DPR's Evaluation of Antifouling Paint Pollution in CA

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Presentation Overview

- Presented previously in July 2007
  - Focus on historical background & prelim. findings of multi-regional study
- Summaries of results from recent CA AFP monitoring studies
- Monitoring studies outside of CA
- Concerns w/ Booster Biocides
- Other factors we considered in our evaluation

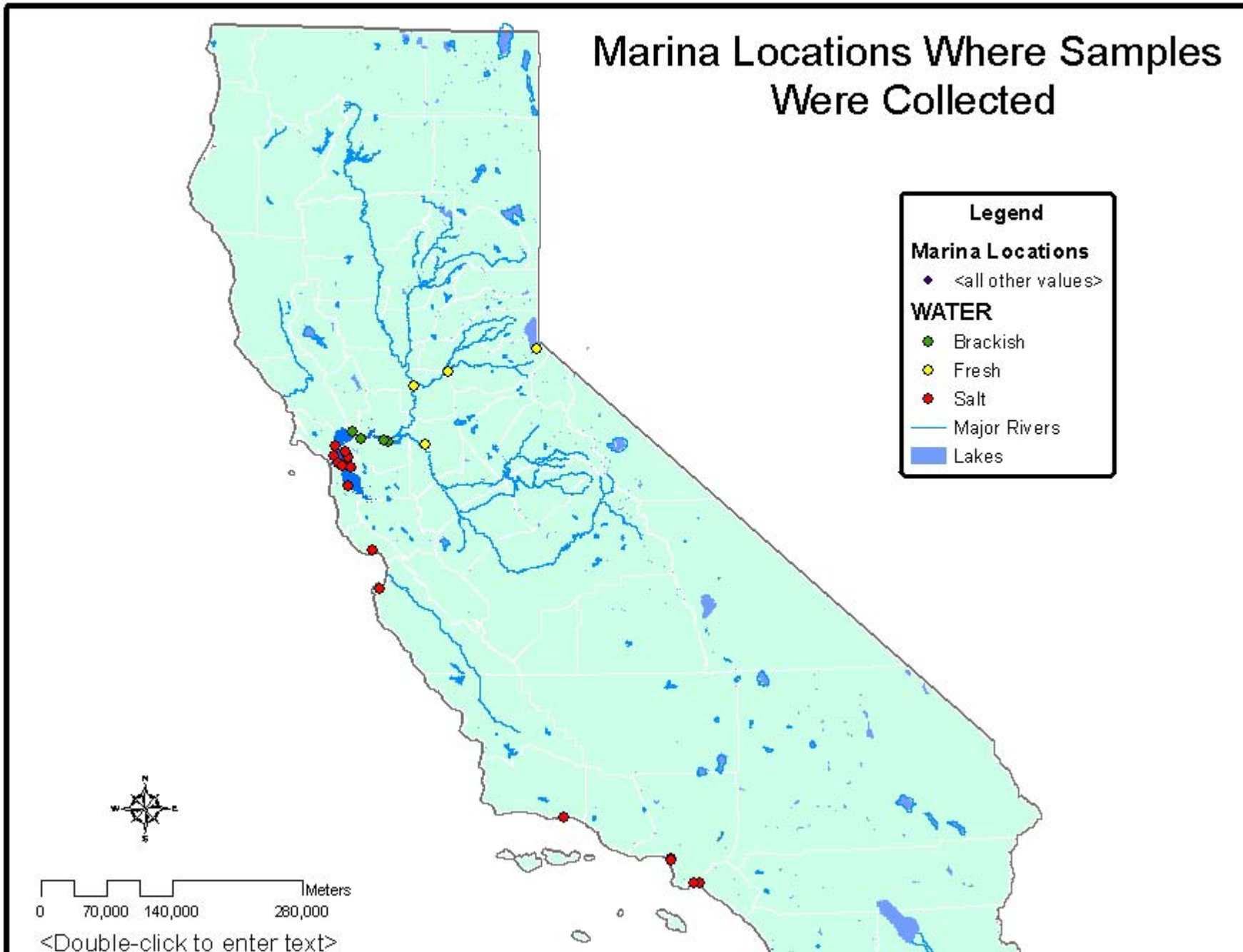
AFP Products in CA

- ~ 170 AFP pesticide products registered
- More than 90% utilizes copper-based biocides
  - Copper oxide, copper hydroxide, copper thiocyanate
- Booster biocides are often co-formulated
  - Zinc pyrithione (a.k.a. omadine)
  - Irgarol 1051
  - Sea-Nine (DCOI)

