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Release and Detection of Nanosized Copper from a Commercial Antifouling Paint

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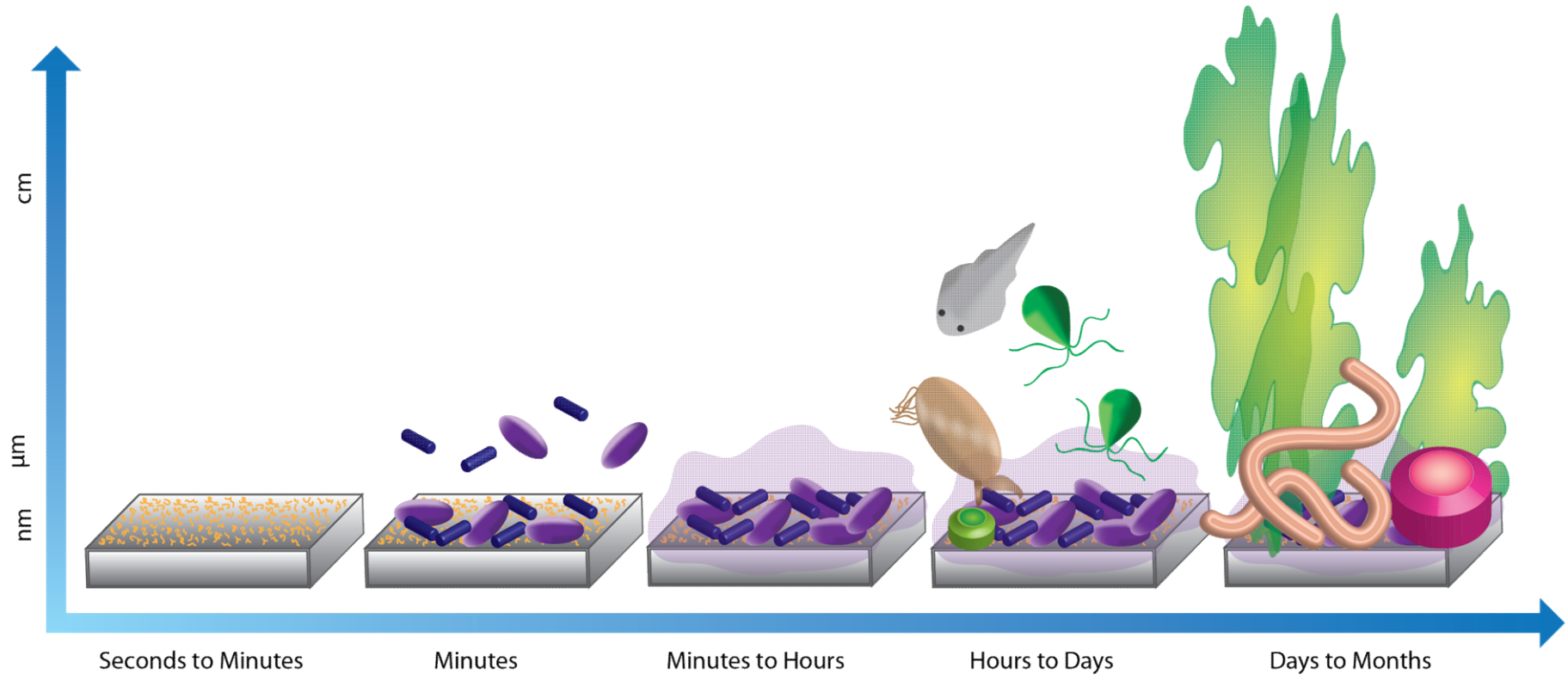
Biofouling

- The accumulation of organisms (micro and macro) on surfaces submerged in water.
- Increases hydrodynamic drag; conceals structural defects
- Reduces speed, fuel economy, and stability of vessels.
- Very costly!
  - E.g., It costs US Navy ~$1 billion annually in extra fuel costs and cleaning

Valkirs *et al.* Marine Poll Bull. 2003, 46(6): 763-779
Schiff *et al*. Marine Poll Bull 2004, 48(3-4): 371-377
http://www.navy.mil/submit/display.asp?story_id=45984

Biofouling



Source: http://amazingbiotech.blogspot.com/2014/04/bio-fouling.html

Biofouling

Antifouling

- *Chemical*: Toxic (e.g. copper-based antifouling paints) and non-toxic chemicals (e.g. non-stick silicone coatings).

- *Biological*: Low-toxicity microbial enzymes and/or metabolites that prevent fouling; such as isomerase, oxidoreductases, transferases, hydrolase, and lyase.

- *Physical or mechanical*: E.g. electrolysis, and hull surface modification, robotic hull grooming (Hull BUG) etc.

Shan *et al*. Chinese Sci Bull. 2011, 56(7): 598-612
Kristensen *et al*. Biotechnol Adv. 2008, 26(5): 471-481
Dobretsov *et al*. Mar Biotechnol. 2007, 9(3):388–397
Asuri *et al*. Small, 2007, 3(1): 50–53

Antifouling

- Biocide-containing (antifouling) paints are often employed to prevent fouling
  - Over **US$ 5.7 billion** is spent annually to prevent and control marine biofouling

- Common biocides include copper (mostly as Cu_2O), and zinc. Biocides can be organic or inorganic compounds.

Valkirs *et al*. Marine Poll Bull. 2003, 46(6): 763-779
Schiff *et al*. Marine Poll Bull 2004, 48(3-4): 371-377
http://www.navy.mil/submit/display.asp?story_id=45984
http://floatways.com/398/ultimate-detailed-antifouling-boat-bottom-paint-guide/

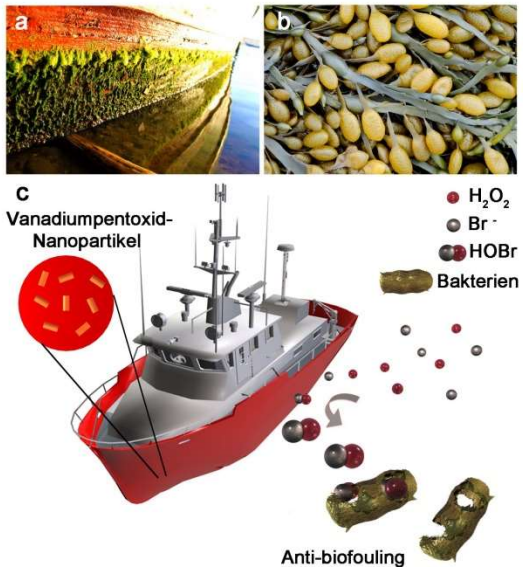
Antifouling

Antifouling paints release biocides directly into waters, which may affect non-target organisms

- VLCC "supertankers" alone release up to 48,000 L of biocides into seawaters annually[1]
- Sediment quality surveys around the US routinely find high [Cu] in marinas and harbors (above federal and state limits)[2]
- Washington State passed a law which may phase out copper-based antifouling coatings on recreational vessels from 2018[3]
- The Unified Port of San Diego is implementing a Cu Reduction/TMDL Program[4]

1. Buskens *et al*. J Coat Technol Res 2013, 10 (1): 29-36
2. Schiff *et al*. Marine Poll Bull 2004, 48(3-4): 371-377
3. http://apps.leg.wa.gov/documents/billdocs/2011-12/Pdf/Bills/Senate%20Passed%20Legislature/5436-S.PL.pdf
4. http://www.waterboards.ca.gov/rwqcb9/water_issues/programs/watershed/souwatershed.shtml

Nano-antifouling



Available Colors:

- White - 4510
- Black - 4505
- Bright Blue - 4502
- Bright Green - 4503

Due to computer monitor color calibration differences, color swatches may not accurately represent the actual paint color.

Overview | Tech Specs | Ways To Buy | Related Products

Copper-Free Nano-Based Technology – 4500 Series

A copper and solvent-free (CSF) ablative, this self-polishing antifoulant is an enhanced, nano-based technology copolymer, biocide release mechanism. Prevents coating buildup and reacts with UV light. Mission Bay may be used on aluminum hulls without the use of a traditional barrier coat system.

