



North Coast Regional Water Quality Control Board

TO: Michael Thomas
North Coast Regional Coordinator
Surface Water Ambient Monitoring Program (SWAMP)

FROM: Chris Watt
Senior Engineering Geologist (Specialist)
Smith River Lily Bulb Order Development Team

DATE: July 21, 2026

SUBJECT: Smith River Plain Surface Water Monitoring Report 2021 – 2024
Data Set and Biotic Ligand Model Result Updates

[Prepared with AI assistance; reviewed and approved by NCRWQCB staff.]

Introduction

In September 2025, North Coast Water Board staff released the Smith River Plain Surface Water Monitoring Study 2021-2024 (2025 SWAMP Report). The report included monitoring data, modeling results, and analyses conducted by North Coast Water Board staff to assess potential pesticide toxicity risk relative to the timing/rates of pesticide applications and precipitation patterns.

Since the release of the report, staff have conducted several targeted follow-up investigations, which have led to needed updates to some of the data, modeling results, and analyses in the 2025 SWAMP Report. This memorandum summarizes a selection of those changes and memorializes them in advance of the public release of proposed General Waste Discharge Requirements for Commercial Lily Bulb Operations in the Smith River Plain (a.k.a. Proposed Lily Bulb Order) to be considered for adoption by the North Coast Water Board at a public hearing on August 6, 2026.

Changes to Data Tables and Modeling Results

Data tables and Biotic Ligand Model (BLM) results presented in Attachment A to the 2025 SWAMP Report have been updated to reflect the results of several recent technical inquiries, including the following:

- A single, previously misreported pesticide concentration has been updated in Attachment A (diuron on 5/16/24 at the Lower Delilah Creek sampling station).

- Provisional sampling results for BLM constituents originally reported in the 2025 SWAMP Report have since undergone the necessary data verification and quality control checks to be considered final under SWAMP and are now publicly available through the California Environmental Data Exchange Network (CEDEN) online database. Previously reported provisional results have been re-checked for conformance with final published values. In some instances, provisional results have been updated and those updates are now reflected in Attachment A.
- Due to the BLM's sensitivity to pH, staff scrutinized all pH monitoring results to ensure all quality assurance / quality control standards were met. Consequently, previously reported pH values for which complete calibration records are not available, or for which calibration standards were not achieved have been removed from Attachment A, as well as BLM results associated with those sampling events. This determination was based on a review of Smith River SWAMP field sonde calibration records for 2021–2024, which found that pH probe performance issues were concentrated in the 2021–2022 period and attributable to a single sonde (YSI600XL, serial 08D100573) that exhibited progressive electrode degradation culminating in full probe failure by June 2022. Sampling events with documented calibration failures, or for which no sonde identification or calibration date was recorded, were excluded from BLM calculations. The basis for each exclusion is documented event-by-event in an internal technical memorandum (Watt, 2026).
- Due to the BLM's sensitivity to Dissolved Organic Carbon (DOC) concentrations when pH levels are sufficiently high, BLM results associated with missing or lost DOC samples have been removed from Attachment A. Previously reported BLM results were based on estimated DOC concentrations.
- Duplicate values in CEDEN for concentrations of calcium, magnesium, and water hardness (which is calculated as a function of calcium and magnesium concentrations) as reported by different laboratories for the same sampling events have been reconciled and appropriately updated in Attachment A. Final revised values for calcium, magnesium, and water hardness, as well as BLM results associated with those events, now consistently reflect values reported by the laboratory using the most appropriate measurement method for the constituent levels present (EPA Method 200.7). Previously reported values included results from either laboratory or averages of the two.
- Dissolved copper concentrations associated with saline sampling conditions (i.e. salinity greater than or equal to 1.0 parts per thousand at the Tillas Slough sampling station) have been removed from Attachment A, as well as BLM results associated with those sampling events. A follow-up study investigating the validity of previously reported copper concentrations during the occurrence of saline conditions concluded that laboratory methodology deficiencies likely led to reports of artificially high dissolved copper concentration results. This determination was based on a targeted verification study in which split samples were collected across a range of salinities at the Tillas Slough station and three

upstream stations and analyzed using interference-corrected methods (EPA Method 200.8 with collision/reaction cell and EPA Method 1640 on-line chelation preconcentration). These methods consistently produced dissolved copper concentrations between 0.27 and 2.0 µg/L, in contrast to the range of 49 to 319 µg/L previously reported for similar saline conditions using standard EPA Method 200.8. Inter-laboratory comparison between two independent laboratories confirmed the low-level results, supporting the conclusion that the previously reported elevated copper concentrations were analytical artifacts caused by polyatomic ion interferences in high-salinity matrices rather than true ambient conditions. Complete information about the study design, results, and quality assurance documentation are provided in an internal technical memorandum (Watt, 2025).

- Where not previously done, missing or lost sample results for BLM constituents have been replaced by average reported values for the sampling station in BLM calculations. Non-detect results have been replaced by the lowest reported concentration for the sampling station in BLM calculations.

Table 1. Updated Range of Dissolved Copper Concentrations and BLM Water Quality Criteria Exceedances at Downstream Monitoring Stations.

Station	Station Code	Range of Measured Cu Values (ug/L)	Total Qualifying Samples	Acute BLM Exceedances	Chronic BLM Exceedances
Lower Delilah	103DE5776	0.77 – 14.8	18	6 (33%)	10 (56%)
Lower Mello	103ME1000	0.98 – 3.19	2	1 (50%)	2 (100%)
Lower Morrison	103MO2500	0.36 – 1.03	14	0 (0%)	1 (7%)
Lower Ritmer	103RI1000	0.45 – 2.14	18	3 (17%)	6 (33%)
Lower Rowdy	103RW0319	0.17 – 0.79	18	0 (0%)	1 (6%)
Tillas Slough	103TL1789	2.03 – 6.81	9	2 (22%)	4 (44%)
Lower Station Totals	--	0.17 – 14.8	79	12 (15%)	24 (30%)

Potential copper toxicity (toxicity unit > 1) was predicted by the BLM at all downstream stations at least once and in approximately 30 percent of samples, with predictions of chronic toxicity twice as common as acute. The BLM predicted a risk of toxicity most frequently in samples collected from Lower Delilah Creek (56% of samples) and Tillas Slough (44% of samples during freshwater conditions).

Changes to Analyses

The 2025 SWAMP report evaluated exceedances of water quality benchmarks using the Water Year (October 1 – September 30) as the standard accounting period. Staff's subsequent review of pesticide application timing and monitoring data revealed that the Water Year framework does not adequately associate benchmark exceedances with the

fields and applications responsible for them. The Water Year boundary — October 1 — falls in the middle of the lily bulb planting/growing/harvesting cycle, splitting pesticide applications for a single crop across two accounting periods and obscuring the relationship between an exceedance event and the fields most likely responsible.

