Life cycle contributions of copper from vessel painting and maintenance activities

Patrick J. Earley[a], Brandon L. Swope[a], Katherine Barbeau[b], Randelle Bundy[b], Janessa A. McDonald[a] & Ignacio Rivera-Duarte[a]

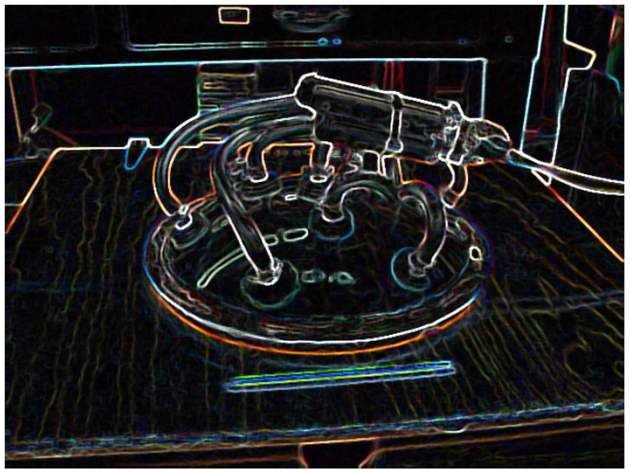
[a] *SPAWAR Systems Center Pacific, San Diego, CA, USA;*

[b] *Scripps Institution of Oceanography/UC San Diego, La Jolla, CA, USA*

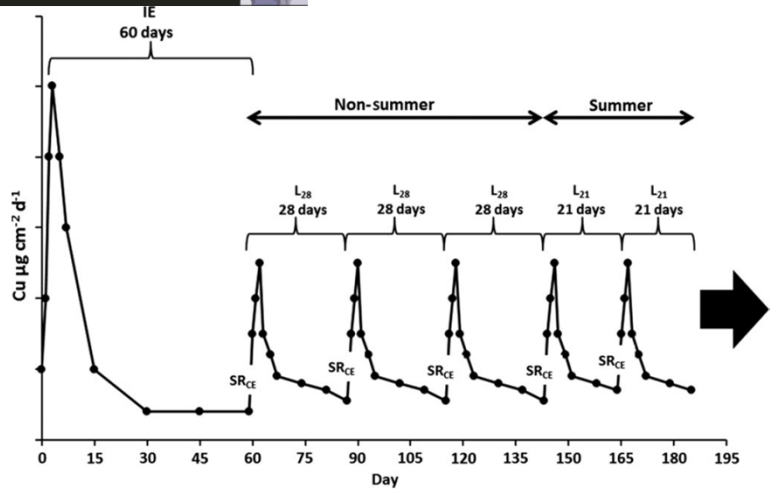
The Journal of Bioadhesion and Biofilm Research,
DOI: 10.1080/08927014.2013.841891

SPAWAR
Systems Center
PACIFIC

Overview



- Exposed Copper antifouling coated panels (Ablative and Epoxy) in Natural environment.
- After 30 days, performed cleaning using (BMP and non-BMP methods).
- Using Navy developed tools, Quantified loading associated with Passive leaching and cleaning activities.
- Measured bioavailibity near paint surface before, during and after cleaning.
- Developed a lifecycle model to quantify annual loading



SPAWAR
Systems Center
PACIFIC

Methods

- In consultation with DPR, 2 Copper Based AF Paints were selected for evaluation.
  - Ablative paint with 38% cupric oxide
  - Epoxy Paint with 65% cupric oxide
  - Coated following industry Standards (2mm dry film thickness)

- Within 48 hours of drying, Panels were exposed at SPAWAR Research Platform located near the mouth of Shelter Island.
  - Triplicate panels, 1 M depth
  - Control (6 panels)
  - Study (6 panels)

SPAWAR
Systems Center
PACIFIC

Methods (cont.)

- Passive Leach Rate measurements by SPAWAR In-Situ Dome Technique.
  - Isolates a set volume of water over the paint surface
  - Aliquots were taken at 0, 15,30 ,45 and 60 min using EPA Clean sampling Techniques
  - Individual samples were analyzed for total and dissolved copper with an ICP/MS.
  - Concentrations were plotted against time and a leach rate is derived from the slope of the line

- Measured throughout the study on Control panels and starting on Day 60 for the study panels.