CA Monitoring Studies

- DPR/SWRCB Multi-Regional Study
- SARWQCB Lower Newport Bay Metals Study
- SDRWQCB South Coast Copper Study
- DBW SIYB Biological Impact Study (in progress)

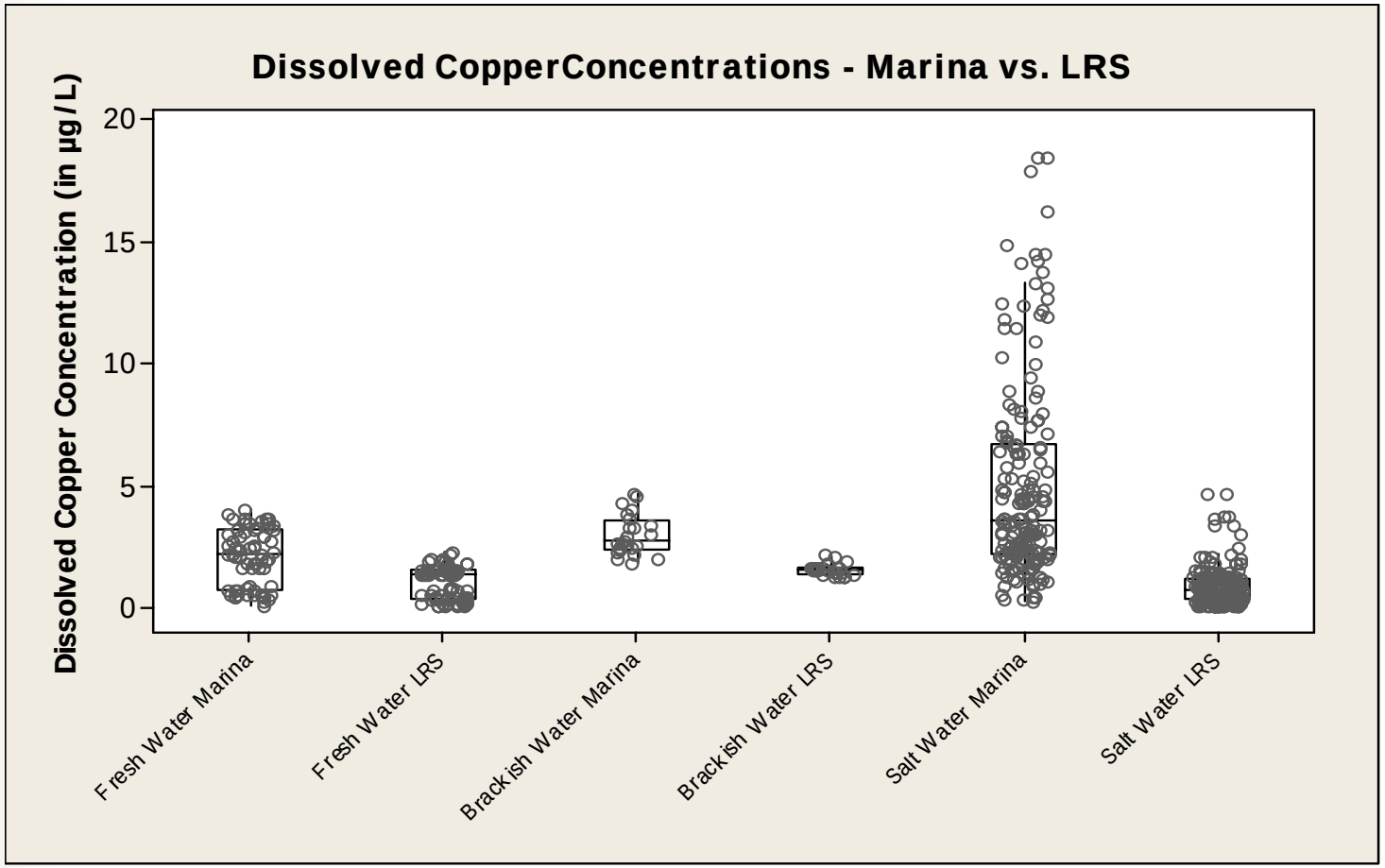
Marina Locations Where Samples Were Collected