To more accurately attribute water quality benchmark exceedances to the planting cycles and fields responsible, staff revised the accounting period to align with the pesticide application cycle for each constituent. Because each pesticide is applied during a different window and is associated with different fields depending on planting status, the revised approach defines exceedance attribution on a constituent-specific basis:

- Copper is applied over the longest window of any monitored constituent, beginning with early applications in February and continuing through the summer growing season. Copper exceedances detected during this interval (February–September) were attributed to fields that were planted in lily bulbs in areas tributary to the monitoring station. Copper exceedances detected after harvest and during the late fall and early winter (October–January) were attributed to those same (i.e. most recently harvested) fields.
- Imidacloprid is typically applied during the spring and summer growing season. Like copper, imidacloprid exceedances detected between February and September were attributed to fields that were planted in lily bulbs. Because imidacloprid is relatively persistent in the environment, exceedances detected after harvest between October and January were attributed to the previous growing season's (i.e. most recently harvested) fields, as residues from the prior application season are mobilized by storm runoff.
- Diuron is typically applied between November and May following planting. Exceedances detected from November through harvest were attributed to fields that were planted in lily bulbs for that growing season.
- Ethoprop is typically applied between September and November to newly planted fields. Exceedances detected from September through harvest were attributed to fields that were planted in lily bulbs for that growing season.

This constituent-specific approach resolves the key limitation of the Water Year framework. Under the prior approach, for example, a copper exceedance during a November sampling event triggered Adaptive Management for all planted fields tributary to the monitoring station, even though the exceedance was more likely associated with recently harvested fields, as copper is not typically applied to newly planted lily bulb fields until February. Similarly, an ethoprop exceedance during the same November event would properly be associated with newly planted fields, as ethoprop is applied in the fall. The Water Year accounting period made no such distinctions.

By aligning exceedance attribution with each constituent's application cycle and the planting status of fields at the time of the exceedance, the revised approach narrows the

scope of Adaptive Management to the fields most likely responsible, reducing the burden on growers whose fields were not associated with the exceedance while maintaining accountability for fields that were. To evaluate the implications of this change, staff re-analyzed the 2021–2024 monitoring data set using the revised constituent-specific, planting-cycle-based accounting periods. The results are presented in Tables 2–5 below.

REFERENCES:

2025 SWAMP Report. North Coast Regional Water Quality Control Board. Surface Water Ambient Water Quality Monitoring Program. Smith River Plain Surface Water Monitoring Report 2021-2024. September 2025.

Watt, C. (2026, April 13). Recommendation for pH Data Exclusion in Smith River BLM Copper Toxicity Analysis – Sonde Calibration Record Review [Internal technical memorandum to D. Kuszmar]. North Coast Regional Water Quality Control Board. (Attached)

Watt, C. (2025, October 20). Tillas Slough Copper Verification Study – Results [Internal memorandum to D. Kuszmar]. North Coast Regional Water Quality Control Board. (Attached)

REVISED 2025 SWAMP REPORT APPENDICES:

Revised 2025 SWAMP Report Appendix A. Smith River Plain Surface Water Monitoring Results (Data Tables)

Table 2. Re-analyzed Benchmark Exceedances by Planting Cycle – Dissolved Copper.

Planting Cycle	Tillas (chronic)	Tillas (acute)	Delilah (chronic)	Delilah (acute)	Ritmer (chronic)	Ritmer (acute)	Rowdy (chronic)	Rowdy (acute)	Morrison (chronic)	Morrison (acute)	Mello (chronic)	Mello (acute)
2020–21	0	0	2	1	0	0	0	0	0	0	1	1
2021–22	2	1	1	1	1	0	0	0	0	0	—	—
2022–23	1	1	5	4	5	3	1	0	1	0	1	0
2023–24	1	0	2	0	0	0	0	0	0	0	—	—

Benchmark Criteria: BLM Toxicity Units > 1.0 (Chronic and Acute)

Accounting Period: February – January

Table 3. Re-analyzed Benchmark Exceedances by Planting Cycle – Imidacloprid.

Planting Cycle	Tillas (chronic)	Tillas (acute)	Delilah (chronic)	Delilah (acute)	Ritmer (chronic)	Ritmer (acute)	Rowdy (chronic)	Rowdy (acute)	Morrison (chronic)	Morrison (acute)	Mello (chronic)	Mello (acute)
2020–21	0	0	1	0	0	0	0	0	0	0	0	0
2021–22	0	0	0	0	0	0	0	0	0	0	—	—
2022–23	2	0	7	0	0	0	0	0	0	0	—	—
2023–24	1	0	2	0	0	0	0	0	0	0	—	—

Benchmark Criteria: Chronic = 0.01 ug/L, Acute = 0.385 ug/L

Accounting Period: February – January

Table 4. Re-analyzed Benchmark Exceedances by Planting Cycle – Diuron.

Planting Cycle	Tillas (chronic)	Tillas (acute)	Delilah (chronic)	Delilah (acute)	Ritmer (chronic)	Ritmer (acute)	Rowdy (chronic)	Rowdy (acute)	Morrison (chronic)	Morrison (acute)	Mello (chronic)	Mello (acute)
2020–21	—	—	—	—	—	—	—	—	—	—	—	—
2021–22	0	0	0	0	0	0	0	0	0	0	—	—
2022–23	0	0	1	0	0	0	0	0	0	0	—	—
2023–24	1	0	1	0	0	0	0	0	0	0	—	—

Benchmark Criteria: Chronic = 0.83 ug/L, Acute = 87.5 ug/L

Accounting Period: November – October

Table 5. Re-analyzed Benchmark Exceedances by Planting Cycle – Ethoprop.

Planting Cycle	Tillas (chronic)	Tillas (acute)	Delilah (chronic)	Delilah (acute)	Ritmer (chronic)	Ritmer (acute)	Rowdy (chronic)	Rowdy (acute)	Morrison (chronic)	Morrison (acute)	Mello (chronic)	Mello (acute)
2020–21	—	—	—	—	—	—	—	—	—	—	—	—
2021–22	0	0	0	0	0	0	0	0	0	0	0	0
2022–23	0	0	0	0	0	0	0	0	0	0	0	0
2023–24	0	0	1	0	0	0	0	0	0	0	—	—

Benchmark Criteria: Chronic = 0.37 ug/L, Acute = 22.0 ug/L

Accounting Period: September – August

ATTACHMENT 1

Watt, C. (2026, April 13). Recommendation for pH Data Exclusion in Smith River BLM Copper Toxicity Analysis – Sonde Calibration Record Review [Internal technical memorandum to D. Kuszmar]. North Coast Regional Water Quality Control Board.

**NORTH COAST WATER QUALITY CONTROL BOARD
INTERNAL TECHNICAL MEMORANDUM**

TO: David Kuszmar, Southern Agriculture Unit Supervisor

FROM: Chris Watt, Senior Specialist

DATE: April 13, 2026

RE: Recommendation for pH Data Exclusion in Smith River BLM Copper Toxicity Analysis — Sonde Calibration Record Review

[Prepared with AI assistance; reviewed and approved by NCRWQCB staff.]