- Water-Based Bottom Paint
- Safest, environmentally-friendly antifouling paint on the market
- Over 80% lower VOC's than solvent-based
- Completely eliminates the leaching of copper compounds into the environment
- Ablative and self-polishing
- No barrier coat needed over most antifouling paints
- Ideal for all types of craft – fiberglass to aluminum
- Helps prevent electrolysis
- Five brilliant colors
- No mud cracking

http://phys.org/news/2012-07-coatings-bactericidal-agent-nanoparticles-combat.html
http://www.seahawkpaints.com/product/mission-bay-csf/

Toxicity: Size matters

- Toxicity of biocides depends on their chemical state (Cu, Zn) and physical state (free ions, complexed ions, nanosized or bulk particles).

- Recent studies suggest that toxicity of copper depends a lot on its physicochemical state.[1-5]

- Most existing biocide release studies determined total and/or "dissolved Cu" (0.45 µm filtrate).

1. Shi *et al*. Environ Pollut 2011, 159:1277-1282
2. Thit *et al*. Toxicity in Vitro 2013, 27:1596-1601
3. Bielmyer *et al*. Environ Sci Technol 2014, 48:13443-13450
4. Siddiqui *et al*. Aquatic Toxicology 2015, 160:205-215
5. Torres-Duarte et al. Nanotoxicology 2016, 10: 671-679

Research Objectives

a. To determine if there are nano-sized biocides in conventional antifouling paints

b. To develop a simple method for assessing release of antifouling paint biocides

c. To estimate release of different forms of biocides (ionic, nano, bulk) from paint matrix

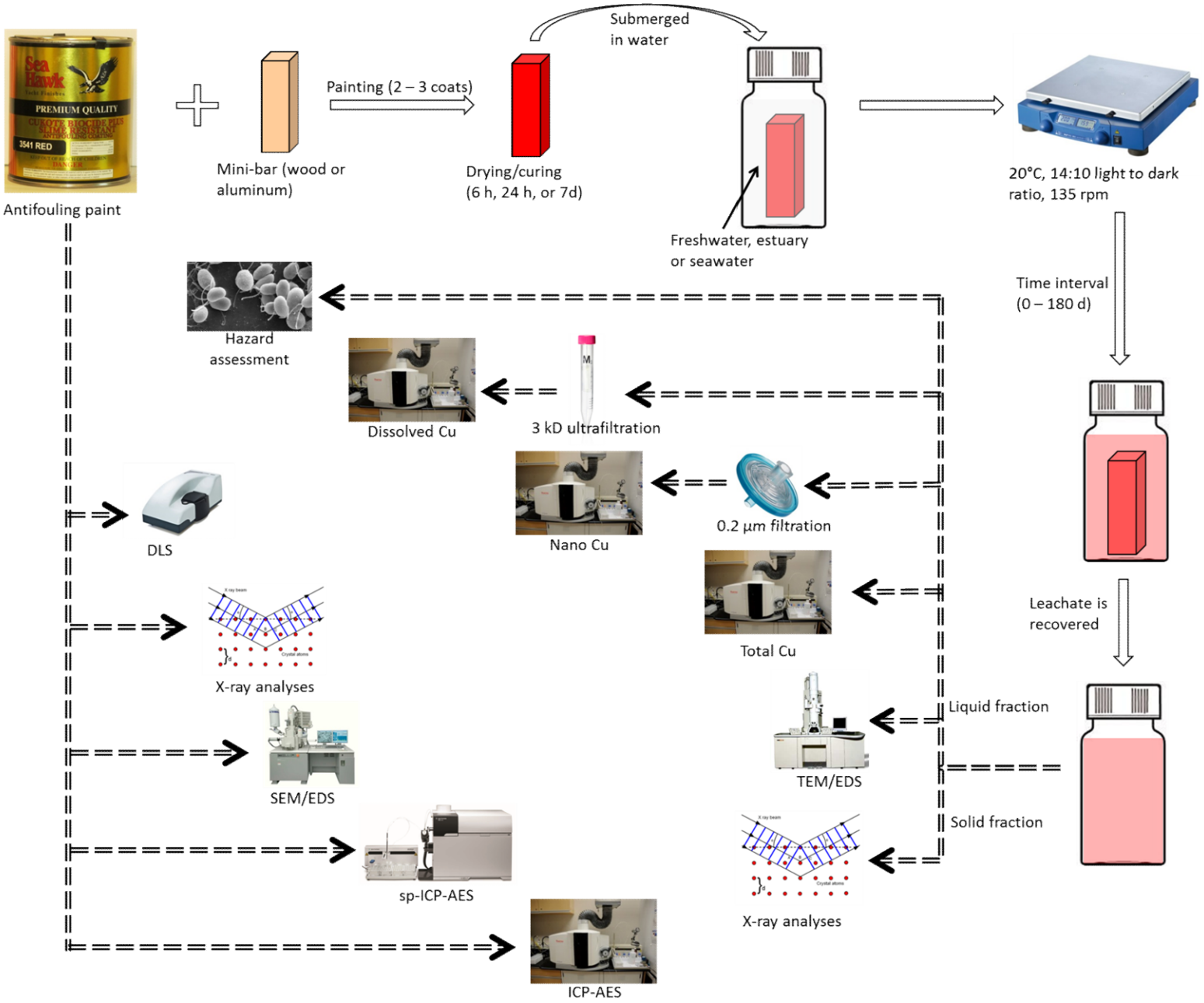
d. To assess the effect of leachate on aquatic organisms

Materials & Methods

CHEMICAL DESCRIPTION: CUPROUS OXIDE PAINT
FORMULA: 6600 SERIES RED, BLACK, BLUE

SECTION TWO – HAZARDOUS INGREDIENTS

CHEMICAL	%	CAS NO.	TLV	PEL	SARA 302	SARA 313	CERCLA RQ#
CUPROUS OXIDE	47.57%	1317-39-1	.1MG/M3	N/A	N	N	N
AROMATIC HYDROCARBON	12.8–1.42%	6472-95-6	100ppm	100ppm	N	Y	Y
POLYMER	3.5-3.8%	60381-61-5	N/A	N/A	N	N	N
ROSIN	6.9-7.7%	8050-09-7	N/A	N/A	N	N	N
RED IRON OXIDE	0-8.3%	1309-37-1	15mg/m3	5mg/m3	N	N	N
BLACK IRON OXIDE	0-8.3%	1317-61-9	15mg/m3	5mg/m3	N	N	N
MAGNESIUM SILICATE	7.3-8.3%	14807-96-6	N/A	20mg/m3	N	N	N
ZINC OXIDE	5.4%	1314-13-2	5mg/m3	5mg/m3	N	N	N
N-CYCLOPROPYL-N-(DIMETHYLENE)-6-(METHYLTHIO) 1, 3, 5-TRIAZINE	2.02%	28159-98-0	N/A	N/A	N	N	N



A summary of the methodology of this study

Adeleye *et al*. Water Research 2016, 102: 374-382

Fwd: nano paint Inbox x

Robert Miller <rjmiller1@gmail.com>
to me

FYI

---------- Forwarded message ----------
From: Kim Ibson <kim@seahawkpaints.com>
Date: Tue, Dec 24, 2013 at 5:25 AM
Subject: RE: nano paint
To: Robert Miller <rjmiller1@gmail.com>

No we don't have nano particles in our paint. Sorry.

