

# **WATER QUALITY SAMPLING**

**Stormwater Enforcement Workshop**

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# *Purpose of the Workshop*

- ❖ Basics of sampling at stormwater facilities
- ❖ Elements of stormwater sampling plans
- ❖ Laboratory analyses and field parameters
- ❖ Maintaining sample and data integrity for enforcement actions

# *Presentation Overview*

- ❖ Sampling Plans
- ❖ Chain-of-Custody Procedures
- ❖ Chain of Continuous Sample Integrity
- ❖ Chemistry
  - General, Toxics, Other Pollutants
- ❖ Quality Assurance
- ❖ Web Links

# *Sampling Plans*

- ❖ The sampling plan, when properly executed, must answer the appropriate questions that lead to successful enforcement action
- ❖ The plan is necessary to organize the methods that develop a legally-defensible enforcement case

# *Sampling Questions*

- ❖ What to sample?
- ❖ Where to sample?
- ❖ How to sample?
- ❖ When to sample?

# *Sampling Questions (Cont'd)*

- ❖ Why are you sampling?
- ❖ What question are you trying to answer?
- ❖ What field parameters and analytes to measure?
- ❖ Where do you sample to characterize sources and build a case?
- ❖ How do you collect, preserve, store, and ship samples in a legally and scientifically defensible manner?
- ❖ When is a sample representative?

# *Typical Enforcement Question*

- ❖ Are discharges of pollutants above regulatory limits being released from the facility?

# *Attitude*

- ❖ **Be professional, polite, but  
Never, Ever, Trust the Discharger**
- ❖ **Assume that the details of sampling and  
analysis will be used scrutinized in court**

# *Typical Sampling Locations are:*

UPSTREAM, DOWNSTREAM, SOURCE

- Other considerations: nature of storm water discharge, news media relations

# *NPDES Samples*

Storm water samples should be taken at a storm water point source. A 'point source' is defined as any discernible, confined, and discrete conveyance, including (but not limited to) any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, concentrated animal feeding operation, landfill leachate collection system, vessel, or other floating craft from which pollutants are or may be discharged (as per 40 CFR 122.2).

Tahoe  
DAILY TRIBUNE

PAGE ONE

TUESDAY, JUNE 8  
1999

# Caltrans will stop the slush

By Andy Bouelle  
Tribune Staff Writer

If you didn't like the California Department of Transportation's slushing-out, snow-removal technique used during the winter, you're not alone — and you won't have to worry about it next year.

The Lahontan Regional Water Quality Control Board has issued a notice of violation to Caltrans for its slushing out, stating that the action hurts the water quality of Lake Tahoe.

"They have an opportunity to come back and say what they intend to do. If it's inadequate, we can conceivably raise it to a higher level of enforcement," said Alan Miller, water resources control engineer of Lahontan. "A notice of violation is kind of a starting point, saying we were not happy with what happened last winter."

Dale Ten Broeck, Caltrans' district division chief for maintenance, said he wants to follow Lahontan's advice.

"We won't be slushing the snow in the future. It's a lot cheaper that way, but let's face it: We have to do our share to help protect the lake," he said. "I estimate it could cost as much as half a million dollars to remove snow in the Tahoe Basin because of not slushing. But my feeling is Caltrans is going to have to step up to the plate. I don't have the extra resources to cover that, but I'll find them."

When Caltrans slushes out, according to Lahontan workers add significant amounts of road salt to the snow. The layers of snow and sand are plowed into the center lane. Then, when the weather warms up, Caltrans crews spread the snow over the road so it melts quickly.

The quickly melting snow creates a rapid onrush of snowmelt that overwhelms stormwater treatment traps. They are unable to treat all of the runoff.

Unacceptable amounts of sand, nitrogen, phosphorous,

*"We have to do our share to help protect the lake."*

— Dale Ten Broeck  
Caltrans' district chief for maintenance

See Slush Page 2A

Sampling Notes: Samples were collected from the following locations per schematic below.