Purpose

This memorandum documents a review of Smith River Surface Water Ambient Monitoring Program (SWAMP) field sonde calibration records (2021–2024) and provides recommendations for which sampling events should have their pH data — and by extension, Biotic Ligand Model (BLM)-derived copper toxicity unit (TU) results — excluded from, or flagged within, the data and analyses presented in the Smith River Plain Surface Water Monitoring Study 2021-2024 (2025 SWAMP Report). These recommendations are based on calibration logs, CEDEN database entries, and field data sheet annotations compiled and reviewed by Mike Thomas (Senior Environmental Scientist, Regional Monitoring Coordinator) and Catherine Davila Arenas (Environmental Scientist, SWAMP/FHAB Lead), as documented in the email correspondence and calibration log data cited in the References section. Raw calibration log data supplied by Mike Thomas are presented in Attachment 2.

Background

BLM-based copper toxicity calculations are highly sensitive to pH, which governs copper speciation and the derivation of site-specific water quality criteria. Measurement error in pH — even on the order of ± 0.2 to 0.3 units — can materially affect calculated toxicity units. It is therefore essential that pH data used in BLM calculations be supported by documented, passing sonde calibration records.

Mike Thomas reviewed all 2021–2024 Smith River field data sheets and calibration logs archived in SharePoint, compiled findings in a spreadsheet (Attachment 1), and communicated findings via email on April 2 and April 8–9, 2026. He subsequently provided the underlying raw calibration log data (Attachment 2). Key contextual findings include:

- SWAMP data entry transitioned to a shell-based system around 2020, after which ComplianceCode defaults to “Pend” and BatchVerification defaults to “NR” for all field data. These codes do not indicate data quality problems.
- A calibration date of “1/1/1950” in CEDEN is a default placeholder and may be used for: situations where field crews did not identify the sonde that was used for the sampling event; sensors that are not routinely calibrated (e.g., temperature); and for visual observations like stream velocity.
- pH probe issues are concentrated in the 2021–2022 period and are associated with sonde 08D100573 (YSI600XL series). The transition to EXO-1 sondes beginning mid-2023 corresponds with a uniformly clean calibration record.
- The raw calibration logs (Attachment 2) document a progressive decline in pH electrode response for sonde 08D100573, with pH1 mV values shifting from approximately –10.9 mV (June 2021) to –59.7 mV (May 2022 pre-cal) — well outside acceptable tolerance — before full probe failure in June 2022.

Recommendations

Tier 1 — Definitively Exclude

June 1, 2022 — Sonde 08D100573 failed pre-calibration (5/31/2022) and post-calibration (6/29/2022) for pH. The 5/31/2022 pre-calibration log (Attachment 2) records pH1 mV for standard 7.00 = –59.7 (fail) and pH2 mV for standard 10.01 = –230.1 (fail), with DO gain of 3.044 also failing. The 6/29/2022 post-calibration records a complete probe failure (PF) across all pH channels. “PF” is explicitly noted on the calibration log. Despite documented failure, no QA flag was entered into CEDEN for pH; this is the only event where a flag should have been entered in CEDEN for pH but was not (Thomas email, 4/8/2026). Recommendation: **Exclude all BLM/TU results from this event.**

Tier 2 — Exclude

August 30, 2022 — Sonde model and serial number both recorded as “NR” (not recorded) on field data sheets, and no calibration date was entered into CEDEN. No corresponding entry appears in the raw calibration log (Attachment 2). Without this information, Mike Thomas specifically identified this event as having questionable data (Thomas email, 4/9/2026). Recommendation: **Exclude.**

December 12, 2022 — Same as 8/30/2022: sonde NR, no calibration records, CEDEN calibration date not entered (Thomas email, 4/9/2026). No corresponding entry appears in Attachment 2. Field data sheet check marks on pH mV values provide informal assurance but cannot substitute for calibration documentation. Note: this event would otherwise register as an exceedance at Lower Delilah Creek (chronic TU = 3.5; acute TU = 2.17), making retention without documentation particularly indefensible. Recommendation: **Exclude.**

July 19, 2022 — Pre-calibration passed (7/18/2022, one day prior; pH1 mV = -32.4, Attachment 2). Post-calibration explicitly failed approximately four weeks later (8/15/2022) with “pH probe failure” annotated on the log and full PF recorded across all pH channels; DO gain also failed at 3.052. The same instrument (08D100573) failed both calibrations on 6/1/2022, just six weeks earlier. The progressive mV drift documented in Attachment 2 (from -10.9 mV in June 2021 to -59.7 mV in May 2022, followed by full PF by June 2022) is consistent with ongoing electrode degradation that would not necessarily be arrested by an intervening passing pre-calibration. No CEDEN pH flag entered. Recommendation: **Exclude based on probe history and post-calibration failure.**

Tier 3 — Include in Sensitivity Analysis; Flag or Exclude

April 13, 2022 — Pre-calibration passed (4/12/2022; pH1 mV = -36.2, Attachment 2). Post-calibration failed (5/5/2022) with pH1 mV = -53.4 (fail); all other parameters passed. The 22-mV shift between pre-calibration (4/12/2022) and the next available post-calibration check (5/5/2022) indicates that the pH electrode was starting to degrade during this period. However, the 4/12/2022 pre-calibration passed acceptably and the exact onset of failure cannot be pinpointed. CEDEN flag entered for DO only; no pH flag. This event produces some of the highest TU values in the dataset (Lower Delilah chronic TU = 10.19; Lower Morrison = 4.62; Lower Ritmer = 4.38). Recommendation: **Include in sensitivity analysis to assess the effect of inclusion versus exclusion on overall conclusions. Based on results, exclude from dataset or flag in 2025 SWAMP Report with uncertainty notation.**

Retain with Notation

All remaining events (see Attachment 1) are recommended for retention. Events where pre-calibration logs were not found but the pH probe passed post-calibration, the field data sheet contains a pH check mark, and a calibration date is entered in CEDEN are considered sufficiently documented for use, consistent with the guidance provided by Mike Thomas (email, 4/8/2026). The 2/12/2023 sampling event is noted: the 2/11/2023 pre-calibration log (Attachment 2) shows pH passing but DO and SpCond failing; pH data from this event are usable. Events 6/20/2024 and 9/25/2024 lack CEDEN calibration date entries but have discoverable calibration logs; CEDEN corrections are in progress and these data are usable per Thomas (email, 4/9/2026).

Endnotes

* Post-calibration for 10/25/2021 (12/1/2021 log, Attachment 2): DO failed (PF) but both pH channels passed. pH data from this event are usable.

† Pre-calibration for 2/12/2023 (2/11/2023 log, Attachment 2): DO and specific conductance failed, but pH passed. pH data from this event are usable.