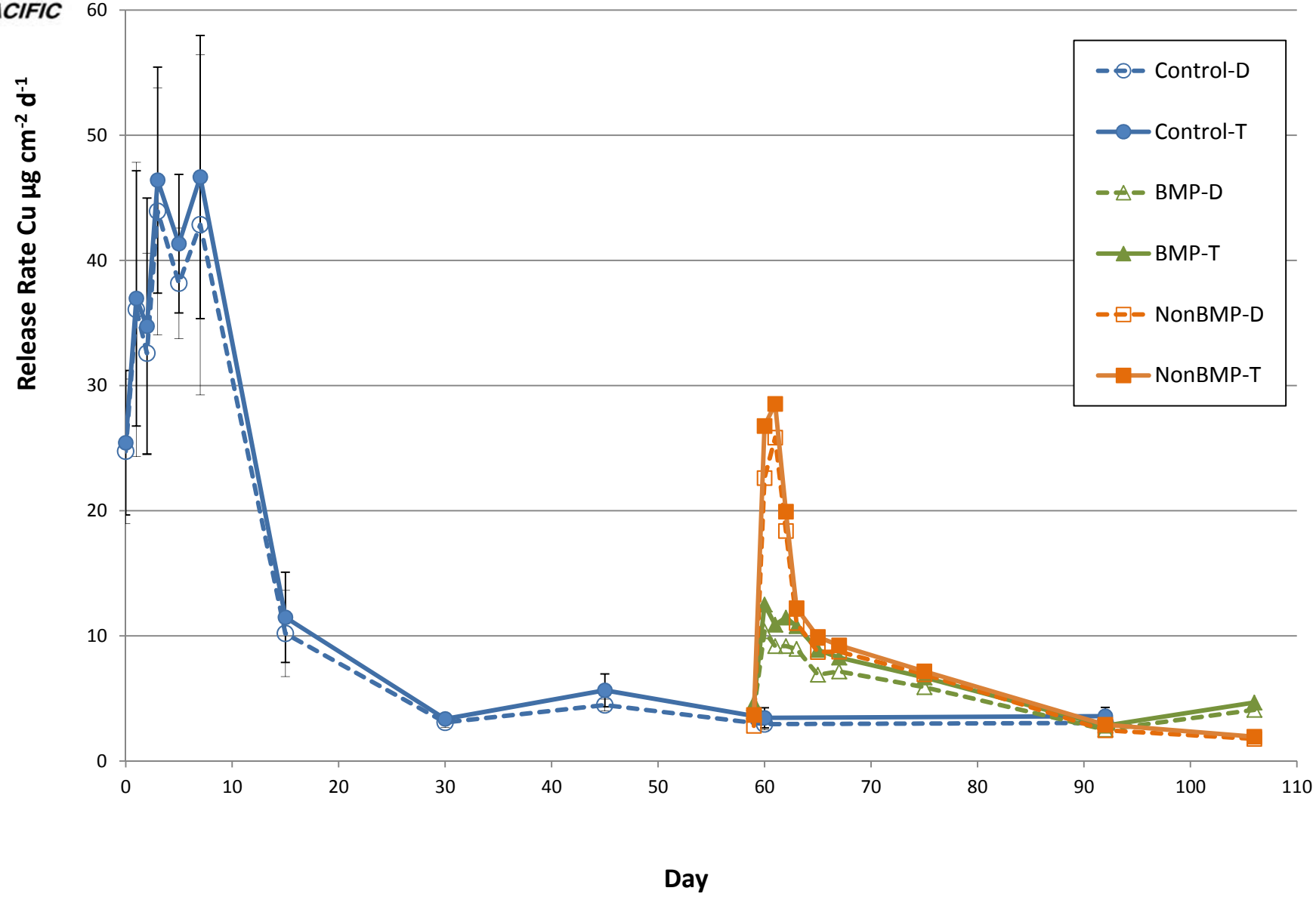
SPAWAR
Systems Center
PACIFIC

Methods (cont.)

- Cleaning Event
  - Study Panels were cleaned with In-Situ Hull sampling device using 2 different BMP methods
    - Soft Pile Carpet
    - Medium Duty Scotch-Brite™ Pad
  - Each panel was cleaned in 3 different locations (totaling 9 samples for each paint and each BMP)
    - Samples were filtered and analyzed for dissolved and particulate loading values
  - Passive Leach Rate Dome measurements were taken 1 hour after cleaning and incrementally for an additional 60 days
  - Additional samples were taken for determination of the free copper ion (Cu2+) on Days 1, during the cleaning event and 24 hours after the cleaning event.

