of less than 0.25 inches of rain (Appendix E). Nearly forty storm events meeting the criteria occurred during the study period. Diuron and imidacloprid concentrations recorded at each monitoring station were plotted with the reference storms and rainfall accumulation across

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¹⁰ A Water Year is from October 1 to September 30.

the lily bulb cultivation annual cycle (August to August). Refer to Appendix F Pesticide Concentration and Storm Event Charts.

Review of the Pesticide Concentration and Storm Event Charts suggests the highest concentrations of diuron and imidacloprid recorded during the study are strongly associated with major storm events. Notably, elevated concentrations of imidacloprid seem to be more persistent than diuron following storms. Persistent elevated concentrations of diuron and imidacloprid are associated with the typical storm season with lower concentrations recorded from mid-summer to early fall. Diuron above the aquatic life criterion (1.3 μ g/L) was recorded only once (Lower Deliah monitoring station) and appears to be associated with the onset of runoff from a large storm in early March 2023. In contrast, imidacloprid above the water quality criterion (0.016 μ g/L) was recorded eight times (Lower Deliah and Tillas Slough monitoring stations).

A similar analysis of copper toxicity and rainfall patterns indicates 1.5 to 3 times higher predicted chronic and acute copper toxicity occurrence rates, respectively, during the storm season as compared to the dry season (Copper Toxicity Charts – Appendix G). Lower Deliah monitoring station recorded the most frequent occurrence of predicted copper toxicity – in more than 50 percent of samples. Outside the storm season, predicted copper bioavailability typically becomes subtoxic (although higher than background) in downstream monitoring stations.

A primary driver in elevated predicted copper toxicity at downstream sampling locations during the storm season appears to be depressed pH (<6.5 pH units) associated with storm events resulting in higher predicted dissolved copper bioavailability rather than a large increase in dissolved copper concentrations. See Tables 13-15 for a statistical comparison. Note: p values of less than 0.05 indicate a significant correlation between data sets.

Table 13. Seasonal pH Means (Upper vs Lower Monitoring Stations)

Stream System	Upper Station Wet Season	Upper Station Dry Season	Lower Station Wet Season	Lower Station Dry Season	Sample Sizes (UW/UD/LW/LD)
Delilah	6.90	7.03	6.52	7.04	12/12/11/12
Morrison	7.02	6.82	6.76	6.70	12/9/12/7
Ritmer	7.19	7.20	6.84	6.87	12/13/12/12
Rowdy	7.35	7.25	7.13	6.94	11/13/12/11

Table 14. pH Units Spatial Differences (Upper vs Lower Monitoring Stations)

Creek System	West Season Spatial Difference	Dry Season Spatial Difference	Wet Season Significance	Dry Season Significance
Delilah	+0.38	-0.01	p < 0.05	p > 0.05
Morrison	+0.26	+0.12	p < 0.05	p > 0.05
Ritmer	+0.35	+0.33	p < 0.05	p < 0.05
Rowdy	+0.22	+0.31	p > 0.05	p > 0.05

Table 15. pH Units Temporal Differences (Wet vs Dry Season)

Creek System	Upper Station Temporal Difference	Lower Station Temporal Difference	Upper Temporal Significance	Lower Temporal Significance
Delilah	-0.13	-0.52	p > 0.05	p < 0.01
Morrison	+0.20	+0.06	p > 0.05	p > 0.05
Ritmer	-0.01	-0.03	p > 0.05	p > 0.05
Rowdy	+0.10	+0.19	p > 0.05	p > 0.05

6.2 Copper/Pesticide Application Rates

Application rates of copper and the synthetic pesticides imidacloprid, diuron, and ethoprop were calculated for the tributary watersheds to the six downstream monitoring stations. Application rates for each tributary watershed to the downstream stations (see Figure 3) were then normalized by tributary area in acres. Refer to Copper/Pesticide Normalized Application Rate Charts – Appendix C and Table 16 below for a summary.