Summary of BLM Chronic Toxicity Units Affected by pH Data Exclusions

The table below identifies all chronic copper BLM TU values at lower Smith River Plain stations (Tillas Slough excluded) corresponding to sampling events subject to exclusion or flagging under the recommendations above. Values are drawn from 2025 SWAMP Report Appendix A (Data Tables). Cells featuring an (E) indicate exceedances of the 1.0 TU regulatory threshold.

Sampling Date	Disposition	Lower Delilah	Lower Morrison	Lower Ritmer	Lower Rowdy	Notes
4/13/2022	Tier 3 — Flag or Exclude (per sensitivity analysis)	10.19 TU (E)	4.62 TU (E)	4.38 TU (E)	0.33 TU	Highest chronic TU event in dataset at 3 stations; pH post-cal failed 5/5/2022.
6/1/2022	Tier 1 — Definitively Exclude	0.71 TU	1.06 TU (E)	1.05 TU (E)	0.43 TU	Pre- and post-cal both failed; no CEDEN flag entered.
7/19/2022	Tier 2 — Exclude	0.77 TU	1.07 TU (E)	0.56 TU	0.52 TU	Post-cal pH probe failure 8/15/2022; same probe as 6/1/2022 failure.
8/30/2022	Tier 2 — Exclude	0.42 TU	No data	0.57 TU	0.13 TU	Sonde NR; no calibration records; all values below threshold.
12/12/2022	Tier 2 — Exclude	3.50 TU (E)	0.45 TU	0.47 TU	0.14 TU	Sonde NR; exceedance at Delilah Creek makes exclusion analytically critical.

The following observations are drawn from the table above and are relevant to the interpretation of copper exceedance frequency at lower Smith River Plain stations:

- The 4/13/2022 event (Tier 3 flag or exclude) dominates the exceedance picture at Lower Delilah Creek (10.19 TU), Lower Morrison (4.62 TU), and Lower Ritner (4.38 TU) — the three largest chronic TU values in the entire 2021–2024 dataset. Whether these values are retained or excluded will have a greater effect on exceedance frequency and any threshold-based conclusions than all Tier 1 and Tier 2 exclusions combined.
- The 12/12/2022 event (Tier 2 exclude) is the only excluded event that produces a threshold exceedance, at Lower Delilah Creek (3.50 TU). Its exclusion removes an above-threshold observation that cannot be supported by any calibration documentation.
- The 6/1/2022 and 7/19/2022 events (Tier 1 and Tier 2 exclude) each produce marginal above-threshold values at Lower Morrison (1.06 TU and 1.07 TU respectively). Excluding these events removes two borderline observations at that station.
- The 8/30/2022 event (Tier 2 exclude) produces no above-threshold values at any retained station; its exclusion does not affect exceedance count but is required for data integrity.
- Lower Rowdy Creek is unaffected by any exclusion or flag — all values at this station during affected events are well below 1.0 TU.

Note on Sonde 08D100573 Electrode Degradation Trajectory

The raw calibration log data (Attachment 2) document a coherent, progressive decline in pH electrode performance for YSI600XL sonde 08D100573. pH1 mV values at the pH 7 buffer standard shifted as follows: -10.9 mV (6/25/2021) → -31.8 mV (12/1/2021) → -42.0 mV (3/14/2022) → -36.2 mV (4/12/2022) → -53.4 mV fail (5/5/2022) → -59.7 mV fail (5/31/2022) → full PF (6/29/2022). Following apparent recovery on 7/18/2022 (-32.4 mV, pass), the electrode again reached full PF by 8/15/2022. This pattern is consistent with a deteriorating junction or reference electrode that intermittently recovered with reconditioning but was fundamentally compromised by mid-2022. The transition to instrument 02A0591AB (YSI600XL) in March 2023 and then to EXO-1 instruments beginning June 2023 coincides with stable, passing calibration records through the end of the sampling period. This instrument-level trajectory supports treating the 2022 exclusions as a coherent data quality finding rather than isolated anomalies.

References

2025 SWAMP Report. North Coast Regional Water Quality Control Board. Surface Water Ambient Water Quality Monitoring Program. Smith River Plain Surface Water Monitoring Report 2021-2024. September 2025.

Thomas, M. (2026, April 2). RE: Question re: calibration records [Email to C. Watt and C. Lopez, with C. Davila Arenas and others cc'd]. North Coast Regional Water Quality Control Board, Planning & Stewardship Division.

Thomas, M. (2026, April 8). RE: Question re: calibration records (Updated Spreadsheet — pH Summary) [Email to C. Watt, C. Lopez, and B. Zabinsky, with C. Davila Arenas, B. Thompson, and K. Carter cc'd]. North Coast Regional Water Quality Control Board, Planning & Stewardship Division.

Thomas, M. (2026, April 9). RE: Question re: calibration records (Correction — 9/20/2024 Calibration Date) [Email to C. Watt and crew]. North Coast Regional Water Quality Control Board, Planning & Stewardship Division.

Thomas, M. (2026, April 13). Smith River SWAMP Sonde Calibration Log Data, 2021–2024 [Spreadsheet provided to C. Watt]. North Coast Regional Water Quality Control Board, Planning & Stewardship Division.

Marshall, T. and Fojut, T. (2026, April 2). RE: Question re: calibration records [Email chain, SWAMP IQ / OIMA Helpdesk response to M. Thomas]. State Water Resources Control Board.

Attachment 1 — Smith River SWAMP Sonde Calibration Summary (2021–2024)

Sample Date	Sonde Model	Sonde No.	Pre-Cal Log	Pre-Cal Date	Pre-Cal pH	Post-Cal Log	Post-Cal Date	Post-Cal pH	CEDEN Flag	CEDEN Cal Date	Recommendation
10/25/2021	YSI600XL	08D100573	Original log lost	10/24/2021	Unknown	Yes	12/1/2021	Pass*	None	10/24/2021	Retain w/ notation
1/18/2022	YSI600XL	08D100573	Original log lost	1/17/2022	Unknown	No	--	--	None	1/17/2022	Retain w/ notation
2/9/2022	YSI600XL	02B0044AB	Original log lost	2/8/2022	Unknown	No	--	--	VFIF (DO)	2/8/2022	Retain w/ notation
3/15/2022	YSI600XL	08D100573	Yes	3/14/2022	Pass	Yes	3/28/2022	Pass	None	3/14/2022	Retain
4/13/2022	YSI600XL	08D100573	Yes	4/12/2022	Pass	Yes	5/5/2022	FAIL	Q (DO)	4/12/2022	FLAG or EXCLUDE (per sensitivity analysis)
6/1/2022	YSI600XL	08D100573	Yes	5/31/2022	FAIL	Yes	6/29/2022	FAIL	None	5/31/2022	EXCLUDE
7/19/2022	YSI600XL	08D100573	Yes	7/18/2022	Pass	Yes	8/15/2022	FAIL	None	7/18/2022	EXCLUDE
8/30/2022	NR	NR	None	--	--	No	--	--	Q (Ritmer cond.)	Not entered	EXCLUDE
11/15/2022	YSI600XL	08D100573	Original log lost	11/15/2022	Unknown	No	--	--	None	11/15/2022	Retain w/ notation
12/12/2022	NR	NR	None	--	--	No	--	--	None	Not entered	EXCLUDE
2/12/2023	YSI600XL	08D100573	Yes	2/11/2023	Pass†	No	--	--	None	2/11/2023	Retain w/ notation
3/5/2023	YSI600XL	02A0591AB	Yes	3/5/2023	Pass	Yes	3/7/2023	Pass	None	3/5/2023	Retain
5/15/2023	YSI600XL	02A0591AB	Yes	5/15/2023	Pass	Yes	5/15/2023	Pass	None	5/15/2023	Retain
6/20/2023	EXO-1	22F104013	Yes	6/14/2023	Pass	No	--	--	None	6/20/2023	Retain