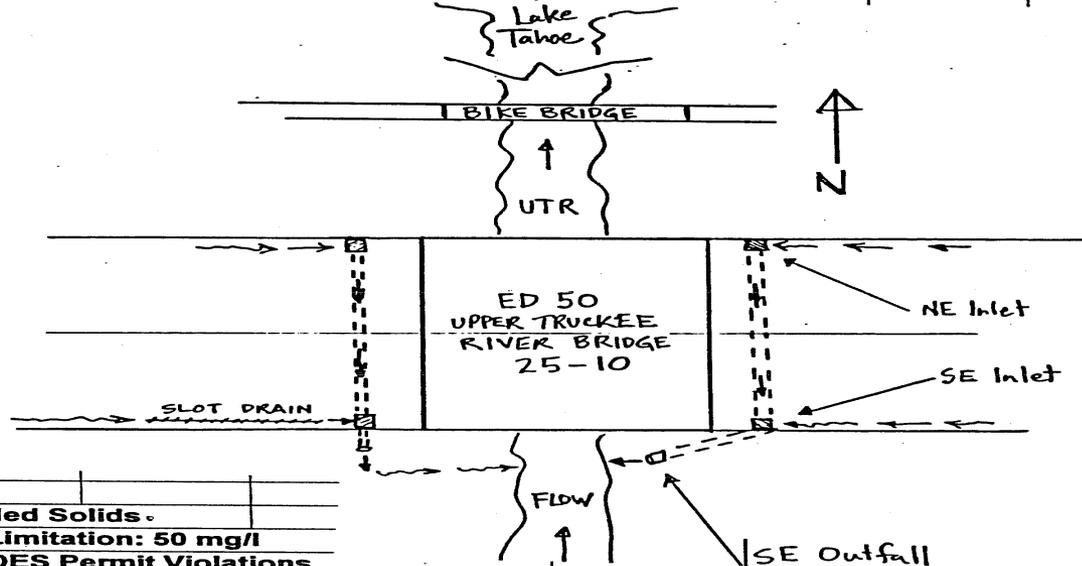
All locations in the vicinity of Upper Truckee River (UTR) Bridge 25-10, 50 ED Postmile 7643.

NE inlet: Grated inlet on northeast side of 25-10; drainage from US 50 west of Sierra Blvd to UTR.

The outflow from the NE inlet crosses 50 ED to SE INLET.

SE inlet: Grated inlet on southeast side of 50 ED; drainage from US 50 west of Sierra Blvd to UTR.

SE outfall: 18-inch culvert outfall to UTR upstream of SE corner 25-10; discharge from NE and SE inlets.



Parameter: Suspended Solids.

Effluent Discharge Limitation: 50 mg/l

Bold Values are NPDES Permit Violations

ID No.	Date	Time	Location	Concentration (mg/l)	Ratio of Concentration to Limitation
41	2/16/99	14:15	NE inlet	3577	71.5
56	2/26/99	15:30	SE outfall	<b>577</b>	11.5
57	2/26/99	16:00	SE inlet	765	15.3
60	3/9/99	14:32	SE outfall	<b>2078</b>	41.6
61	3/9/99	14:35	SE inlet	1931	38.6
64	3/9/99	15:27	SE outfall	<b>1936</b>	38.7
66	3/9/99	15:35	SE inlet	2269	45.4
97	4/9/99	12:20	NE inlet	2373	47.5
98	4/9/99	12:22	SE outfall	<b>2713</b>	54.3
99	4/9/99	12:24	SE inlet	2937	58.7
100	4/9/99	14:50	SE outfall	<b>2041</b>	40.8
101	4/9/99	15:00	SE inlet	433	8.7
102	4/9/99	15:10	NE inlet	2641	52.8

# *Field and Lab QA/QC*

- ❖ Blanks
- ❖ Replicates
- ❖ Splits
- ❖ Blinds and Double Blinds
- ❖ Matrix Spikes