Kim

-----Original Message-----
From: Robert Miller [mailto:rjmiller1@gmail.com]
Sent: Monday, December 23, 2013 [illegible] PM
To: [illegible]
Subject: nano paint

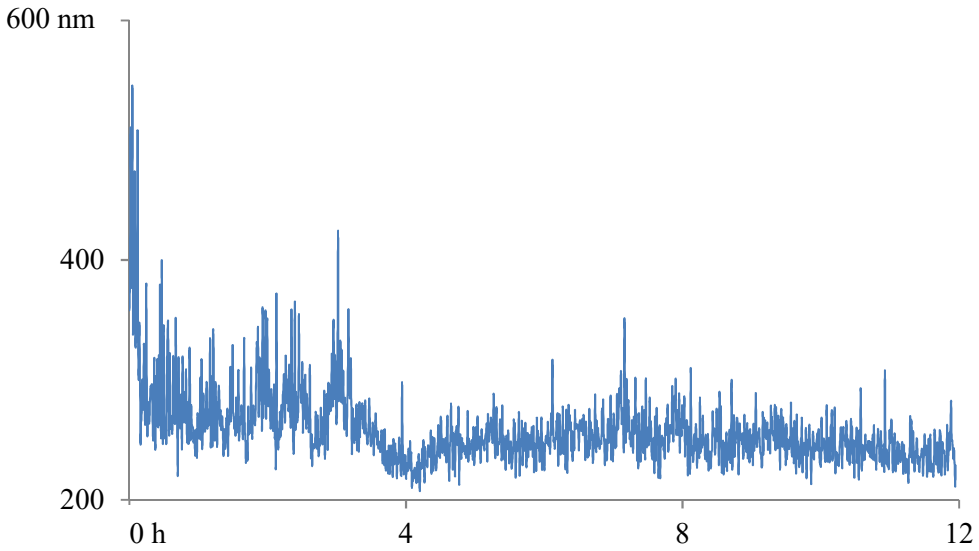
Hi,
I was wondering if you sell an antifouling paint with copper nanoparticles in it. I have heard that the copper will last longer in that form.
thank you,
Bob Miller

--
Robert J. Miller
Marine Science Institute
University of California Santa Barbara
Santa Barbara CA 93106-6150
(805) 893-6174

No we don’t have nano particles in our paint. Sorry.

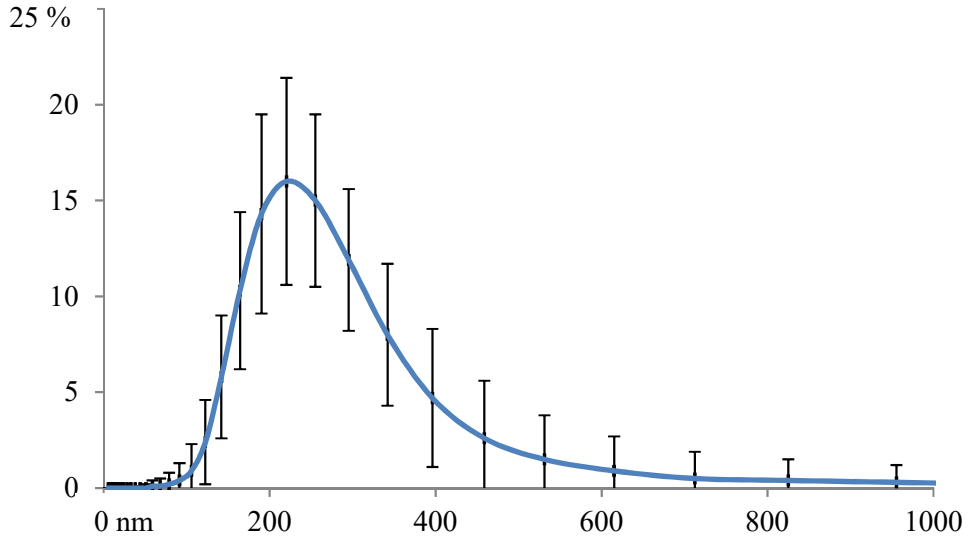
Average size of paint particles over 12 h

Hydrodynamic diameter



Size distribution of paint particles over 12 h

Intensity



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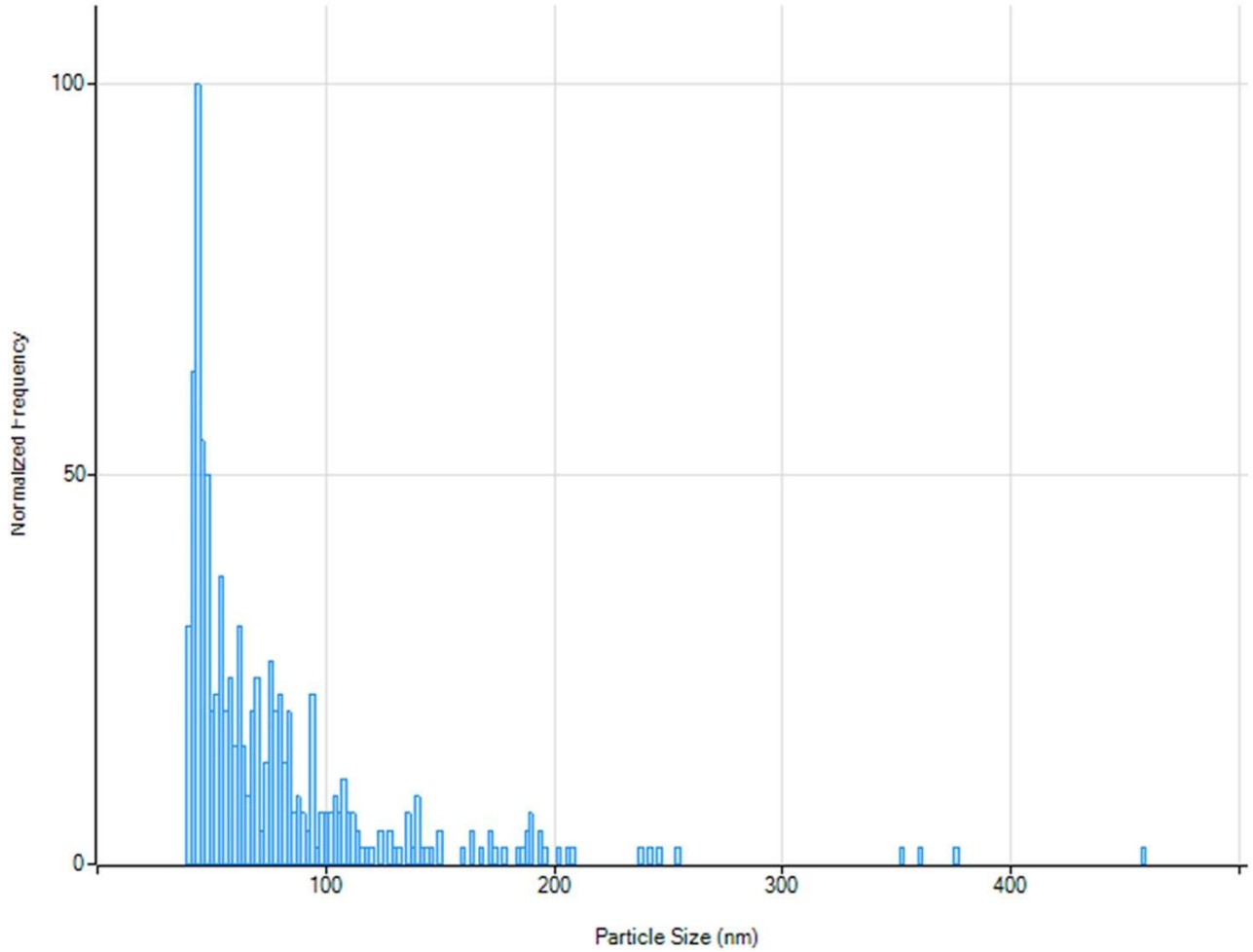
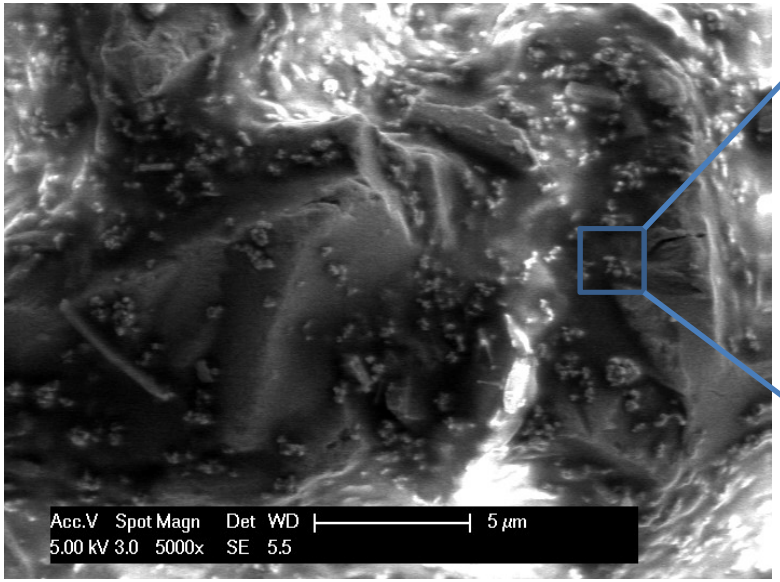
sp-ICP-MS