Cu Findings - DPR/SWRCB Multi-Regional Study

- Medians for salt, brackish & fresh marina sites were 3.7, 3.1, 1.6 ppb, respectively
- Medians for corresponding background were 0.6, 1.6, 0.7 ppb, respectively
- Differences in marina vs. background conc. are statistically significant (nested ANOVA) for salt water marinas
- In salt & brackish water areas, 15 of 17 marinas exceeded CTR chronic stds. (3.1 ppb); 10 of these 15 marinas also exceeded acute stds. (4.8 ppb)

Dissolved Copper Monitoring Results – Multi-Regional Study



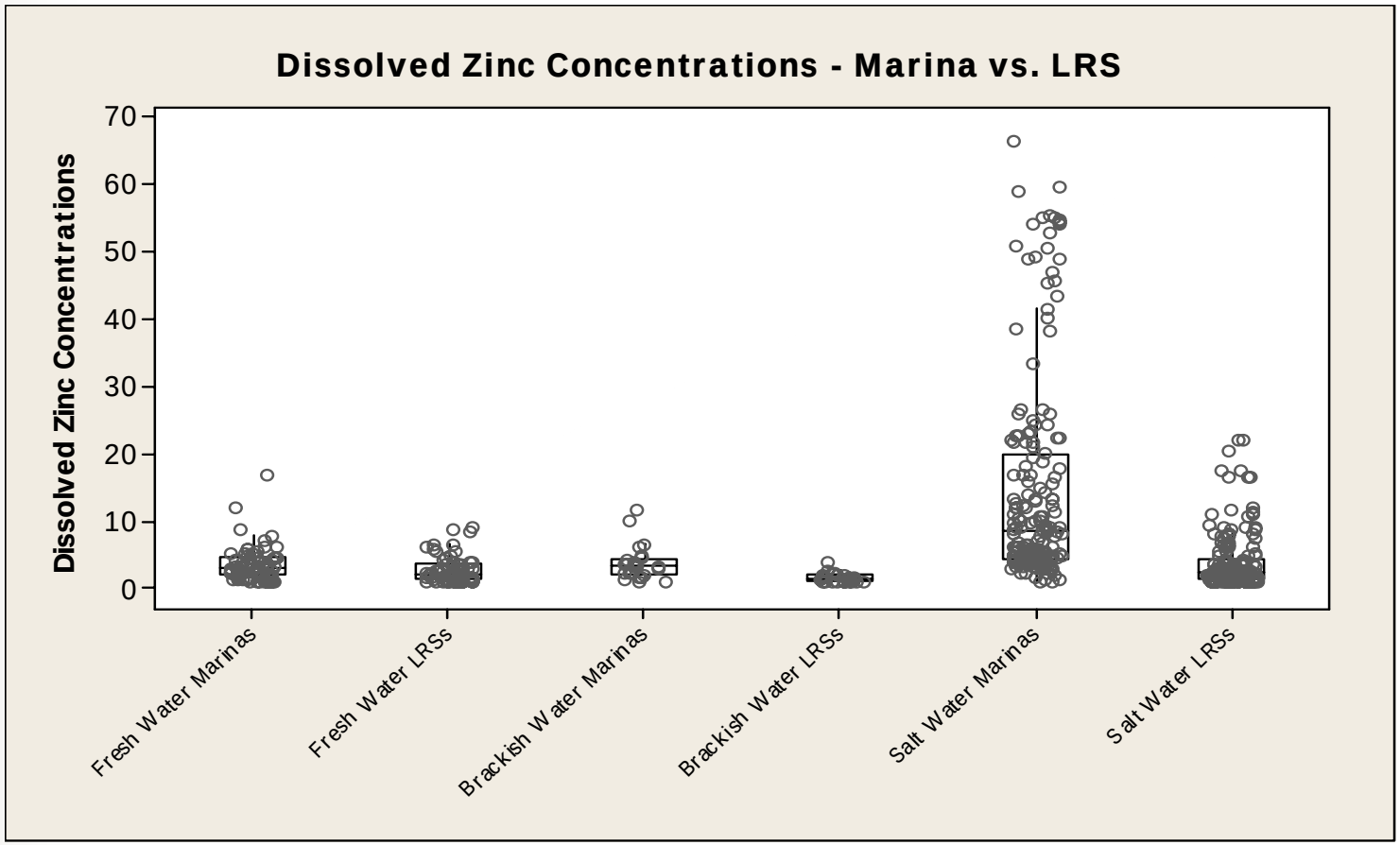
Cu Findings - DPR/SWRCB Multi-Regional Study (cont.)