Sample Date	Sonde Model	Sonde No.	Pre-Cal Log	Pre-Cal Date	Pre-Cal pH	Post-Cal Log	Post-Cal Date	Post-Cal pH	CEDEN Flag	CEDEN Cal Date	Recommendation
7/10/2023	EXO-1	22F104013	Yes	7/10/2023	Pass	Yes	7/11/2023	Pass	None	7/10/2023	Retain
8/14/2023	EXO-1	22F104013	Yes	8/11/2023	Pass	Yes	8/16/2023	Pass	None	8/11/2023	Retain
9/11/2023	EXO-1	13K101204	Yes	9/9/2023	Pass	Yes	9/11/2023	Pass	None	9/9/2023	Retain
10/15/2023	EXO-1	13K101204	Yes	10/14/2023	Pass	Yes	10/16/2023	Pass	None	10/14/2023	Retain
11/5/2023	EXO-1	22F104013	Yes	11/4/2023	Pass	Yes	11/8/2023	Pass	None	11/4/2023	Retain
12/12/2023	EXO-1	22F104012	Yes	12/11/2023	Pass	No	3/1/2024	Pass	None	12/11/2023	Retain
1/14/2024	EXO-1	13K101204	Yes	1/13/2024	Pass	Yes	1/15/2024	Pass	None	1/13/2024	Retain
4/21/2024	EXO-1	13K101204	Yes	4/20/2024	Pass	Yes	4/22/2024	Pass	None	4/20/2024	Retain
5/16/2024	EXO-1S	24B104329	No	None	Unknown	Yes	6/18/2024	Pass	None	5/14/2024	Retain w/ notation
6/20/2024	EXO-1S	24B104329	Yes	6/18/2024	Pass	Yes	6/21/2024	Pass	None	Not entered (logs found)	Retain
9/25/2024	EXO-1	22F104012	Yes	9/24/2024	Pass	Yes	10/24/2024	Pass	None	Not entered (logs found)	Retain

Note: See Attachment 2 and Endnotes in memo (Recommendations) for 10/25/2021 and 2/12/2023 events.

Attachment 2 — Raw Sonde Calibration Log Data Provided by Mike Thomas (pH Parameters)

This table presents pH-relevant columns from the raw calibration log data. FAIL or PF indicates a recorded failure. NR indicates no record. Full calibration data including DO and specific conductance parameters are available from Mike Thomas / SharePoint. Cal By initials: RF = Rich F.; JF = J. Fryer; MT = Mike Thomas; CL = Carrieann Lopez; MH = M. Harms; PS = P. Stropes; MG = M. Garcia.

Cal Date	Sonde Model	Sonde No.	Cal By	Project	pH1 Std	pH1 Init	pH1 Cal	pH1 mV	pH1 Rng	pH2 Std	pH2 Init	pH2 Cal	pH2 mV	pH2 Rng	pH Slope	Slope Rng	Post-Cal	Notes
6/25/2021	YSI600XL	08D100573	RF	Scott River	7.00	7.01	7.00	-10.9	pass	10.01	10.01	10.01	-185.3	pass	174.4	pass	see next	NR
12/1/2021	YSI600XL	08D100573	JF	Foss Creek	7.00	7.10	7.00	-31.8	pass	10.01	10.05	10.01	-205.2	pass	173.4	pass	see next	DO FAIL (PF); pH pass
3/14/2022	YSI600XL	08D100573	RF	Smith River	7.00	7.05	7.00	-42.0	pass	10.01	9.97	10.01	-212.8	pass	170.8	pass	see next	NR
3/28/2022	YSI600XL	08D100573	MT	Woody Creek	7.00	6.99	7.00	-38.1	pass	10.01	10.01	10.01	-210.1	pass	172.0	pass	see next	NR
4/12/2022	YSI600XL	08D100573	CL	Jolly Giant	7.00	6.95	7.00	-36.2	pass	10.01	10.02	NR	-210.0	pass	173.8	pass	see next	NR
5/5/2022	YSI600XL	08D100573	RF	Coastal Pathogen	7.00	7.00	7.00	-53.4	FAIL	10.01	9.98	10.01	-223.0	pass	169.6	pass	see next	pH1 mV FAIL; DO gain 1.185
5/31/2022	YSI600XL	08D100573	RF	Smith River	7.00	7.07	7.00	-59.7	FAIL	10.01	10.01	NR	-230.1	FAIL	170.4	pass	see next	Pre-Cal FAIL: pH1+pH2 FAIL; DO gain 3.044
6/29/2022	YSI600XL	08D100573	RF	Gold Ridge	PF	PF	PF	PF	PF	PF	PF	PF	PF	PF	PF	PF	see next	Post-Cal FAIL: Full pH probe failure (PF)
7/18/2022	YSI600XL	08D100573	RF	Smith River	7.00	7.08	7.00	-32.4	pass	10.01	10.04	10.01	-205.7	pass	173.3	pass	see next	NR