# QA/QC Plan

- ❖ QAPP if a “Project”
- ❖ Monitoring Plan (MP) most Important
- ❖ Data Quality Objectives (DQOs) - qualitative or quantitative statements of the precision, bias, representativeness, completeness, and comparability necessary for the data to serve the objectives of the project



# *Industrial Stormwater Analytes*

- ❖ pH
- ❖ TSS
- ❖ TOC
- ❖ SC
- ❖ Toxic Chemicals
- ❖ Other Pollutants

# *Construction Stormwater Analytes*

- ❖ pH
- ❖ TSS
- ❖ SS (Settleable Solids)
- ❖ SSC (Suspended Sediment Concentration)
- ❖ Water Quality Monitoring
- ❖ Turbidity
- ❖ Other Pollutants





*Turbidity*

WALCORE GMH

SCUPPER

5 15 '00

# *Field Parameters*

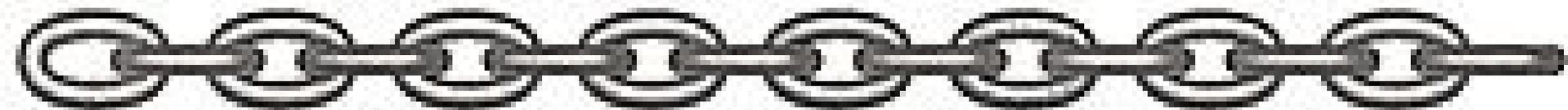
- ❖ temperature must be measured in the field,
- ❖ pH, chlorine, dissolved oxygen, and soluble sulfide have a 15 min. holding time, and must realistically be measured in the field.
- ❖ Other common field parameters are turbidity and electrical conductivity can be measured in the field or in the lab within holding times.

# *Field Activities*

- ❖ Instrument Calibration, Record Keeping + calibration logs and field checks (Handout pH example)
- ❖ Detailed Field Notes

# *Sampling Tips*

- ❖ Label the bottles, not just the lids (lids can be exchanged between bottles)
- ❖ Use a unique sample ID for all samples – e.g. based on FY-ProjectType-sequential number (089RB001)



# *Chains*

- ❖ Chain of Custody—Legal Document to verify unbroken custody of sample / functional document to link sample results with sample metadata (sample location filed conditions, personnel sampling, etc)
- ❖ “Chain” of Sample Integrity—Sampling Protocol, QA/QC, Preservation, Storage, Transport, Analysis, Data Interpretation/Data QA/QC

# Chain-of-Custody Procedures

- ❖ A sample is considered to be under a person's custody if it is
  - ❖ - in the individual's physical possession,
  - ❖ - in the individual's sight,
  - ❖ - secured in a tamper-proof way by that individual, or
  - ❖ - secured by the individual in an area that is restricted to authorized personnel

# COC Procedures

- ❖ Elements of chain-of-custody include the following:
  - ❖ • Sample Identification
  - ❖ • Security seals and locks
  - ❖ • Security procedures
  - ❖ • Chain-of-custody forms/Request for Analysis
  - ❖ • Field Logbook



# *Chain of Continuous Sample Integrity*

- ❖ **Sampling Protocol**
- ❖ bottle selection
- ❖ required sample volumes
- ❖ gloves (latex, nitrile preferred)
- ❖ face upstream when sampling
- ❖ depth of sampling
- ❖ undisturbed, representative sample
- ❖ grab sample, composite (spatial, temporal), autosampling, clean hands, dirty hands, etc.

# *Sample Integrity*

- ❖ Preservation
- ❖ Transport
- ❖ Storage
- ❖ Shipping
- ❖ custody seals
- ❖ chain-of-custody
- ❖ received by lab in time to meet analytical holding times

# *Sample Integrity (Cont'd)*

## **The Laboratory**

- ❖ Sample turn-around
- ❖ Follow-up
- ❖ Internal QA/QC
- ❖ reporting limits must be at or less than discharge limitations, Basin Plan water quality objectives for receiving waters, etc.
- ❖ Labs used must usually be Department of Health Services, Environmental Laboratory Assessment Program (DHS-ELAP) certified for the particular analyses tested  
<http://ww2.cdph.ca.gov/certlic/labs/Pages/ELAP.aspx>