- In fresh water areas, CTR stds. were rarely exceeded (1 of 68 samples)
- Few background samples exceeded CTR stds.
- Particularly elevated levels in Central & South Coast marinas
- Moderately elevated levels in SF Bay Area marinas (note Site Specific Objectives)
- With leaching estimates & source survey, we believe boat AFPs are a major source of Cu, particularly in salt water marinas in dry periods

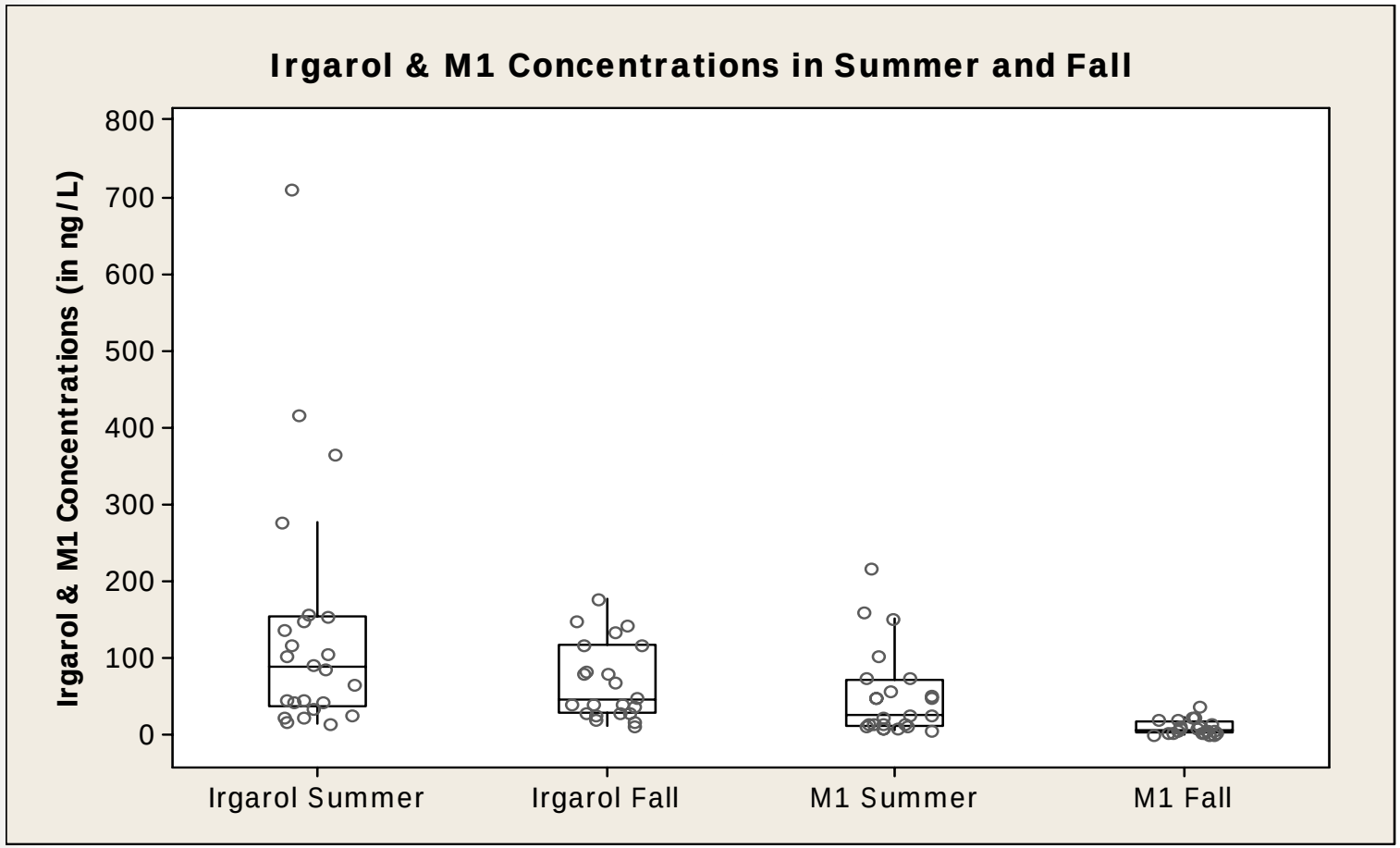
Other Findings - DPR/SWRCB Multi-Regional Study