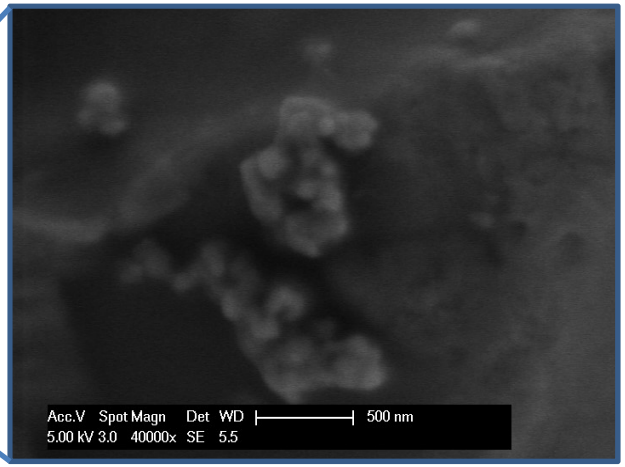


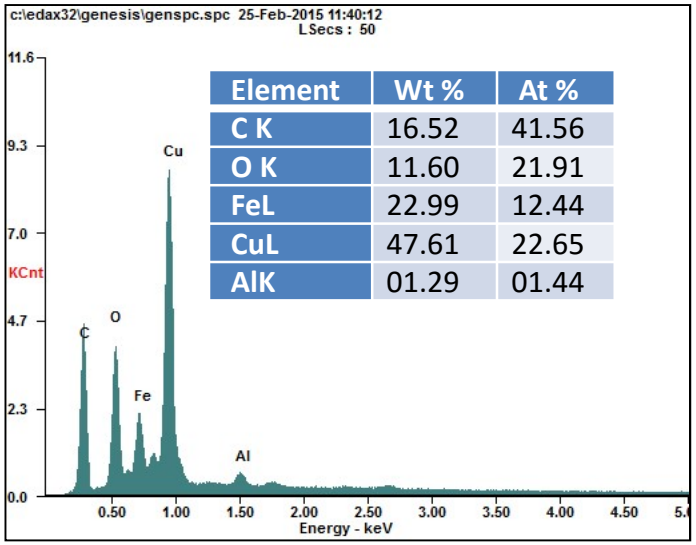
Particle size distribution of Cu_2O (as Cu) present in antifouling paint obtained from single particle-ICP-MS

Adeleye *et al*. Water Research 2016, 102: 374-382

SEM-EDS

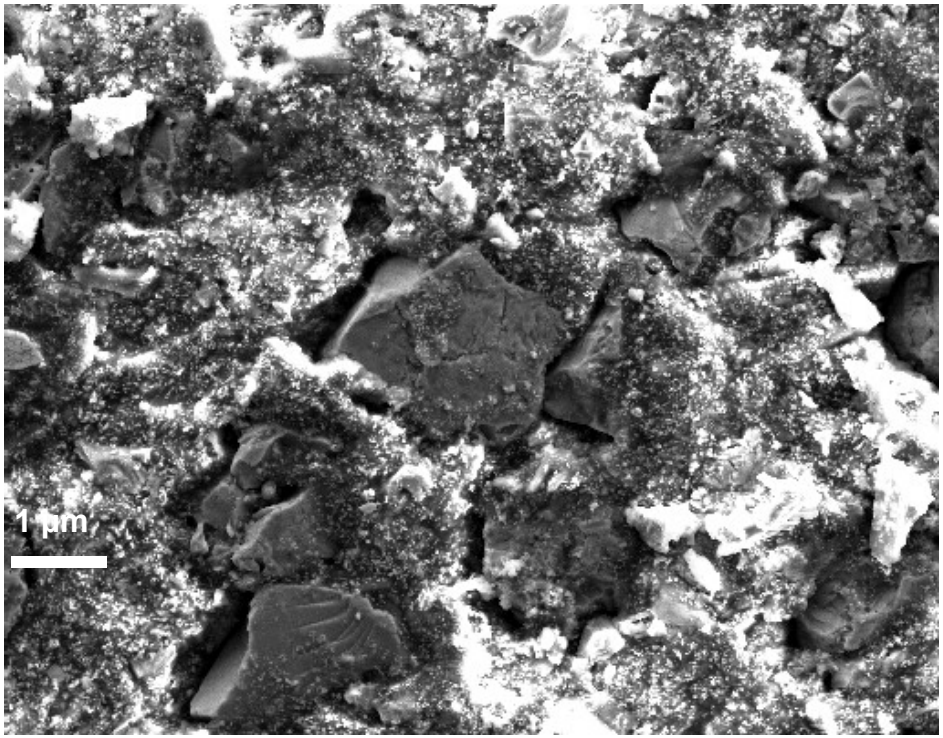




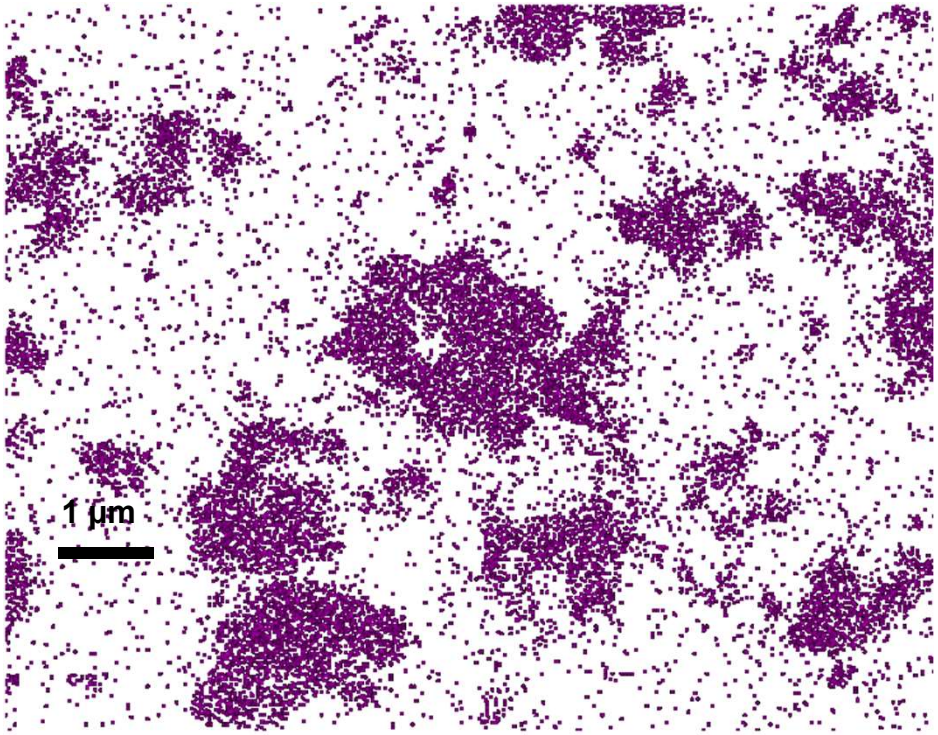


Element	Wt %	At %
C K	16.52	41.56
O K	11.60	21.91
FeL	22.99	12.44
CuL	47.61	22.65
AlK	01.29	01.44