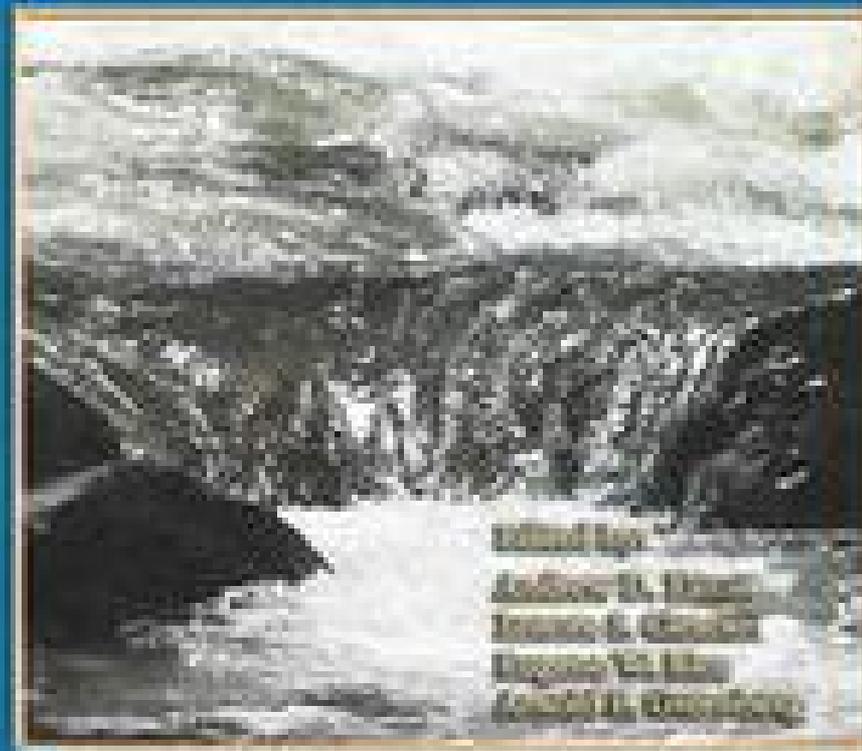
# *Chemistry*

- ❖ EPA Analytical Series
- ❖ 500 Series – Drinking Water
- ❖ 600 series – Environmental / Ambient Samples
- ❖ 8000 Series – Waste Characterization (from SW-846)

21st Edition

# STANDARD METHODS

FOR THE EXAMINATION OF WATER & WASTEWATER



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## 2005

Centennial Edition

# *Toxic Chemicals - Metals*

- ❖ Common methods are AAS, GF, GF-CVF, ICP-AES, ICP-MS
- ❖ Priority Pollutant Metals (13) – Silver (Ag), Arsenic (As), Antimony (Sb), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Nickel (Ni), Selenium (Se), Thallium (Tl), Zinc (Zn)
- ❖ RCRA/TCLP Metals (8) - Arsenic (As), Barium (Ba), Cadmium (Cd), Chromium (Cr), Mercury (Hg), Lead (Pb), Selenium (Se), Zinc (Zn)

# *Toxic Chemicals - Organics*

- ❖ Common methods are Gas Chromatography - Flame Ionization Detection (GC-FID), Gas Chromatography-Electron Capture (GC-EC), Gas Chromatography -Mass spectroscopy (GC/MS), High Pressure Liquid Chromatography (HPLC)
- ❖ Volatiles including Halocarbons
- ❖ Petroleum Fuels
- ❖ Semi-volatiles
- ❖ Polychlorinated Biphenyls (PCBs)
- ❖ Pesticides /Herbicides

# *Parameter Selection Tips*

- ❖ If unknown, Initial investigation “shotgun approach” may be used GC/MS and ICP/MS methods are generally good for this, since they provide positive identification and quantitation of all extracted compounds in the sample.
- ❖ Follow-up investigation – “round up the likely suspects” assuming prior sampling and knowledge of the site and prior pollution can narrow the focus of the investigation.