- 8 of 47 water samples toxic in mussel embryo development tests
- TIE on most toxic samples confirm Cu toxicity – also highest conc. (18.4 ppb)
- Toxicity observed when Cu > 8-10 ppb
- Zn conc. all below CTR (81 & 90 ppb)
- Zn - Significant difference marina vs. background
- Irgarol & M1 ubiquitous sometimes at levels above EC_{50} values

Dissolved Zinc Results – Multi-Regional Study



Irgarol & M1 Results – Multi-Regional Study



2006 Lower Newport Bay Study

- Dissolved Cu (among 9 metals tested) that exceeded CTR stds.
- 52 of 72 samples from marina & yacht basins exceeded chronic CTR
- Of these 52, 20 also exceeded acute CTR
- Average ~ 4.2 ppb; Max of 11.0 ppb
- No water column toxicity (10 samples)

2005 South Coast Study

- Assessment of 30 marina sites between Dana Point Harbor & U.S./Mexico Border
- Majority of samples were > CTR
- Range = n.d. – 21.0 ppb, average ~ 7.0 ppb
- Samples > 10 ppb toxic on mussel embryo development
- Not all samples above CTR were toxic

Monitoring Outside CA

- State of Florida
- State of Maryland
- United Kingdom
- Europe – Mediterranean Sea, Baltic Sea & North Sea
- All studies showed frequently elevated Cu concentrations & occasional toxicity in marinas & other areas w/ heavy boating activities

Ecological Risk Assessments

- 3 comprehensive PERAs conducted
- ERAs 🕓 there is generally low probability of ecological risks; however, higher probabilities of risk exist where boating activities are high
- PNECs
  - Salt water acute ~ 5.6 – 6.3 ppb
  - Fresh water acute ~ 8.2 ppb

Booster Biocide: Zinc Pyrithione ($ZnPt_2$)

- Pose another heavy metal - sediment issue
- Transchelation w/ Cu 🕒 $CuPt_2$ - more stable & toxic
- $ZnPt_2$ hydrolysis stable (although photo sensitive)
- No ambient data
- $ZnPt_2$ & $CuPt_2$ are highly toxic to a variety of aquatic organisms

Selected $ZnPt_2$ & $CuPt_2$ Toxicity Values

$ZnPt_2$, 96 hrs. LC_{50}	4.7 ppb	Crustacean (*M. bahia*)	U.S. EPA, 2004
$ZnPt_2$, 96 hrs. LC_{50}	6.3 ppb	Crustacean (*M. bahia*)	Madsen et al., 2000
$ZnPt_2$, 48 hrs. LC_{50}	8.2 ppb	Crustacean (*D. magna*)	Boeri et al., 1994a
$ZnPt_2$, 96 hrs. LC_{50}	6.3 ppb	Crustacean *(M. bahia)*	Boeri et al., 1993
$ZnPt_2$,7 days, LC_{50} $CuPt_2$, 7 days LC_{50}	8.4 ppb 7.6 ppb	Juvenile rainbow trout (*O. mykiss*)	Okamura et al., 2002
$ZnPt_2$, 96 hrs. LC_{50}	2.6 ppb	Fish (*P. promelas*)	Boeri, et al., 1999