SEM-EDS



Scanning electron microscopy



EDS hypermap for Cu

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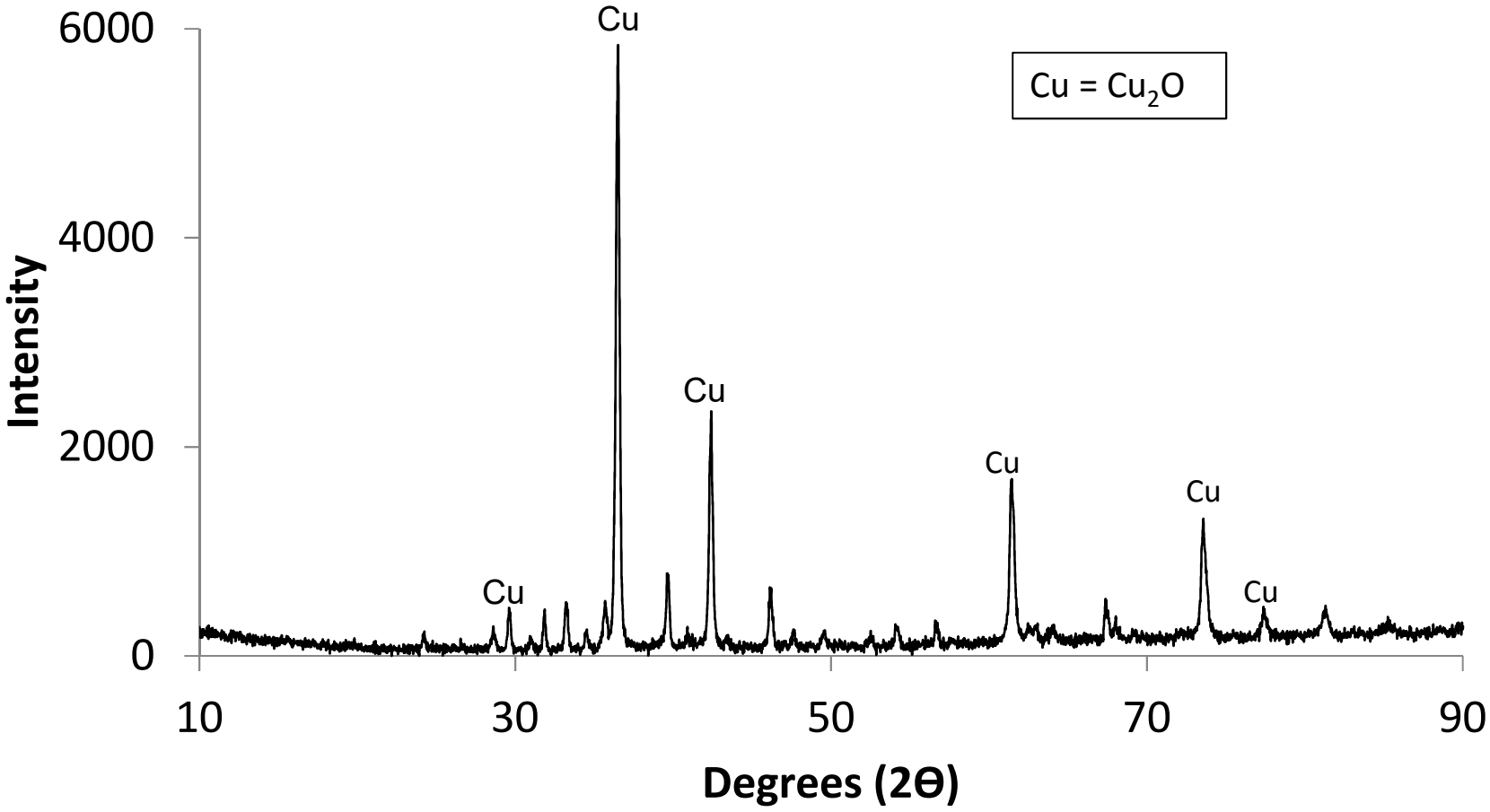
Paint characterization



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Comparison of Release Rate

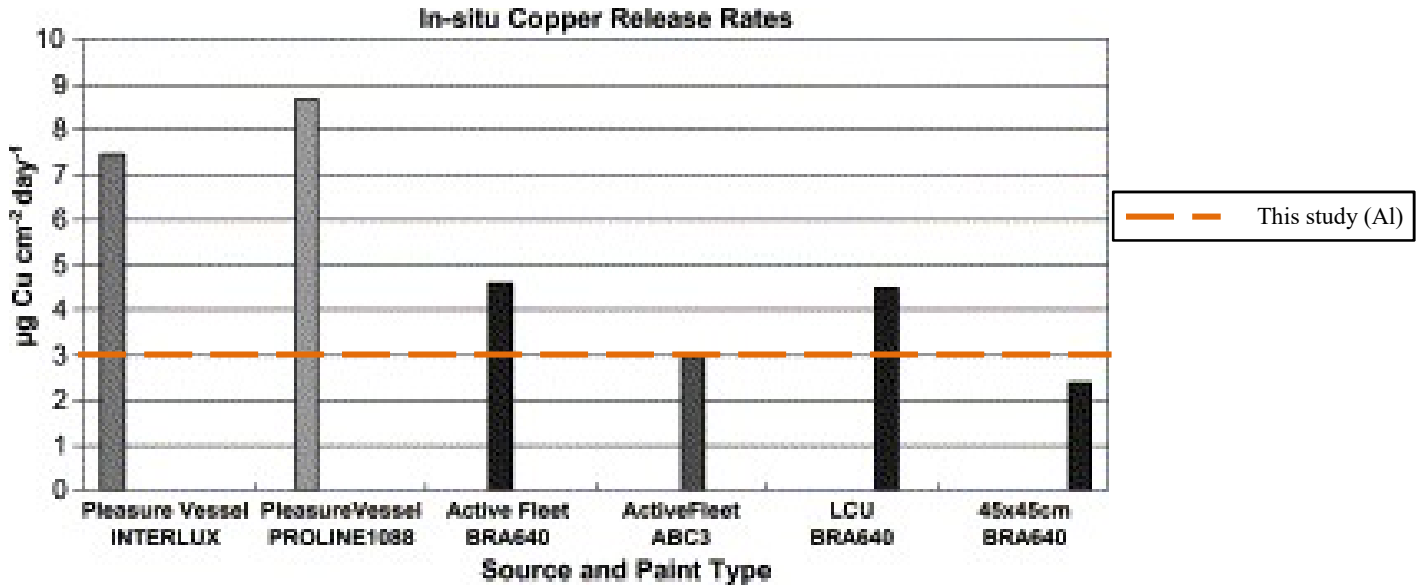
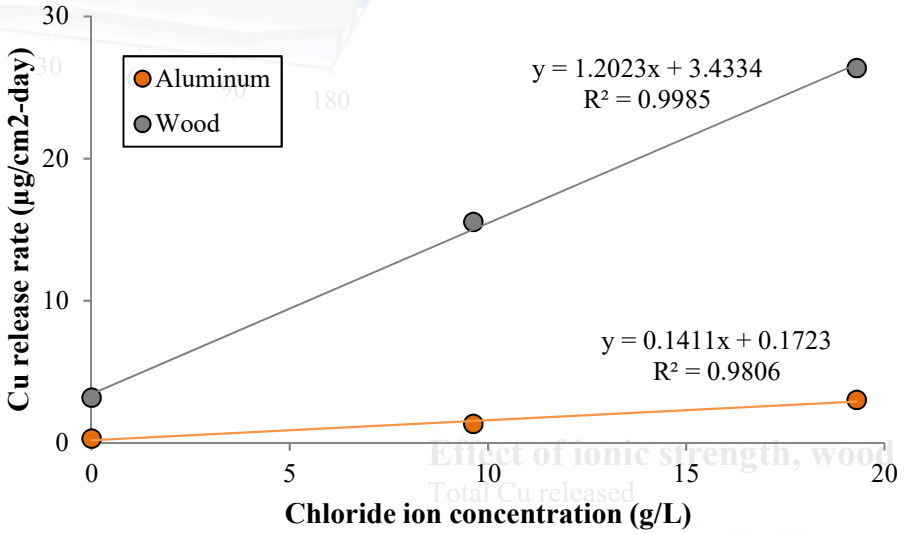


Fig. 14 Mean in situ release rates for pleasure craft, active Navy vessels, and stationary 45 cm × 45 cm panels.