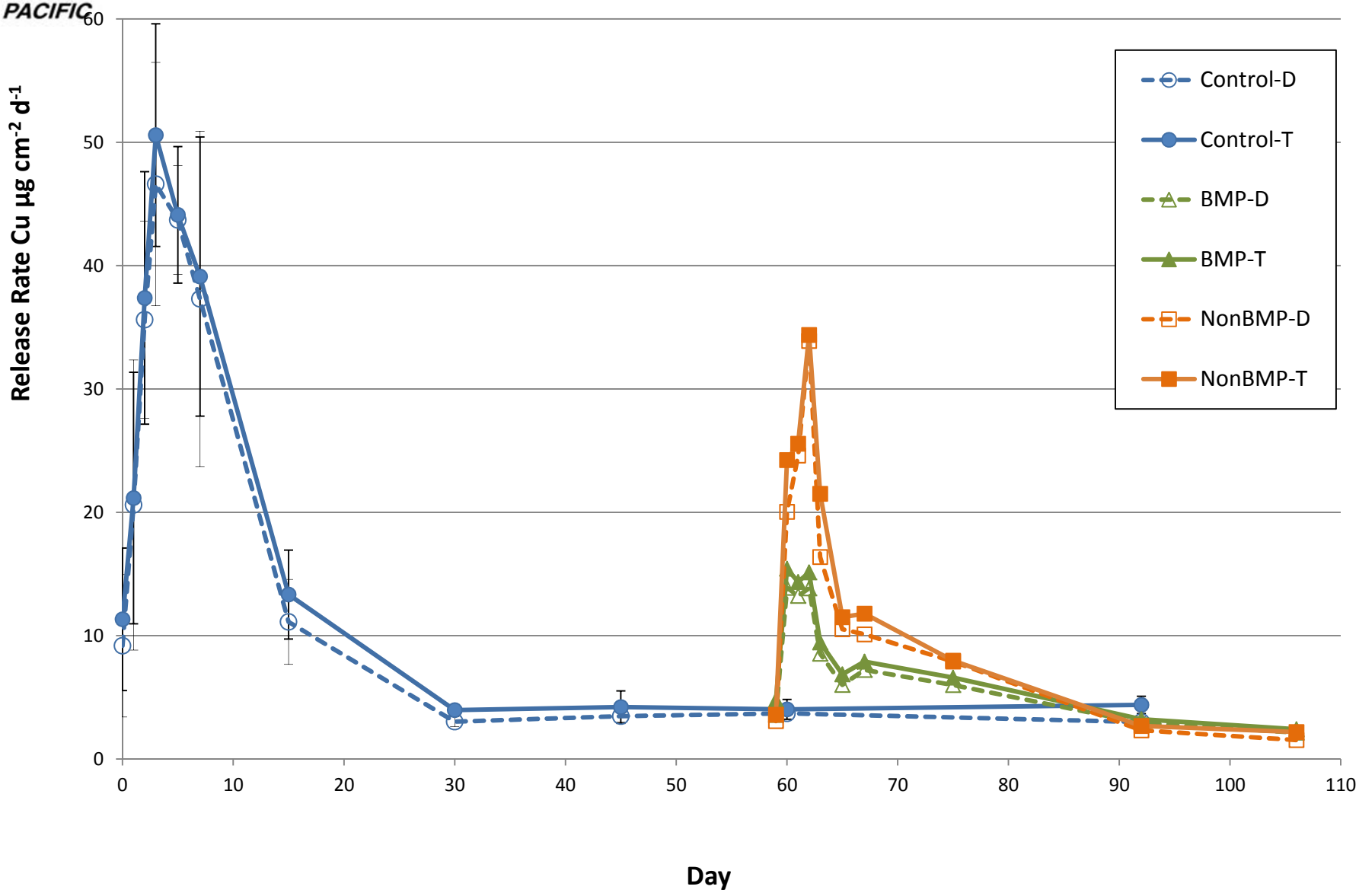
SPAWAR
Systems Center
PACIFIC

Results: Epoxy Coating Release Rates



SPAWAR
Systems Center
PACIFIC

Results: Ablative Coating Release Rates