# *Other Pollutants - General*

- ❖ Five-day Biochemical Oxygen Demand--  
BOD5
- ❖ Chemical Oxygen Demand
- ❖ Alkanlinity
- ❖ Hardness, mg equivalent/L  $\text{CaCO}_3 =$   
 $([\text{Ca}, \text{mg}/\text{l}] * 2.497) + ([\text{Mg}, \text{mg}.\text{l}] * 4.116)$
- ❖ Turbidity
- ❖ Cyanide

# *Other Pollutants - Nitrogen*

- ❖ Total Kjeldahl Nitrogen (TKN) is a measure of both N bound in organic molecules and total ammonium
- ❖ Ammonia,  $\text{NH}_3$  (in reality the prevalent form at normal pH is ammonium,  $\text{NH}_4^+$ ), the aqueous form of the most chemically reduced nitrogen form
- ❖ Nitrate and Nitrite ( $\text{NO}_3 + \text{NO}_2$ ), the oxidized and environmentally mobile form
- ❖ Total Nitrogen (TN) is functionally determined from the sum of  $\text{TKN} + (\text{NO}_3 + \text{NO}_2)$

# *Other Pollutants - Phosphorus*

- ❖ Total Phosphorus (TP) all organic and inorganic forms of phosphorus
- ❖ Ortho-Phosphorus (OP, also know as soluble reactive phosphorus, SRP), the simplest inorganic form of aqueous phosphorus
- ❖ In addition, there are several different other operationally–defined forms of phosphorus

# *Other Pollutants - Pathogens*

## ❖ Microbiological Methods

- Fecal Coliform
- Total Coliform
- E. coli
- Enterococcus

## ❖ Membrane (direct count) versus multiple tube (most probable number, MPN) methods

# *Web Links for Stormwater Quality Enforcement Sampling*

- ❖ USEPA NPDES Storm Water Sampling Guidance Document
  - <http://www.epa.gov/npdes/pubs/owm0093.pdf>
- ❖ Washington State Water Quality Program Inspection Manual
  - <http://www.ecy.wa.gov/pubs/9276.pdf>
- ❖ Washington State Stormwater Sampling Guidance Document
  - <http://www.ecy.wa.gov/pubs/0210071.pdf>

## *Web Links (Cont'd)*

- ❖ Colorado State Stormwater Sampling Guidance Document
  - <http://www.cdphe.state.co.us/wq/PermitsUnit/stormwater/guidancefactsheets/SWSampelingGuidance.pdf>
- ❖ California Stormwater Quality Task Force (SWQTF) Construction SW Sampling and Analysis, Appendix C
  - [http://www.cabmphandbooks.com/Documents/Construction/Appendix\\_C.pdf](http://www.cabmphandbooks.com/Documents/Construction/Appendix_C.pdf)
- ❖ SWRCB Water Quality Order No. 97-03-DWQ NPDES/WDR General Permit for Industrial Activities
  - [http://www.waterboards.ca.gov/water\\_issues/programs/stormwater/docs/induspmt.pdf](http://www.waterboards.ca.gov/water_issues/programs/stormwater/docs/induspmt.pdf)

## *Web Links (Cont'd)*

- ❖ SWRCB Water Quality Order No. 99-08-DWQ NPDES General Permit for Construction Activities
  - [http://www.waterboards.ca.gov/water\\_issues/programs/stormwater/docs/finalconstpermit.pdf](http://www.waterboards.ca.gov/water_issues/programs/stormwater/docs/finalconstpermit.pdf)
- ❖ Statewide Ambient Monitoring Program (SWAMP) Quality Assurance Management Plan (See Appendices E and F for Field Monitoring Standard Operating Procedures (SOPs))
  - [http://www.swrcb.ca.gov/water\\_issues/programs/swamp/qamp.shtml](http://www.swrcb.ca.gov/water_issues/programs/swamp/qamp.shtml)