Valkirs et al (2003), Marine Pollution Bulletin, Volume 46, Issue 6, 2003, 763–779



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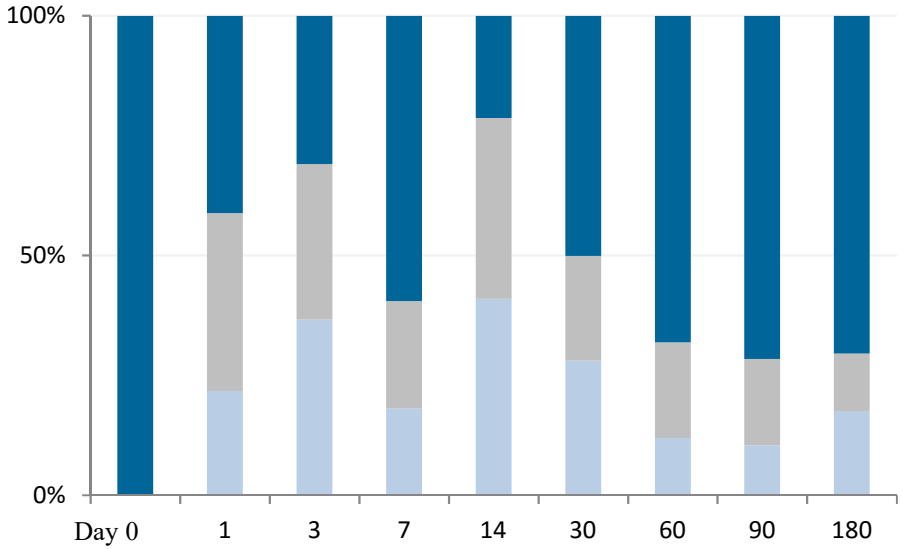
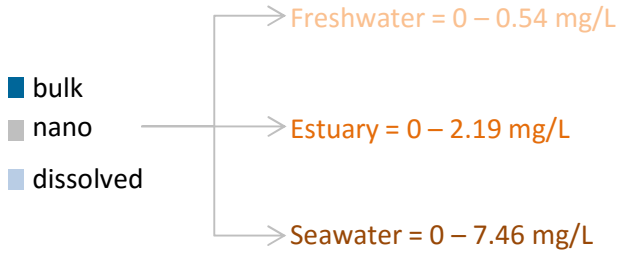
Size fractions of Cu released into freshwater

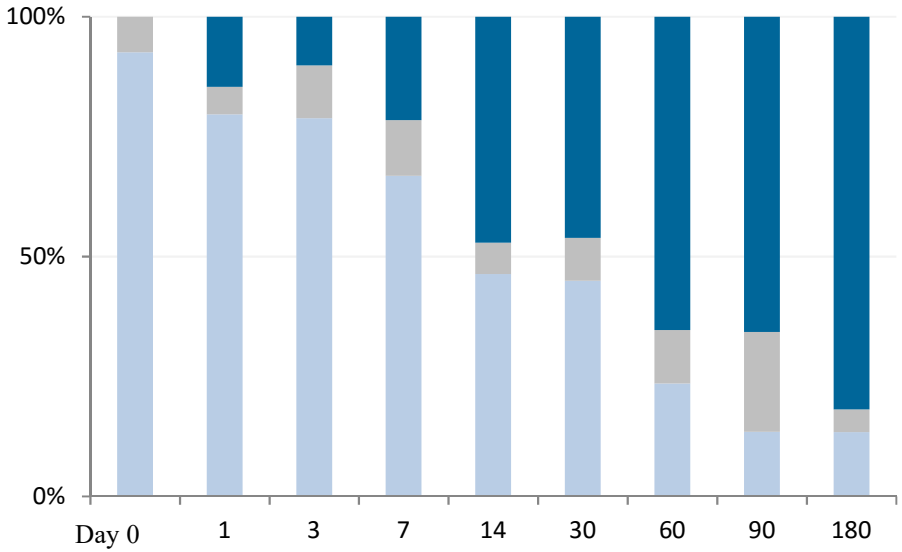
Fraction of Cu released





Size fractions of Cu released into seawater

Fraction of Cu released



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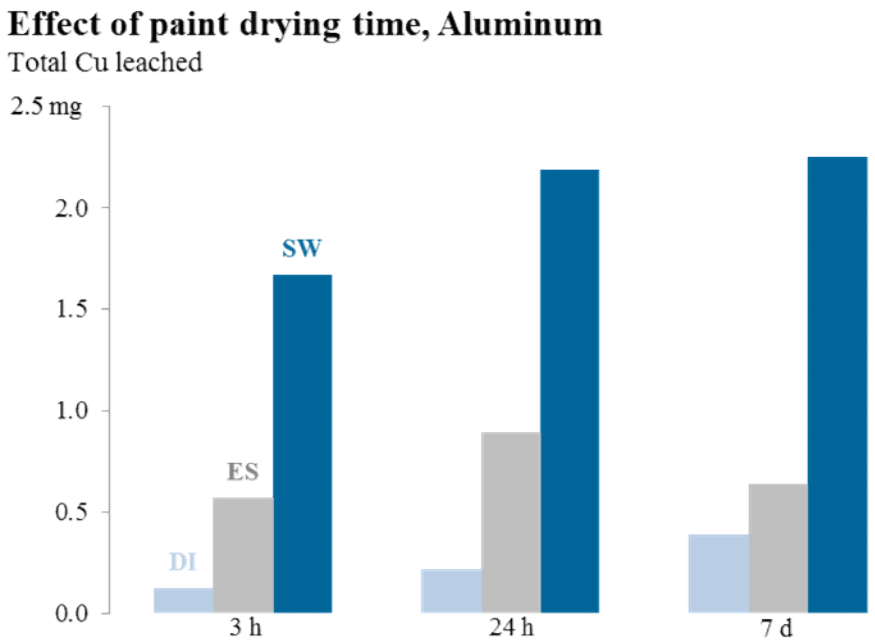