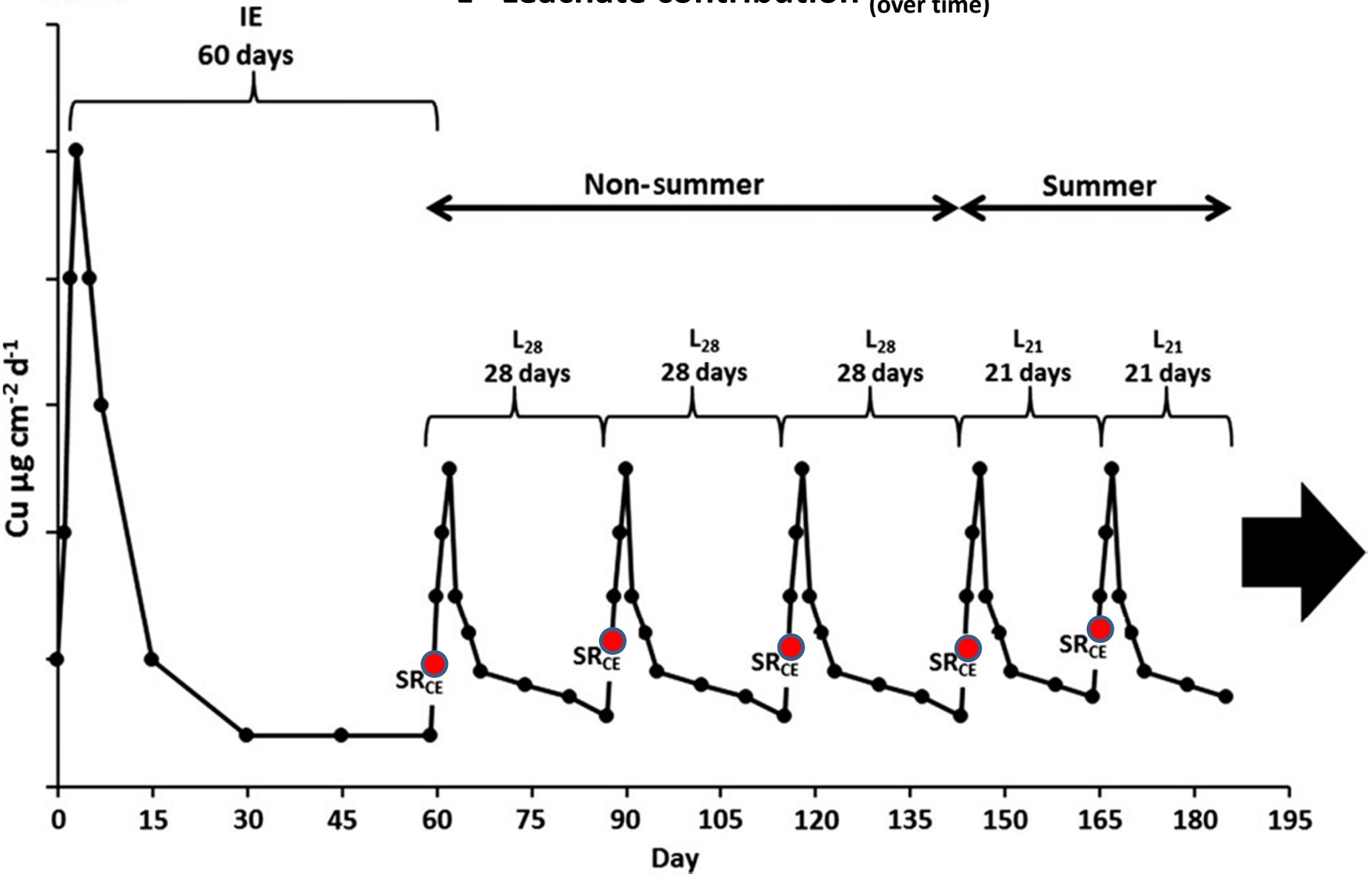
SPAWAR
Systems Center PACIFIC

Lifecycle Model Development

IE= Initial Exposure

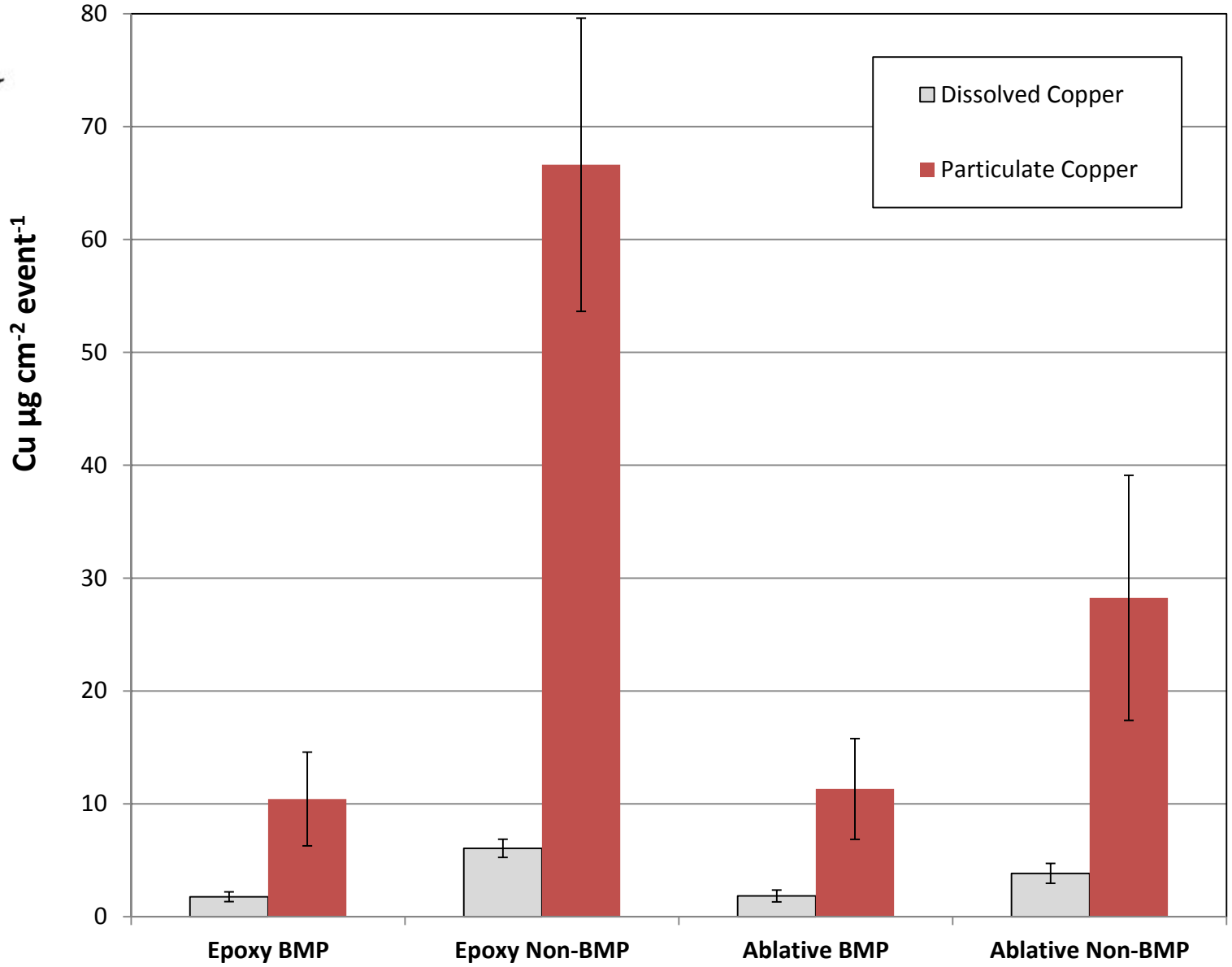
SR_{CE}= Surface Refreshment (cleaning event)