Cal Date	Sonde Model	Sonde No.	Cal By	Project	pH1 Std	pH1 Init	pH1 Cal	pH1 mV	pH1 Rng	pH2 Std	pH2 Init	pH2 Cal	pH2 mV	pH2 Rng	pH Slope	Slope Rng	Post-Cal	Notes
8/15/2022	YSI600XL	08D100573	RF	Scott River	7.00	PF	PF	PF	PF	10.01	PF	PF	PF	PF	PF	PF	see next	Post-Cal FAIL: pH probe failure (PF); DO gain 3.052
2/11/2023	YSI600XL	08D100573	RF	Smith River	7.00	7.01	NR	-1.80	pass	10.01	10.03	NR	-174.5	pass	172.7	pass	see next	pH pass; DO+ SpCond FAIL
3/5/2023	YSI600XL	02A0591AB	MH	Smith River	7.00	7.05	7.01	-11.00	pass	10.01	10.05	10.01	-177.8	pass	166.8	pass	pass	NR
5/15/2023	YSI600XL	02A0591AB	MH	Smith River	7.00	7.19	6.99	-17.30	pass	10.01	9.82	10.00	-184.2	pass	166.9	pass	pass	pH probe should be changed; Post-Cal at 900 ft elev; new DO membrane
6/14/2023	EXO-1	22F104013	RF	Cyano/ Smith River	7.00	7.04	7.00	20.51	pass	10.01	10.01	10.01	-189.7	pass	179.2	pass	see next	NR
7/10/2023	EXO-1	22F104013	PS	Smith River	7.00	7.02	6.99	-21.32	pass	10.01	10.16	10.01	-190.5	pass	NR	PF	pass	NR
8/11/2023	EXO-1	22F104013	PS	Smith River	7.00	7.04	7.00	-23.59	pass	10.01	10.01	10.01	-194.2	pass	170.6	pass	pass	NR
9/9/2023		13K101204	MH	Smith River	7.00	7.09	7.00	-25.40	pass	10.01	10.03	10.01	-196.4	pass	170.7	pass	pass	NR
10/14/2023		13K101204	PS	Smith River	7.00	7.02	6.99	-25.96	pass	10.01	10.00	10.01	-196.2	pass	170.3	pass	pass	NR
11/4/2023	EXO-1	22F104013	PS	Smith River	7.00	8.99	7.00	-24.90	pass	10.01	10.00	10.01	-196.2	pass	171.3	pass	pass	NR
12/11/2023	EXO-1	22F104012	CL/ MT	Smith River	7.00	7.06	7.00	-16.30	pass	10.01	10.04	10.01	-188.5	pass	172.2	pass	see next	NR
1/13/2024		13K101204	MH	Smith River	7.00	7.03	7.00	-26.68	pass	10.01	9.97	10.01	-196.3	pass	169.6	pass	pass	NR
4/20/2024		13K101204	PS	Smith River	7.00	7.09	7.00	-31.39	pass	10.01	10.10	10.01	-202.1	pass	170.8	pass	pass	NR

Cal Date	Sonde Model	Sonde No.	Cal By	Project	pH1 Std	pH1 Init	pH1 Cal	pH1 mV	pH1 Rng	pH2 Std	pH2 Init	pH2 Cal	pH2 mV	pH2 Rng	pH Slope	Slope Rng	Post-Cal	Notes
5/14/2024	EXO-1S	24B104329															see next	No data entered
6/18/2024	EXO-1S	24B104329		Smith River	7.00	7.08	7.00	-13.90	pass	10.01	10.05	10.01	-188.3	pass	174.4	pass	see next	NR
9/24/2024	EXO-1	22F104012	MT	Smith River	7.00	7.10	7.00	-28.60	pass	10.01	10.10	10.01	-201.8	pass	173.2	pass	see next	NR
10/21/2024	EXO-1	22F104012	MG	NR	7.00	7.03	7.00	-30.40	pass	10.01	10.03	10.01	-202.2	pass	171.8	pass	see next	NR

Note: See Attachment 1 and Endnotes in memo (Recommendations) for 10/25/2021 and 2/12/2023 events.

ATTACHMENT 2

Watt, C. (2025, October 20). Tillas Slough Copper Verification Study – Results [Internal memorandum to D. Kuszmar]. North Coast Regional Water Quality Control Board.

**NORTH COAST WATER QUALITY CONTROL BOARD
INTERNAL TECHNICAL MEMORANDUM**

TO: David Kuszmar, Southern Agriculture Unit Supervisor
FROM: Chris Watt, Senior Specialist
DATE: October 20, 2025
RE: Tillas Slough Copper Verification Study – Results

[Prepared with AI assistance; reviewed and approved by NCRWQCB staff.]

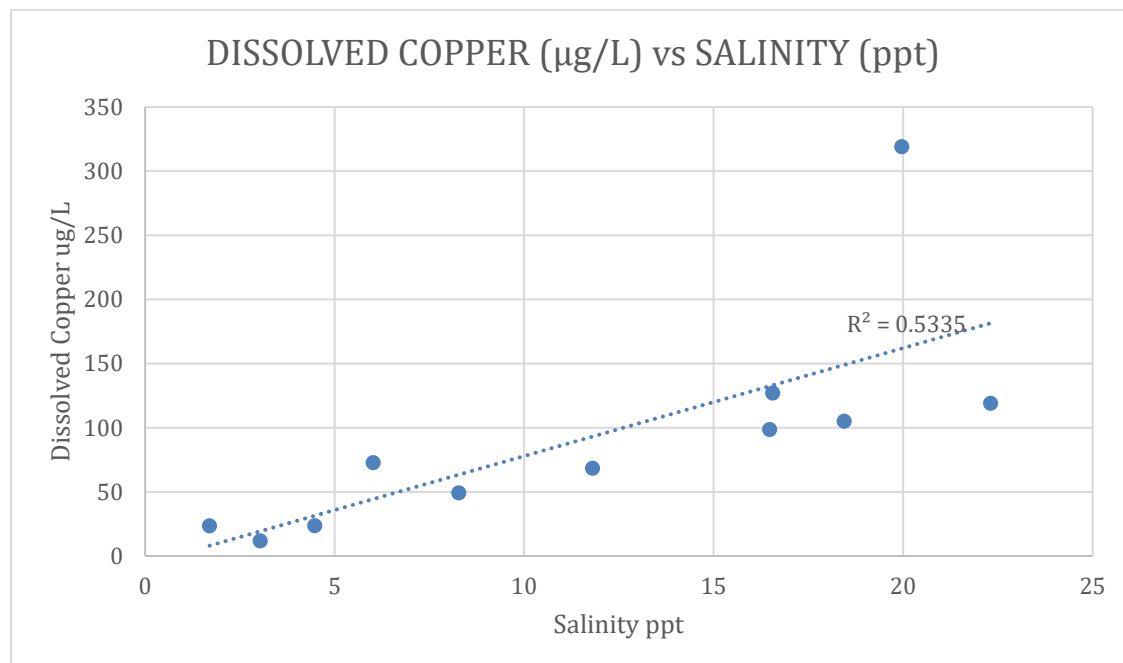
EXECUTIVE SUMMARY

This verification study demonstrates that anomalous elevated dissolved copper concentrations (49-319 µg/L) reported by Moss Landing Marine Labs using EPA Method 200.8 (Inductively Coupled Plasma Mass Spectrometry) for samples collected at the Tillas Slough Tide Gate Sampling Station (Station 103TL1789) between 2022-2024 were most likely analytical artifacts caused by polyatomic interferences in high-salinity matrices (Table 1). The elevated dissolved copper concentrations showed a strong correlation with salinity levels exceeding 1 part per thousand (ppt) (Figure 1). Using interference-corrected analytical methods (EPA 1640 and EPA 200.8 with collision cell), dissolved copper concentrations at Station 103TL1789 and three upstream stations ranged from 0.27 to 2.0 µg/L. This verification study was conducted following a comprehensive Surface Water Ambient Monitoring Program (SWAMP) Monitoring Plan developed in August 2025 (Watt, 2025).

Table 1. Station 103TL1789 Salinity > 1ppt Dissolved Copper Results (2022-2024).

