Copper Source Tracking in Stormwater Using X-Ray Fluorescence and Design of Custom Stormwater BMPs

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Background

- The U.S. Maritime Administration (MARAD) maintains the National Defense Reserve Fleet, a fleet of vessels that serve as a reserve of ships for national defense and national emergency purposes. The Suisun Bay Reserve Fleet in Benicia, California is part of the reserve fleet (aka "Mothball Fleet").
- An investigation into the potential source(s) of dissolved copper in stormwater was conducted on the Mt. Washington, a vessel moored at Benicia.
- Stormwater monitoring data indicated elevated concentrations of copper were present in the stormwater with no known source.
- Total copper concentrations were between 1,000 and 3,000 µg/L, with approximately 90% of the copper in the dissolved form.

Objectives

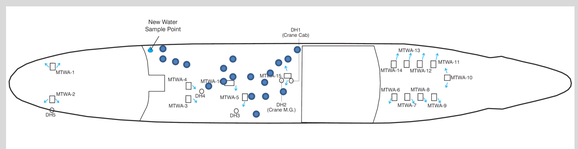
- **Develop and test vessel stormwater BMPs able to reduce copper to target levels.**
  - Identify potential source(s) of dissolved copper in stormwater
  - Confirm the leachability of the copper using a simple field leaching test
  - Develop and test treatment controls to reduce dissolved copper concentrations in stormwater

Approach

XRF test to identify potential copper sources → **Field leach test to confirm copper leachability in identified copper source** → **Bench-scale column test to test removal efficiency and permeability**

XRF Field Test

- A Thermo Scientific Niton XLT 898D x-ray fluorescence (XRF) field analyzer, typically used for screening metals contaminated soils or objects with lead paint, was used to screen deck-mounted equipment and surfaces at 19 locations on the vessel.
- Copper concentrations detected using XRF ranged from non-detect to 864,000 mg/kg.
- The highest copper concentrations were detected on the surfaces of the single anchor leg mooring (SALM) structure located on the central portion of the vessel's main deck.
- The SALM is an underwater anchor for fueling operations, which allows for fueling in high seas.
- Copper concentrations measured on surfaces of the SALM were between one and three orders of magnitude greater than the other measured copper concentrations.
- The storage of the SALM on the deck of the vessel and its large size (approximately 55 feet by 140 feet) allowed for significant contact time and area for rainfall to leach copper from ablative paint.



Copper Concentrations Based on XRF

Sample #	Location/Description	Copper (mg/kg)	Error (±) (mg/kg)
1	Conduit surface beneath stormwater sampling point	11,400	800
2	Deck surface beneath stormwater sampling point	2,436	288
3	Oily connector joint on pipe on main deck near stern	7,009	456
4	Rusted area of deck surface upgradient from stormwater sampling point	74,700	4,000
5	Hatch located on main deck near stern	ND	---
6	Side of SALM where runoff appears to flow onto the main deck toward the stormwater runoff sampling point	**844,600**	8,800
7	Underside of SALM	**864,000**	---
8	Top of SALM	**826,000**	8,000
9	Rubber coated structure bolted to the underside of the SALM	ND	---
10	Blue painted cover of hatch on central portion of main deck	928	196
11	Oil reservoir near on main deck near stern	395	177
12	Yellow painted winch on main deck near stern	6,895	436
13	Connector on a pipe ram on main deck near stern	10,400	900
14	Overhead rusted pipe that runs along central portion of main deck	ND	---
15	Aluminum duct on main deck near central portion of main deck	1,132	554
16	Oil stained area on windless winch on central portion of main deck	4,249	431
17	Oil stained port on supply line on central portion of main deck	ND	---
18	Surface of DH-1/DH-2 dehumidifier on central portion of main deck	ND	---
19	Floor near drain conduit on central portion of main deck	1,394	343

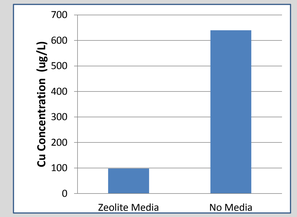
Notes:
mg/kg = milligrams per kilogram
ND = not detected
Copper concentrations were measured using a Thermo Scientific Niton 898XLT x-ray fluorescence analyzer

Field Leaching Test

- Mt. Washington is an off-shore fueling tanker with 100' by 700' surface area. The SALM is 55' by 140' in surface area.
- A simple field-based test was used to confirm the source by applying two gallons of distilled water to the surface area of the potential source area and capturing and analyzing the dissolved copper concentration in the leachate.
- The leachate from the field confirmation test had a dissolved copper concentration of 640 µg/L.

Bench-Scale Column Test

- Zeolites were chosen as a control measure to mitigate copper concentrations before stormwater enters Suisun Bay.
- The zeolite media used was BakerCorp's Z-200 media (impregnated with hexadecyl trimethylammonium chloride)
- Stormwater runoff collected from the SALM of the *Mt. Washington* was poured through a 4 inch column of the modified zeolites and submitted to a laboratory along with the non-treated sample for analysis.
- The resulting analytical data reported an initial dissolved copper concentration of 640 µg/L in the stormwater runoff collected directly from the SALM and a dissolved copper concentration of 98 µg/L in the same runoff after being passed through the modified zeolites in the bench test.
- The filtration media achieved a dissolved copper removal efficiency of greater than 80% in the runoff.



Dissolved Copper Concentrations in Treated and Untreated Stormwater

Summary of Findings

- An innovative use of an XRF field analyzer allowed for quick, cost effective identification of copper sources to stormwater
- The Single Anchor Leg Mooring (SALM) was identified as a significant source of copper in vessel stormwater runoff.
- Field leach testing confirmed that high concentrations of dissolved copper can leach from the SALM.
- Zeolite wattles were tested to be effective in reducing stormwater copper concentrations

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