L= Leachate contribution (over time)



SPAWAR Systems Center PACIFIC

Contributions from Cleaning Event



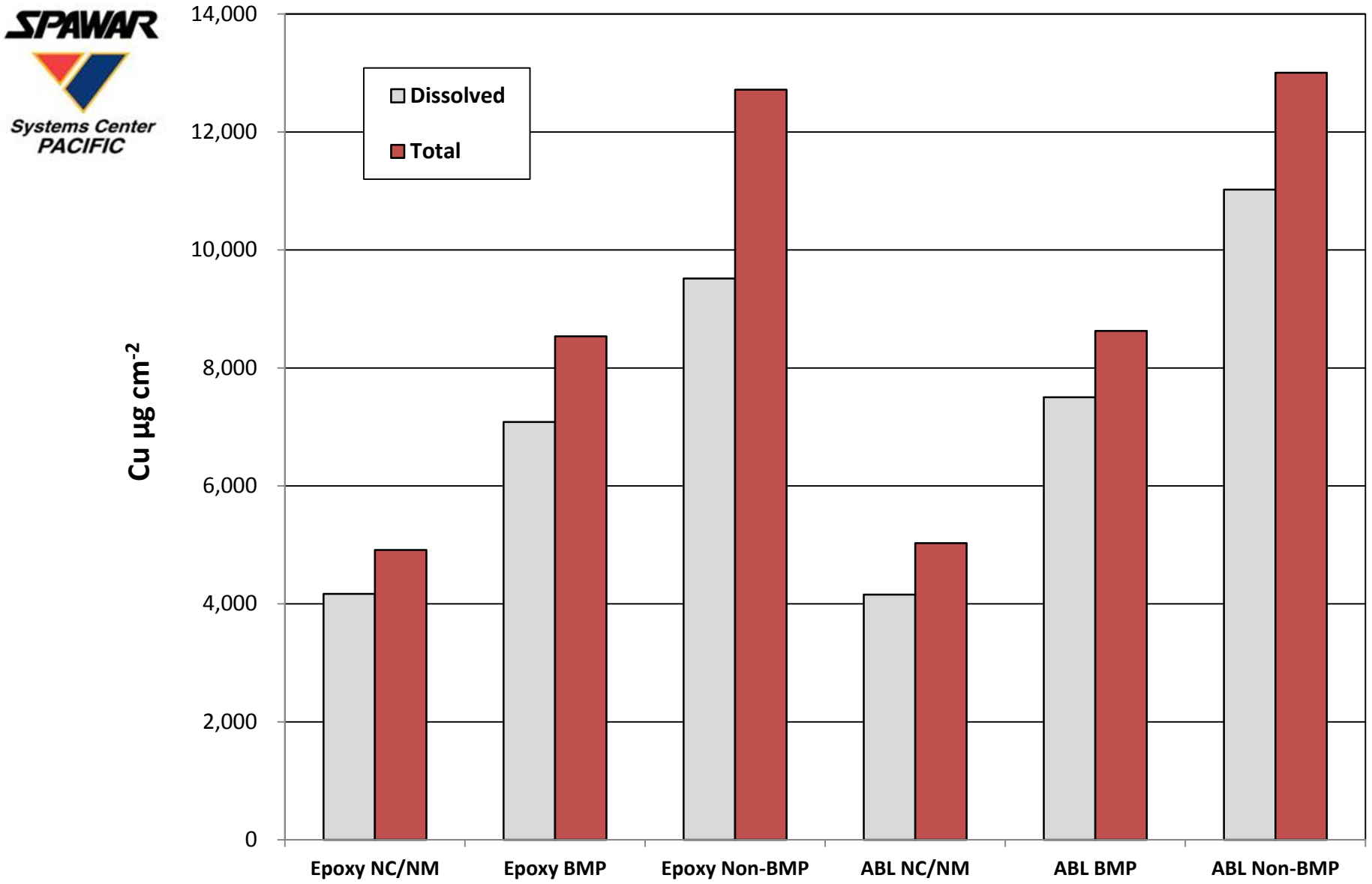
Mass of dissolved and particulate copper (µg cm^{-2} $event^{-1}$) released after the BMPs and non-BMP treatments from the epoxy and ablative coatings.

SPAWAR
Systems Center
PACIFIC

Use of appropriate BMP's

- BMP associated with this level of fouling = Soft pile carpet or soft cloth.