Booster Biocide: $ZnPt_2$

- Rise in $ZnPt_2$ products in registration queue
- Could end up replacing Cu AFP products based on efficacy & cost
- Danish EPA's ERA 🕓 likely a risk of chronic ecotoxic effects in marinas/harbors (assumes high adoption rate)
- U.S. EPA 🕓 $ZnPt_2$ on a conditional registration status until ERA can be completed
- MAM-PEC Modeling 🕓 PEC of 2.2 ppb @ 30% adoption level (note: did not model $CuPt_2$)

Booster Biocide: Irgarol & M1

- Triazine class herbicide
- Sea water half-life ~ 100 days
- In DPR study, Irgarol ubiquitous w/ average of 136 ppt, max. of 712 (11 sites)
- Levels similar to those in Maryland, Florida, Spain, France, and Bermuda
- No W.Q. stds. for Irgarol or M1

Booster Biocide: Irgarol & M1

- Inhibits photosynthesis in range of 50-200 ppt (ng/L)
- Plant toxicity benchmark ~ 136 ppt (Hall *et al*., 1999)
- U.S. EPA updated ERA from 2003 noted
  - high plant toxicity
  - slow degradation rate
  - high plant bioconcentration potential
- U.S. EPA 🕓 Irgarol could have direct effects on producers & indirect effects on consumers

Booster Biocide: Sea-Nine (DCOI)

- Organic isothiazolone-class compound
- Controls bacteria, fungi, diatoms, and green algae (soft fouling)
- Geared toward larger ship applications (commercial & military)
- Only 3 products currently registered w/ DPR; however, no ambient data
- No W.Q. stds. for Sea-Nine

Booster Biocide: Sea-Nine (DCOI)

- Sea water half-life < 1 day
- Does not have bioaccumulation tendencies
- Highly toxic to marine algae & invertebrates
- Effects on sea urchin eggs & embryos in picoliter levels (1 pg/L NOEC)

Selected Sea-Nine Toxicity Values

LC50	2 ppb	Alga (*E. intestinalis*)	Jacobson & Willingham, 2000
48 hrs. LC_{50}	4 ppb	Crustacean (*D. magna*)	Fernandez-Alba et al., 2002
48 hrs. LC_{50}	2 ppb	Bay mussel larvae	Shade et al., 1993
48 hrs. LC_{50}	7 ppb	Oyster larvae	Shade et al., 1993
7-day LC_{50}	14 ppb	Rainbow trout (*O. mykiss*)	Okamura et al., 2002

Booster Biocide: Sea-Nine (DCOI)

- Danish EPA's ERA 🕓 likely a risk of chronic ecotoxic effects in marinas/harbors (assumes high adoption rate)
- EXAMS Model 🕓 PEC of 1 ppt for San Diego Bay
  - For central Bay not marina
  - Leach rate used 20x lower than true rate
- Adjustments suggest NOECs & LOECs may be surpassed w/ high adoption

Other Factors Considered

- Other State regulatory activities/actions
  - SIYB Cu TMDL - Implementation
  - Marina del Rey & Lower NPB metals TMDLs
  - Additional CWA 303(d) listings
  - Any changes to CTR stds.
  - Site Specific Objectives (e.g. SF Bay)
- Federal AFP-Related Activities
  - Cuprous Oxide Reregistration
  - NPDES Permit Requirements for Vessel Discharges
  - UNDS Regulations for Military Vessels
  - Changes to W.Q. criteria for aquatic life

Other Factors Considered

- Available Management Practices
  - Improved Hull Cleaning Practices
  - Hull Slips/Hull Lifts
  - Others?
- Available Alternative Coatings
  - Less toxic/non toxic
  - ?Feasibility? Cost, efficacy, practical?

DPR Policy Decision - AFP

- December 4, 2007 – DPR announced plans to pursue reevaluation of all AFPs based on these findings, data & information
- Reevaluation, if approved, will be divided
  - Copper AFPs – focus on mitigation
  - Non-Copper AFPs – focus on ambient concentrations & water quality impacts

Questions?

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