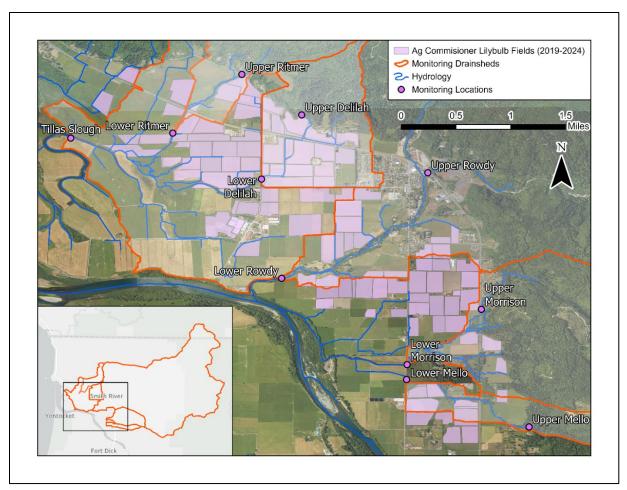


Figure 3. Monitoring Drainsheds in the Smith River Plain

Table 16. Summary of Synthetic Pesticide/Elemental Copper Normalized Application Rates 2020-2024 (lbs/acre/year)

Station Name	Tributary Area (acres)	Diuron	Imidacloprid	Ethoprop	Elemental Copper
Lower Delilah	536	0.340	0.026	0.297	1.3
Tillas Slough	2,780	0.241	0.015	0.184	1.0
Lower Mello	366	0.139	0.009	0.117	0.8
Lower Ritmer	733	0.035	0.001	0.021	0.16
Lower Rowdy	21,922	0.006	0.0004	0.006	0.03
Lower Morrison	1,357	0.047	0.004	0.049	0.30

Normalized annual copper application rate and annual average predicted potential chronic copper toxicity are highly correlated (r=0.832) Refer to Section 5 for a summary of predicted copper toxicity results. During the study period, the approximately 540-acre tributary watershed to the Lower Delilah monitoring station had the highest normalized copper application rate (1.3 lbs/acre/year), the most predicted chronic toxicity occurrences (12x), and the highest recorded level of predicted chronic toxicity (10 TUs). Tillas Slough monitoring station (approx. 2,800-acre tributary area) had the second highest normalized copper application rate (1.0 lbs/acre/year), the second most predicted chronic toxicity occurrences (5x), and the second highest recorded level of predicted chronic toxicity (9.5 TUs).

Normalized annual diuron application rates are weakly correlated (r=0.365 and 0.332) to average annual concentrations and water quality criterion exceedance rates. However, imidacloprid application rates are exceptionally correlated to both (r=0.978 and 0.960). During the study period, the approximately 540-acre tributary watershed to the Lower Delilah monitoring station had the highest normalized diuron application rate (0.340 lbs/acre/year), the only exceedance of the water quality criterion (1.3 μ g/L), the highest normalized imidacloprid application rate (0.026 lbs/acre/year), and the most exceedances (6x) of the water quality criterion (0.016 μ g/L). Tillas Slough (approx. 2,800-acre tributary area) had the second highest normalized diuron application rate (0.241 lbs/acre/year), second highest average diuron concentration (0.188 μ g/L), second highest normalized imidacloprid application rate (0.015 lbs/acre/year), and two exceedances of the water quality criterion (0.016 μ g/L).

Ethoprop (n=64 for lower monitoring stations) was detected most frequently at the Lower Delilah station (3 of 5 detections at the lower monitoring stations) while recording the only water quality criterion (0.37 µg/L) exceedance at 2 µg/L and highest normalized application rate. Lower

Ritmer, Lower Rowdy, and Lower Mello monitoring stations did not record detections of ethoprop. Associations between application rate and reported ethoprop concentrations are inconsistent.

7 CONCLUSIONS

Key outcomes of the monitoring study are understanding pesticide and copper status and trends in surface waters along with agricultural practice and hydrologic relationships/correlations. The study also provides insights in support of developing adaptive management strategies and monitoring requirements for General Waste Discharge Requirements for Commercial Lily Bulbs in the Smith River Plain (Lily Bulb Order).

7.1 Status and Trends

Over the study period, the persistent and highly mobile synthetic pesticides diuron and imidacloprid were commonly detected below the water quality criteria downstream of bulb fields. Periodically, monitoring stations at Lower Delilah and Tillas Slough recorded exceedances of the respective water quality criteria. Ethoprop, a volatile and low-persistence synthetic pesticide, was rarely (5%) detected downstream of bulb fields with a singular occurrence above the water quality criterion. Dissolved copper concentrations above background occur year-round downstream of bulb fields with copper bioavailability frequently predicted above potentially toxic levels during the storm season.