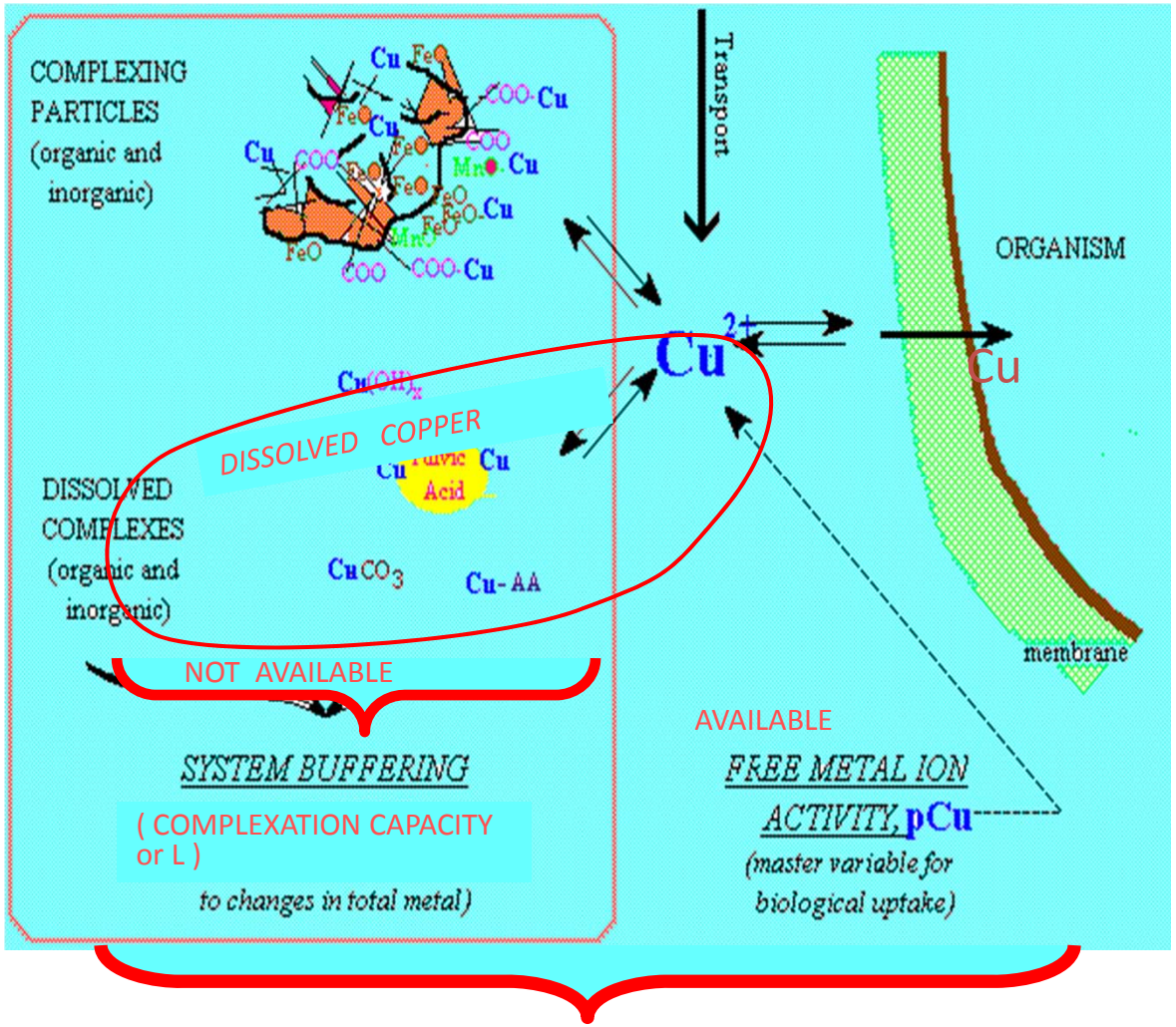
- Use of a Medium Duty Scotch-Brite™ Pad for this level of fouling would result in:
  - Damage to the paint surface
  - Premature coating failure
  - Higher copper loading to the environment



Life cycle loading values for the epoxy and ablative coatings under different cleaning scenarios. NC/NM = no cleaning/no movement. ABL = ablative coating.

Understanding the Free copper ion (Cu^{2+}) Model

- In aquatic systems metal toxicity IS NOT well related to Cu_{total} or $Cu_{dissolved}$.
- Metal toxicity IS better related to the free ion activity ($(Cu^{++})_{aq,}$ pCu).
- Free ion activity is related to both total metal concentration and buffering capacity (CuCC or L).
- High concentrations of organic copper-binding ligands in coastal estuaries have been shown to effectively buffer copper toxicity even at relatively high copper loadings



Buffle, *et al.*, 1990.