Sample Date	Sample Time	Salinity (ppt)	Tide Height (ft)	Dissolved Cu (µg/L)
07/19/22	11:45	8.28	1.0	49.2
08/30/22	08:00	16.56	0.6	127
11/15/22	10:00	4.48	4.1	23.6
06/21/23	08:45	6.02	-0.75	72.7
07/10/23	12:45	11.81	1.6	68.4
08/14/23	17:30	18.45	3.2	105
09/10/23	15:45	16.48	3.4	98.5
10/15/23	17:15	22.31	1.0	119
11/05/23	12:30	3.04	4.0	11.7
06/19/24	15:30	1.70	3.3	23.5
09/26/24	13:15	19.97	3.7	319

Figure 1. Station 103TL1789 Dissolved Copper vs Salinity (2022-2024).



Analytical Interference Concerns

In ICP-MS (Inductively Coupled Plasma Mass Spectrometry) analysis, copper determination can be significantly affected by polyatomic interferences, particularly on isotopes ^{63}Cu and ^{65}Cu . These interferences arise from the formation of polyatomic ions involving argon from the plasma gas and other elements present in the sample matrix, such as sodium and magnesium commonly found in saline waters. Common interfering species include $^{40}\text{Ar}^{23}\text{Na}^+$ and $^{40}\text{Ar}^{25}\text{Mg}^+$ on ^{63}Cu and ^{65}Cu respectively, which can lead to overestimation of copper concentrations as their signals are indistinguishable from the copper isotopes in the mass spectrometer without appropriate interference correction technology.

Key observations from 2022-2024 sampling results prompting this verification study:

- Ten of eleven samples with salinity >1 ppt showed copper >20 µg/L
- Highest copper (105-319 µg/L) occurred at highest salinities (16-22 ppt)
- Strong positive correlation between salinity and reported copper
- Pattern consistent with known interference mechanisms

STUDY DESIGN

Project Personnel and Responsibilities

This verification study was conducted under the oversight of Chris Watt (North Coast Regional Water Quality Control Board), with technical support and field work performed by Chris Watt, Brenna Sullivan, David Kuszmar, and Carrieann Lopez. Analytical

services were provided by Babcock Laboratories, Inc. (Riverside, CA) and Weck Laboratories, Inc. (Hacienda Heights, CA).

Sampling Strategy and Locations

Surface water samples were collected at four locations during both high and low tides on two dates to capture varying salinity conditions.

The primary location was selected because it is the SWAMP monitoring location where elevated copper concentrations strongly correlated with salinity were previously detected by Moss Landing Marine Labs using EPA Method 200.8.

- Station 103TL1789 – Tillas Slough at Tide Gate

Three tributary locations were selected to characterize potential upstream sources of copper and distinguish between agricultural inputs versus possible salinity interference. All tributary sampling points were located to capture near-field conditions prior to tidal mixing.

- Station 103TL3482 – Tillas Slough above Ritmer/Delilah Creeks
- Station 103RI0011 – Ritmer Creek Confluence with Delilah Creek
- Station 103DE0010/103DE0377 – Delilah Creek Confluence with Tillas Slough

Analytical Methods

All samples were analyzed by Babcock Laboratories, Inc. (Riverside, CA) using the following methods. Split samples from Station 103TL1789 were analyzed by Weck Laboratories, Inc. (Hacienda Heights, CA) for inter-laboratory comparison.

EPA Method 200.8 with Collision/Reaction Cell Technology: A collision or reaction cell is placed between the plasma and the mass analyzer. An appropriate collision gas is introduced into the cell, causing collisions with interfering polyatomic ions ($^{40}\text{Ar}^{23}\text{Na}^+$, $^{40}\text{Ar}^{25}\text{Mg}^+$) that fragment or remove them from the ion beam, while copper ions are less affected due to their different collision cross-sections and chemical properties.

EPA Method 1640 On-line Chelation Preconcentration: This method uses on-line chelation preconcentration coupled with ICP-MS for ultra-trace level determination of copper in ambient waters. The technique involves using a chelating agent to selectively bind to copper ions, concentrating them from the sample matrix. This enhances sensitivity by reducing matrix interferences and improving detection limits, making it particularly suitable for measuring copper at or below EPA water quality criteria levels in complex matrices including seawater.

RESULTS

Table 2. September 3, 2025 – High Tide Results.

Station	EPA 1640 Diss Cu (µg/L)	EPA 1640 Total Cu (µg/L)	EPA 200.8 Diss Cu (µg/L)	EPA 200.8 Total Cu (µg/L)	Time	Salinity (ppt)
103TL1789	0.43	0.78	0.6 (J)	0.8 (J)	12:03	24.03
103TL3482	0.93	1.6	0.8 (J)	1.5	13:32	16.93
103RI0011	1.1	2.5	1.0	2.5	12:43	15.01
103DE0010	0.74	1.6	0.8 (J)	1.5	13:00	17.78

Laboratory: Babcock Laboratories, Report C5I0819

Table 3. September 3, 2025 – Low Tide Results.

Station	EPA 1640 Diss Cu (µg/L)	EPA 1640 Total Cu (µg/L)	EPA 200.8 Diss Cu (µg/L)	EPA 200.8 Total Cu (µg/L)	Time	Salinity (ppt)
103TL1789	1.0	1.5	1.0	1.4	16:06	16.53
103TL3482	1.2	1.5	1.2	1.5	17:19	15.46
103RI0011	2.0	3.1	2.0	3.2	16:35	12.59
103DE0010	1.5	1.9	1.6	1.8	16:52	13.78

Laboratory: Babcock Laboratories, Report C5I0791

Table 4. September 17, 2025 – High Tide Results.

Station	EPA 1640 Diss Cu (µg/L)	EPA 1640 Total Cu (µg/L)	EPA 200.8 Diss Cu (µg/L)	EPA 200.8 Total Cu (µg/L)	Time	Salinity (ppt)
103TL1789	0.27	0.59	0.4 (J)	0.8 (J)	11:45	27.65
103TL3482	0.92	1.5	0.9 (J)	1.4	13:50	17.73
103RI0011	0.84	1.5	0.9 (J)	1.5	12:45	17.31
103DE0377	0.81	1.4	0.8 (J)	1.3	13:15	17.14

Laboratory: Babcock Laboratories, Report C5I2693

Table 5. September 17, 2025 – Low Tide Results.

Station	EPA 1640 Diss Cu (µg/L)	EPA 1640 Total Cu (µg/L)	EPA 200.8 Diss Cu (µg/L)	EPA 200.8 Total Cu (µg/L)	Time	Salinity (ppt)
103TL1789	1.1	1.5	1.0	1.6	16:40	18.25
103TL3482	1.0	1.8	1.0	1.7	18:45	18.31
103RI0011	0.67	2.9	0.7	2.8	18:00	5.56
103DE0377	0.68	1.2	0.6	1.1	18:30	6.10

Laboratory: Babcock Laboratories, Report C5I2702

(J) = Estimated value

Method Agreement

As illustrated in the results presented above, agreement between EPA Methods 200.8 and 1640 for dissolved copper (salinity > 1ppt) was acceptable across all samples, with differences typically <0.2 µg/L.