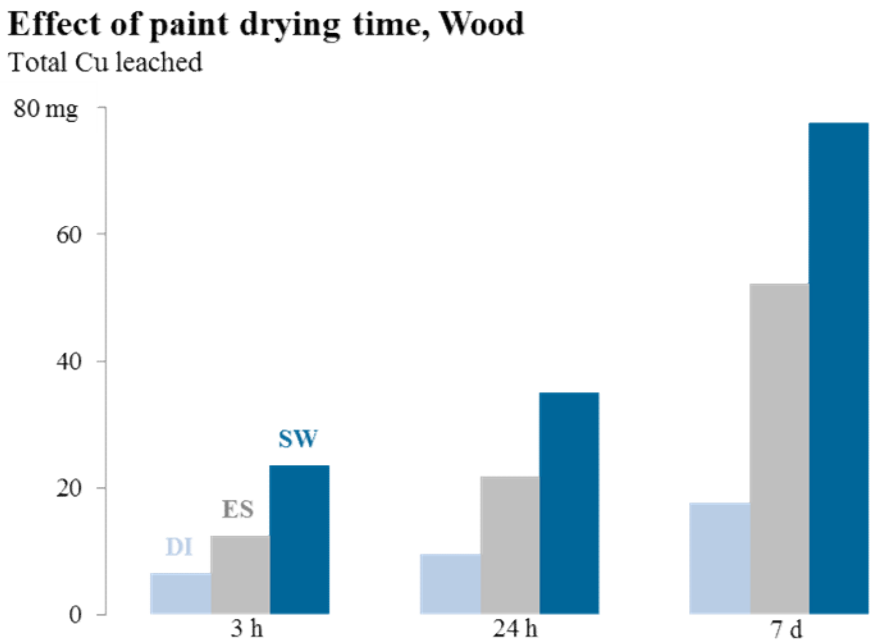

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Particle Transformation

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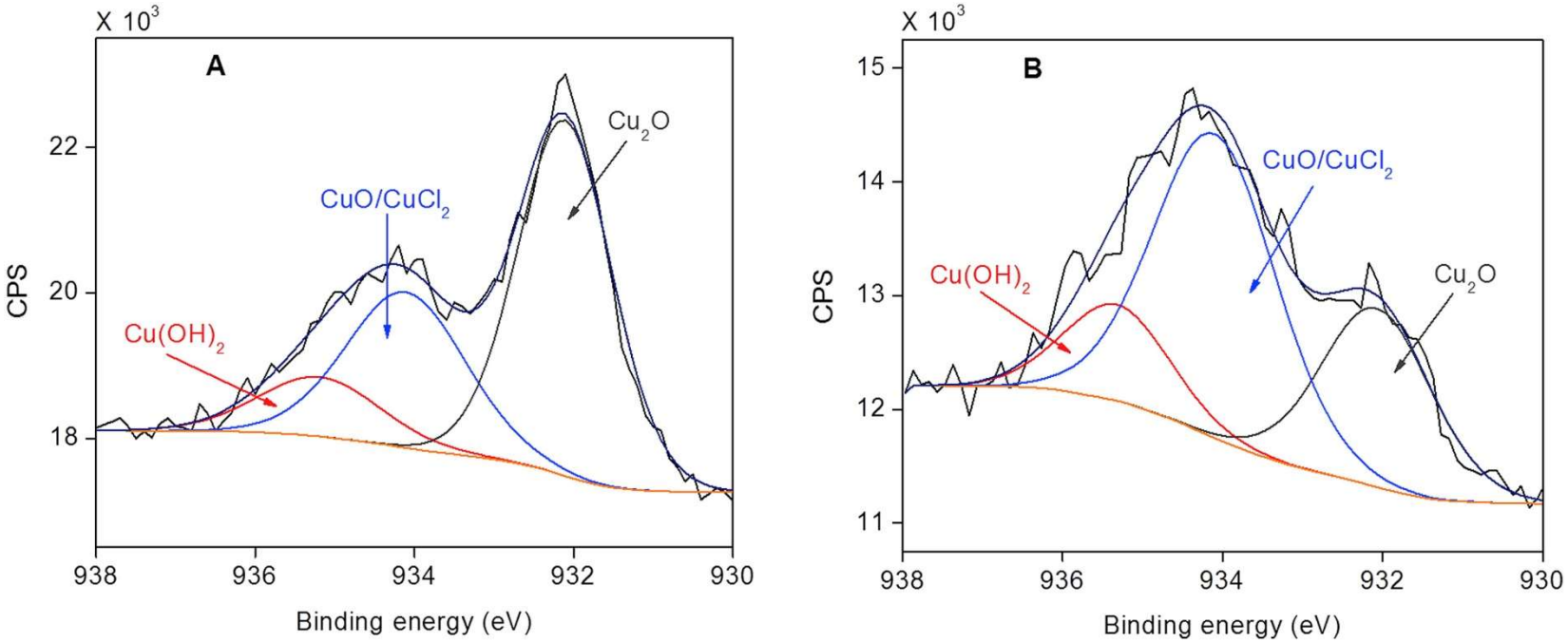

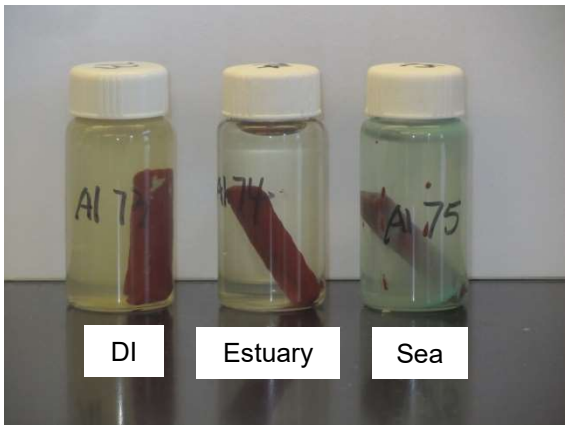

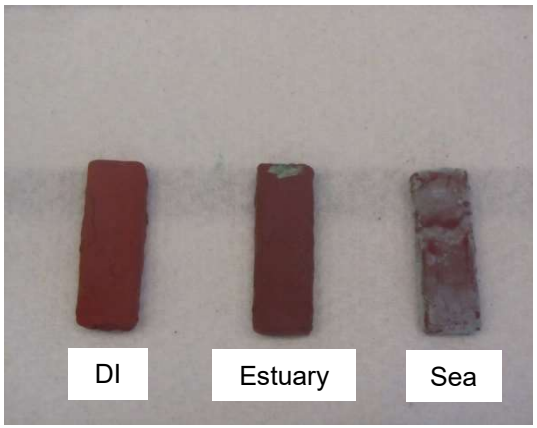

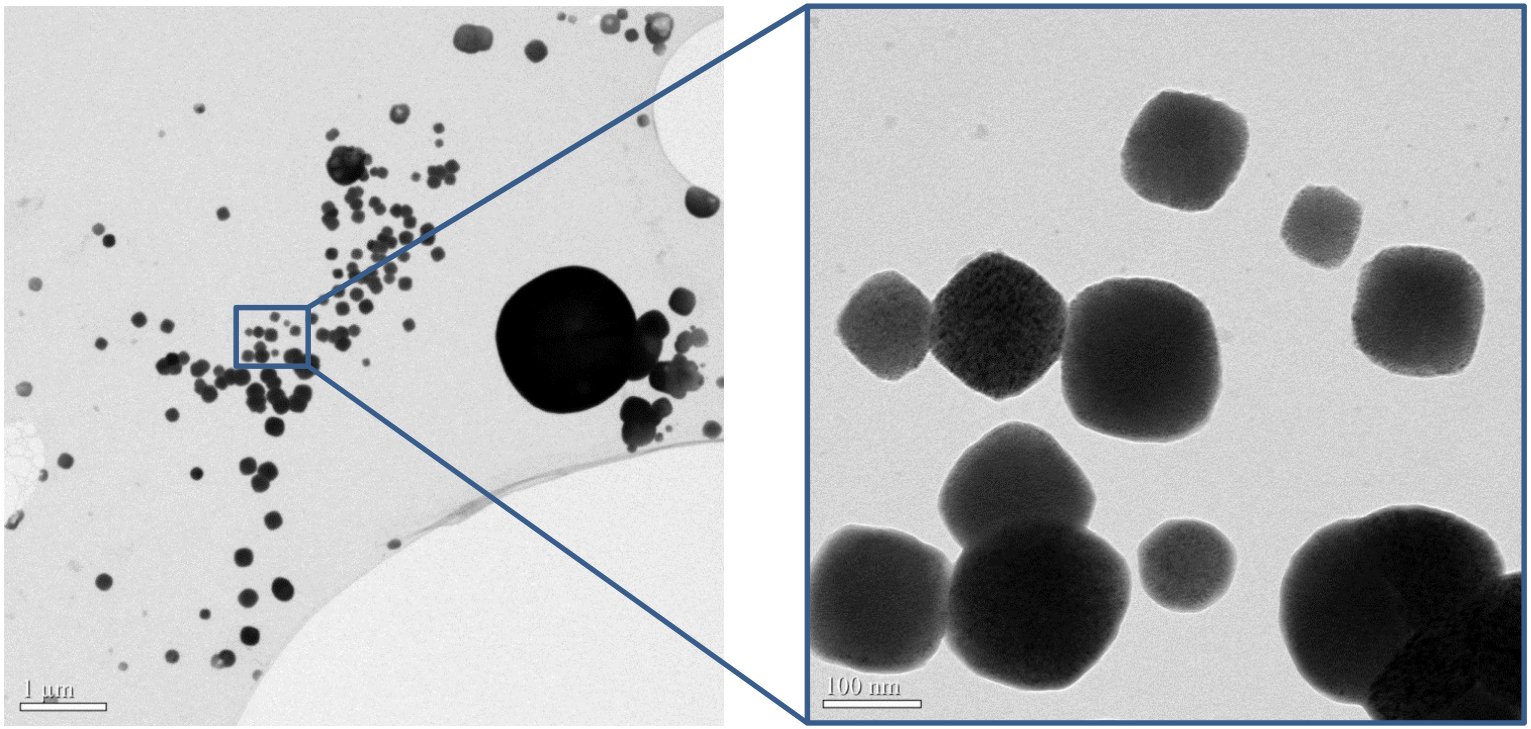

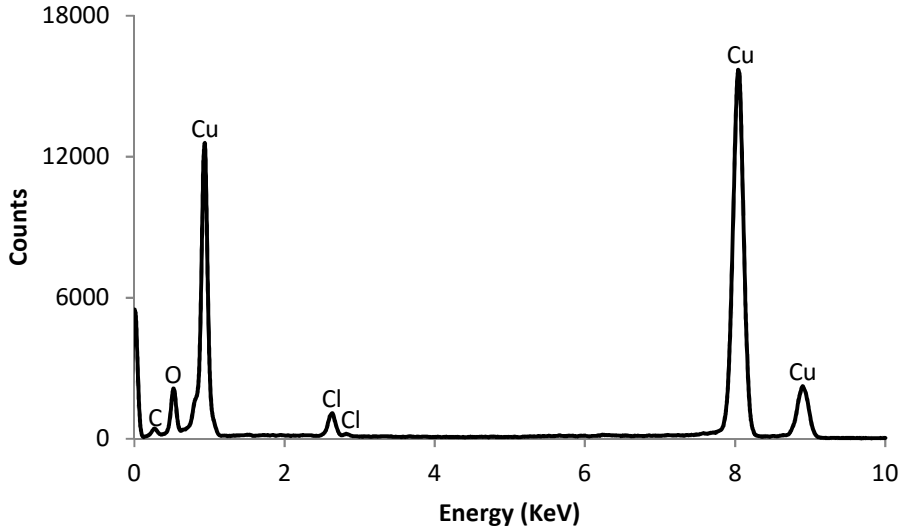

Element	Weight%	Atomic%
C K	2.01	7.93
O K	7.88	23.3
Cl K	2.83	3.77
Cu K	87.28	64.99