7.2 Hydrologic Factors

Although the data set is limited, imidacloprid and diuron concentrations downstream of bulb fields appeared to sharply peak during early stages of overland flow from larger storms (>2 inches in 3 days) prior to dilution from increasing overland flow and a rise in streamflow. With cessation of overland flow and a presumed drop in streamflow, diuron and imidacloprid concentrations appeared to transition to moderate levels, possibly associated with a post-storm rise in shallow groundwater flow to the tributary streams, which may continue for weeks following larger storms. Outside the typical storm season, persistent detections (below the water quality criteria) downstream of bulb fields suggest subsurface transport of imidacloprid and diuron via shallow groundwater baseflow to streams is a possibility.

During the storm season, predicted copper bioavailability frequently increased to potentially toxic levels downstream of bulb fields and typically dropped to subtoxic levels outside the storm season. Fate and transport of dissolved copper appears to follow a similar pattern as diuron and imidacloprid. Depressed pH and a rise in dissolved copper concentrations downstream of bulb fields during the storm season appear to be the primary factors causing an increase in potential copper bioavailability and toxicity predicted by the BLM. North Coast Water Board staff are working on a hypothesis for the observed pH depression which may be associated with a longterm decline in groundwater pH within the Smith River Plain aquifer near the town of Smith River. The following chart illustrates a trend in Smith River Plain groundwater pH dropping from slight alkaline (pH values of 7-8) to slightly acidic (pH values of 6-6.5) over the last 50 years, as measured in wells located near the town of Smith River - data are from the State Water Board Groundwater Ambient Monitoring and Assessment Program (Figure 4). Additionally, North Coast Water Board staff recorded pH values during monitoring of domestic wells near the town of Smith River in 2015 and 2025. The average pH in 2015 was 6.1 and the average in 2025 was 5.7. Groundwater elevations in the Smith River Plain have been stable since at least 1973 (Figure 5).

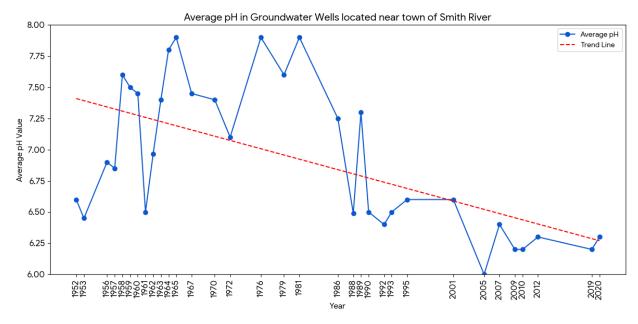


Figure 4. Time Series of Groundwater pH Near Town of Smith River

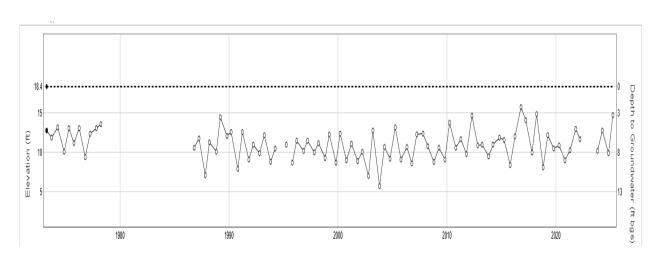


Figure 5. Time Series of Groundwater Elevations Near Town of Smith River (State Well No. 18N01W27P003H).

7.3 Agricultural Factors

Dissolved copper concentrations downstream of bulb fields are higher (year-round) than background concentrations. Apart from two occurrences at the upper monitoring stations, predicted acute and chronic copper toxicity only occurred downstream of bulb fields and rarely outside the storm season. Normalized elemental copper application rates greater than 1 lb/acre/year are associated with frequent occurrences of predicted copper toxicity during the storm season.

Diuron and imidacloprid are commonly detected downstream of bulb fields (year-round) and normalized application rates in excess of 0.3 and 0.01 lbs/acre/year, respectively are associated with exceedances of water quality criteria during the storm season.

8 RECOMMENDATIONS

North Coast Water Board staff have the following recommendations for data analysis, adaptive management, and water quality monitoring:

- 1. Reduce diuron, imidacloprid, and copper normalized application rates in watersheds with exceedances of water quality criteria.
- 2. Identify management practices which will decrease copper, diuron, and imidacloprid transport from lily bulb fields to surface waters (e.g., increased soil organic carbon content.)
- 3. Identify possible mechanisms causing depressed pH associated with stream reaches receiving baseflow from alluvial sediments and lily bulb fields.
- 4. Focus surface water monitoring on storm season sampling of stream reaches with elevated normalized pesticide and copper application rates and associated exceedances of water quality criteria.
- 5. Time storm season monitoring to capture both initial overland flows to streams and dry periods following storms after cessation of overland flow.

9 REFERENCES

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