Inter-Laboratory Comparison – Station 103TL1789

Split samples from Station 103TL1789 were analyzed by both Babcock and Weck Laboratories, as summarized in the following tables.

Table 6. September 3, 2025 Inter-Laboratory Comparison – Station 103TL1789.

Date/Tide	Laboratory	EPA 1640 Diss Cu (µg/L)	EPA 1640 Total (Cu) (µg/L)	EPA 200.8 Diss (Cu) (µg/L)	EPA 200.8 Total (Cu) (µg/L)
Sept 3 High	Babcock	0.43	0.78	0.6 (J)	0.8 (J)
	Weck	0.39	0.56	ND	ND
Sept 3 Low	Babcock	1.0	1.5	1.0	1.4
	Weck	0.47	1.1	0.78	1.3

Table 7. September 17, 2025 Inter-Laboratory Comparison - Station 103TL1789.

Date/Tide	Laboratory	EPA 1640 Diss Cu (µg/L)	EPA 1640 Total (Cu) (µg/L)	EPA 200.8 Diss (Cu) (µg/L)	EPA 200.8 Total (Cu) (µg/L)
Sept 17 High	Babcock	0.27	0.59	0.4 (J)	0.8 (J)
	Weck	0.20	0.58	ND	0.51
Sept 17 Low	Babcock	1.1	1.5	1.0	1.6
	Weck	0.96	1.6	0.85	1.4

Note: Weck Laboratory EPA 200.8 results reporting limit = 0.5 µg/L. ND indicates results below the method detection limit (MDL).

(J) = Estimated value

Inter-laboratory agreement between Babcock and Weck was acceptable across all samples and both sampling dates, with differences for dissolved copper (salinity > 1 ppt) ranging between 0.04 and 0.53 µg/L. Both laboratories consistently reported copper concentrations in high-salinity samples well below historically reported values, confirming the likelihood that previously reported elevated copper concentrations were analytical artifacts caused by polyatomic ion interferences in high-salinity matrices rather than true ambient conditions at Station 103TL1789.

QUALITY ASSURANCE

Quality Assurance Objectives

All samples were collected and analyzed following quality assurance objectives established in the SWAMP Monitoring Plan (Watt, 2025):

- Precision: Relative percent difference between split samples should be $\leq 15\%$ for concentrations $> 10\times$ detection limit.
- Accuracy: Laboratory control samples and matrix spikes should meet method-specified criteria (85-115% recovery).
- Detection Limits: Both EPA Methods 200.8 and 1640 should achieve $\leq 0.1 \mu\text{g/L}$ for dissolved copper (ultra-trace capability).

Babcock Laboratories QC Summary

All quality control samples met acceptance criteria:

- Method blanks: All ND (not detected)
- Laboratory Control Samples: 85-106% recovery
- Matrix Spike recoveries: 85-112% recovery
- Duplicate samples: RPD 2-8%
- All holding times met

Weck Laboratories QC Summary

All quality control samples met acceptance criteria:

- Method blanks: All ND (not detected)
- Laboratory Control Samples: 94-106% recovery
- Matrix Spike recoveries: 89-112% recovery
- Duplicate samples: RPD 2-7%
- All holding times met

DISCUSSION

Evidence for Analytical Interference

This verification study provides the following compelling evidence that questionable elevated dissolved copper concentrations in samples collected in Tillas Slough from 2022-2024 with salinity $> 1\text{ppt}$ were analytical artifacts:

Consistent low-level results: All samples from both sampling dates and all tidal conditions showed dissolved copper concentrations $< 2.0 \mu\text{g/L}$ using interference-corrected methods.

Method agreement: EPA 1640 and EPA 200.8 with collision cell produced comparable results (differences generally $<0.2 \mu\text{g/L}$), demonstrating effective interference elimination.

Inter-laboratory confirmation: Weck and Babcock laboratories produced consistent results for split samples, with differences generally $<0.5 \mu\text{g/L}$ for EPA 1640.

CONCLUSIONS

- 1. Questionable Elevated Concentrations Were Analytical Artifacts.** The difference between dissolved copper concentrations reported by Moss Landing ($49\text{--}319 \mu\text{g/L}$) to this study's results ($0.27\text{--}2.0 \mu\text{g/L}$) for samples where the salinity was >1 ppt, combined with excellent method agreement and inter-laboratory confirmation, suggest that previously reported elevated dissolved copper concentrations were most likely caused by polyatomic interferences ($^{40}\text{Ar}^{23}\text{Na}^+$ and $^{40}\text{Ar}^{25}\text{Mg}^+$) in high-salinity matrices.
- 2. Interference-Corrected Methods Are Essential.** Both EPA Method 1640 (on-line chelation) and EPA Method 200.8 with collision cell technology successfully eliminated polyatomic interferences, producing comparable low-level results.
- 3. Inter-Laboratory Agreement Confirmed.** Split sample analysis by Weck Laboratories confirmed Babcock's results, with excellent agreement between laboratories for EPA 1640 analyses.

RECOMMENDATIONS

1. Exclude or appropriately flag anomalous elevated dissolved copper data associated with salinity > 1 ppt at Station 103TL1789 (Tillas Slough at Tide Gate) – and by extension, Biotic Ligand Model (BLM)-derived copper toxicity unit (TU) results – presented in the Smith River Plain Surface Water Monitoring Study 2021-2024 (2025 SWAMP Report).
2. Use interference-corrected analytical methods (EPA Method 200.8 with collision cell or EPA Method 1640) to ensure accurate copper determinations in high-salinity estuarine environments.
3. Contact Moss Landing Marine Labs to confirm analytical methodology used during 2022-2024 monitoring and recommend transition to interference-corrected methods for future estuarine copper analyses.
4. Update monitoring protocols to require specification of collision cell use or alternative interference correction for all ICP-MS copper analyses in saline matrices (>1 ppt).
5. Use this case study in training materials to illustrate the importance of proper analytical method selection in high-salinity matrices and the potential for polyatomic interferences to generate false positive results.

REFERENCES:

Watt, C. (2025). SWAMP Monitoring Plan: Tillas Slough Copper Verification Study. North Coast Regional Water Quality Control Board, Santa Rosa, CA. August 18, 2025.

2025 SWAMP Report. North Coast Regional Water Quality Control Board. Surface Water Ambient Water Quality Monitoring Program. Smith River Plain Surface Water Monitoring Report 2021-2024. September 2025.

ANALYTICAL REPORTS:

Babcock Laboratories, Inc., Riverside, CA

Reports: C5I0819, C5I0791, C5I2693, C5I2702

Report Dates: September 30, 2025 and October 15, 2025

Weck Laboratories, Inc., Hacienda Heights, CA

Reports: C5I1247, C5I1248, C5I2705, C5I2706

Report Dates: October 6, 2025 and September 30, 2025