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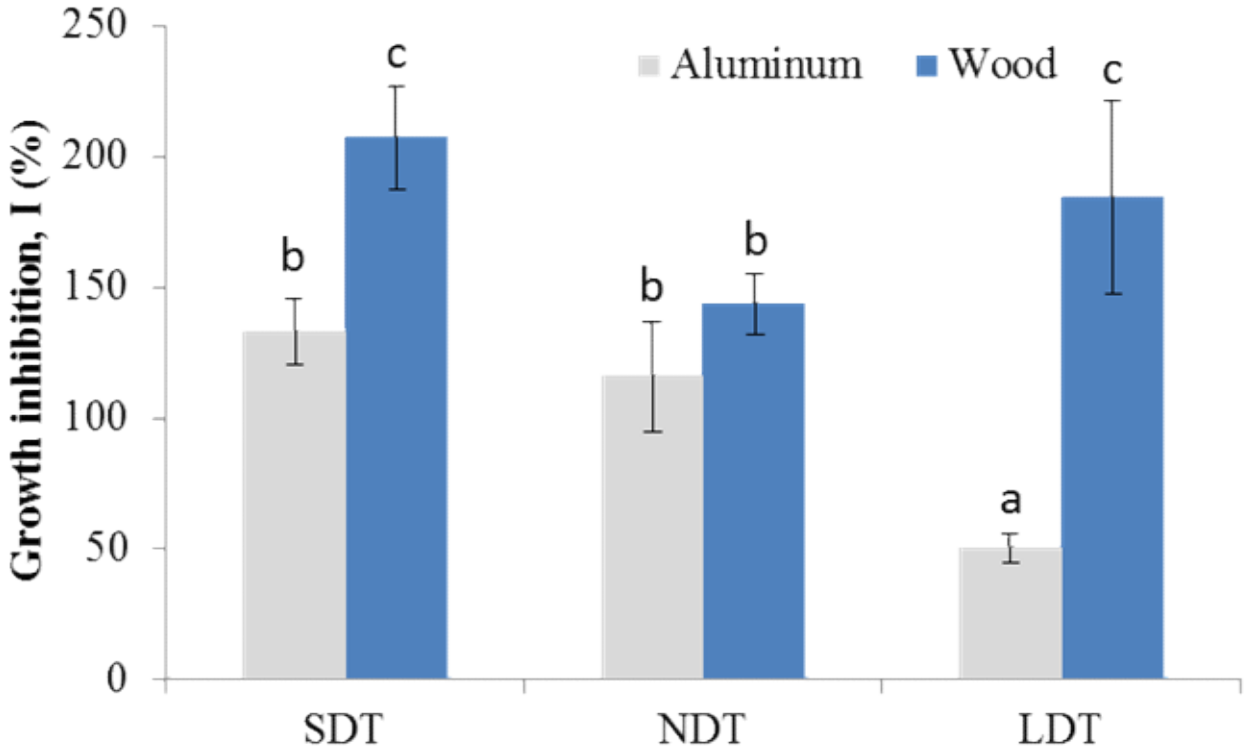
Effect on Isochrysis galbana



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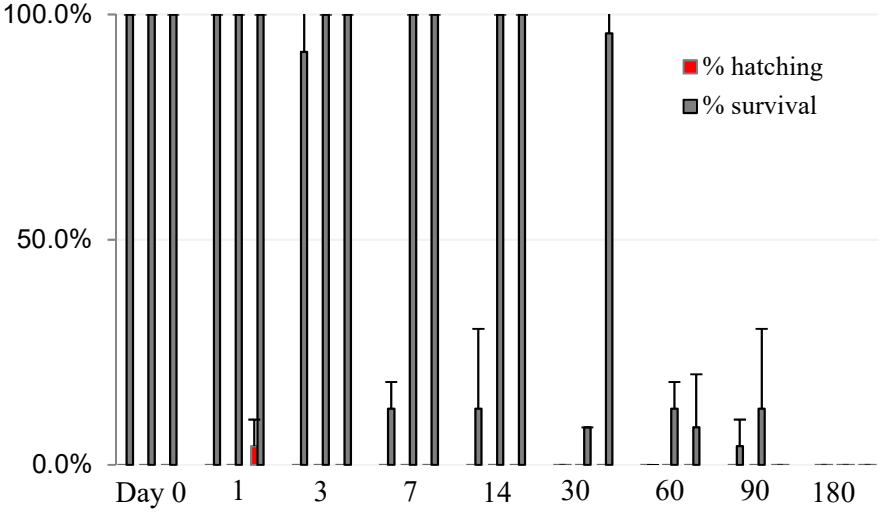
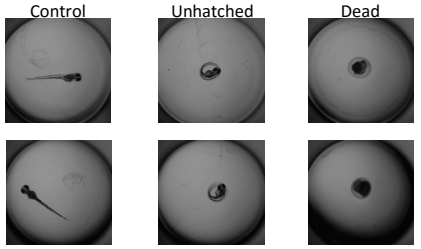
Effect of paint leachate on zebra fish embryos

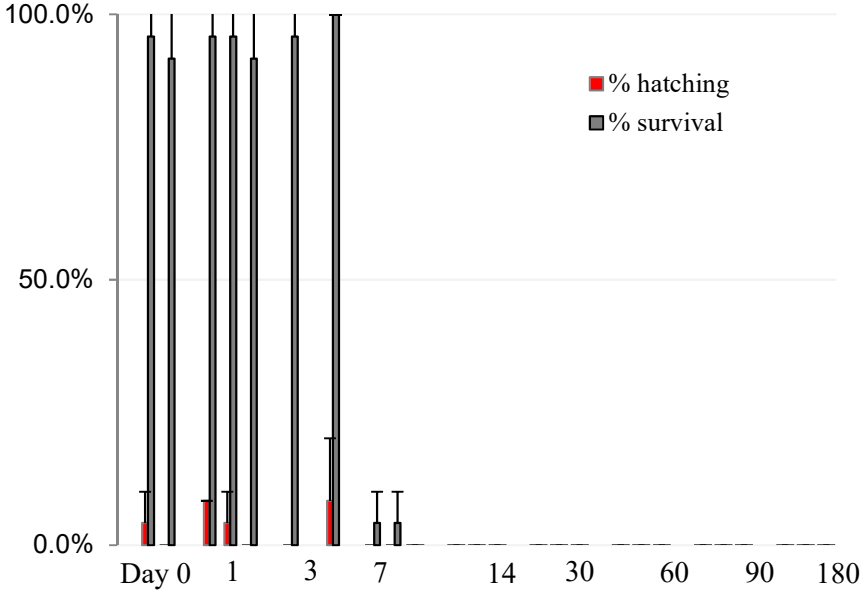
Aluminum





Effect of paint leachate on zebra fish embryos

Wood



Conclusions

- Nanosized Cu_2O was detected in a *unlabeled* antifouling paint and its leachate

- Release of Cu was strongly dependent on:
  - Material painted
  - Salinity
  - Drying time

- Transformation of Cu_2O is in orders of weeks or months

- Paint leachate exhibited toxicity to algae and zebra fish embryos

Acknowledgements

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Mengya Tao
Sage Davis
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