SPAWAR
Systems Center
PACIFIC

Cu^{2+} > Ligands

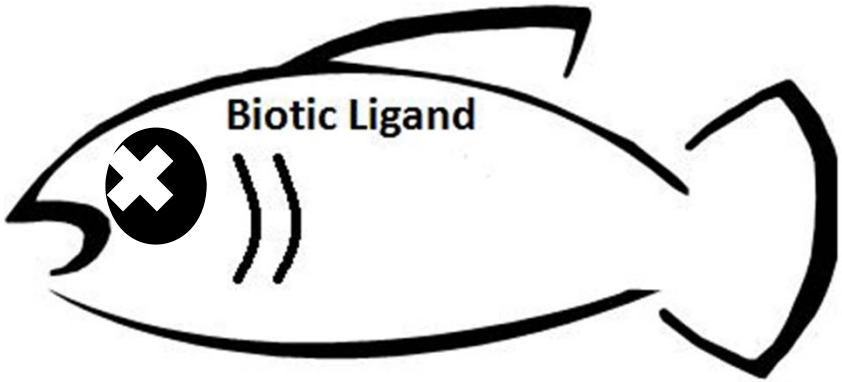
Competing Cations

Na^+

Organic Ligands

DOM

Cu^{2+}



CO_3^-

Inorganic Ligands

SPAWAR
Systems Center
PACIFIC

Cu^{2+} = Ligands

Competing Cations

Na^{+}

DOM

DOM

CO_3^{-}

Organic Ligands

DOM

Cu^{2+}

Cu^{2+}

Cu^{2+}

CO_3^{-}

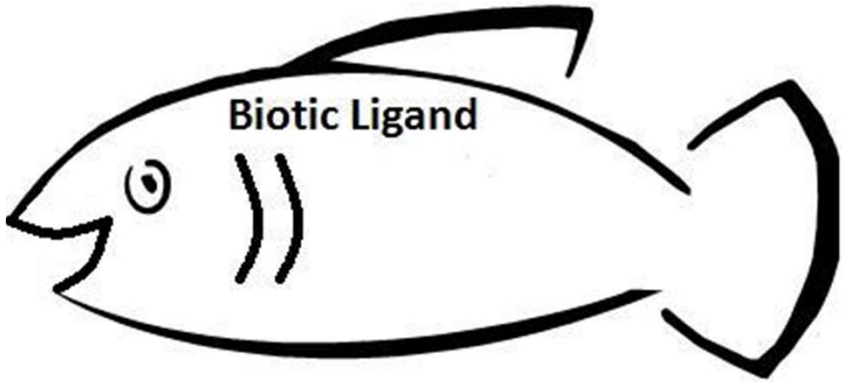
Cu^{2+}

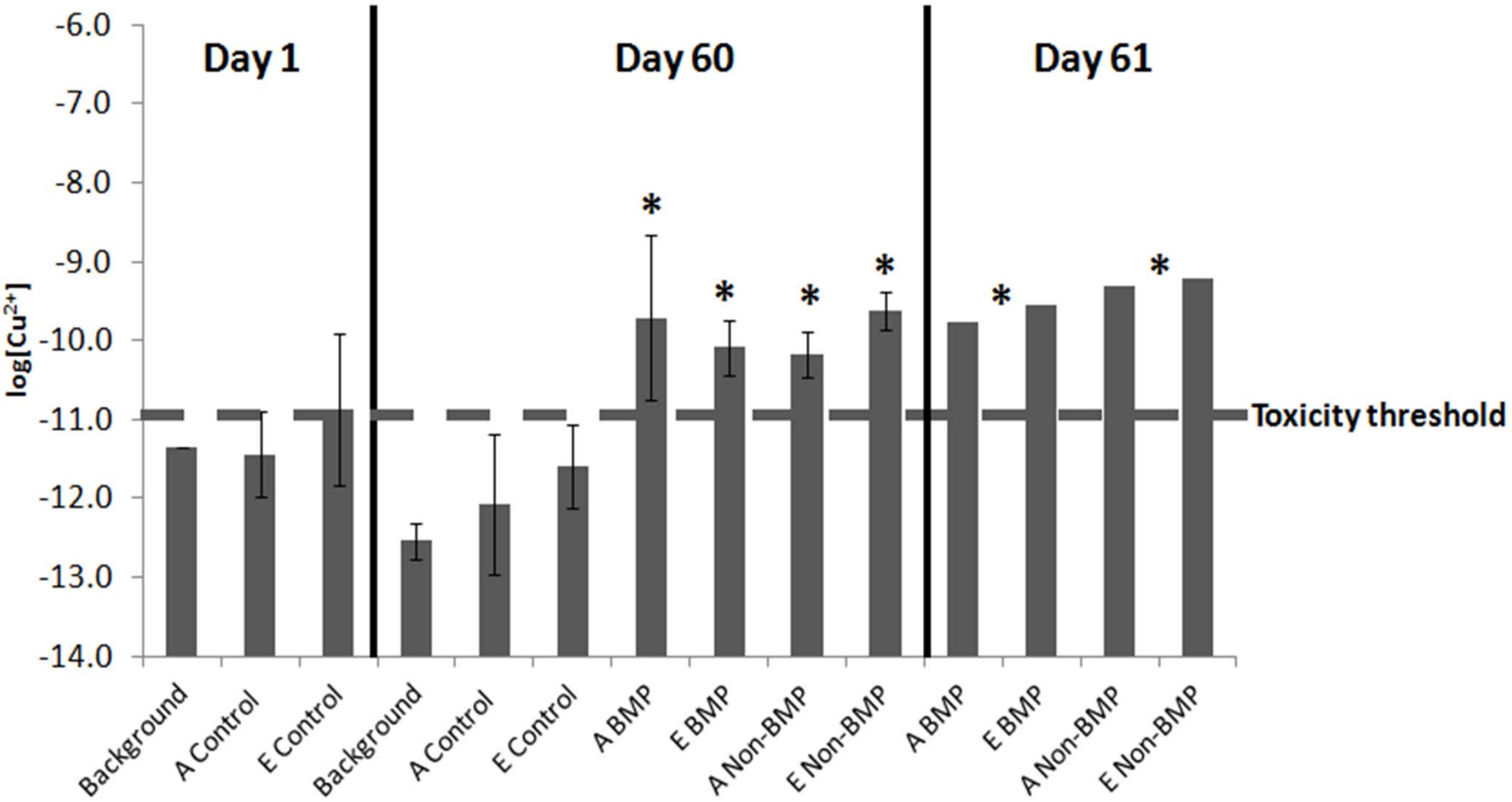
Cu^{2+}

Cu^{2+}

CO_3^{-}

Inorganic Ligands





Average free copper (log[Cu2+]) concentrations on days 1, 60, and 61 in all treatments. The dashed line denotes the toxicity threshold for free copper in the marine environment. The * denotes statistical significance from the ambient for that sampling day at the 95% confidence interval (t-test), except in the case of day 61 when no ambient sample was taken. A denotes ablative coating, and E denotes epoxy coating.

SPAWAR
Systems Center
PACIFIC

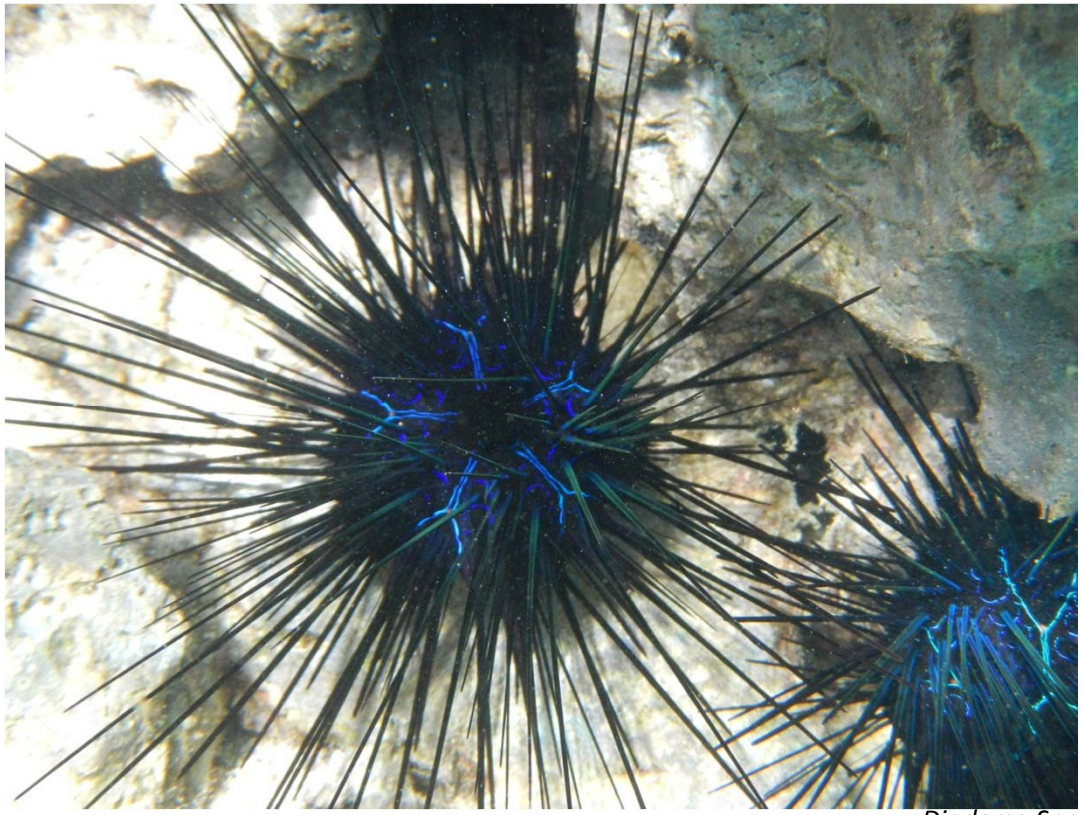
Conclusions

- All of the variables measured are interdependent and require careful consideration before parsing the information out for separate use.

- BMP's are important-
  - The selection and use of BMPs for maintaining AF coatings can have a substantial impact on these loading values. On average, the use of BMPs resulted in one-third less copper loading than non-BMP practices.
  - Improper BMPs can shorten the life of the paint, and increase environmental loading with no benefit.

- Cleaning activities (regardless of method) result in a greater toxicity potential than initial paint exposure despite the lower dissolved copper release rates associated with cleaning vs Initial Exposure.

Questions?



Diadema Spp

Acknowledgements

This work was conducted under requirements established by The California Department of Pesticide Regulation in conjunction with Nan Singhasemanon and funded by The American Coatings Association. The authors wish to acknowledge the efforts of Jeff Kagan, Sara Melvin, and Marissa Brand of SPAWAR Systems Center Pacific and Adam Darer of Scripps Institution of Oceanography for their support during peak sampling activities throughout the study as well as Bryan Blain from San Diego State University Foundation for his assistance in equipment configuration and vigilance over the test equipment during the experiment. The laboratory of Lihini Aluwihare at Scripps Institution of Oceanography is acknowledged for the DOC measurements. Mention of any company or product does not constitute eendorsement by SPAWAR Systems Center Pacific, The Department of the Navy, or Scripps Institution of Oceanography.