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## **Supplemental Material**

## **Advancing Alternative Analysis: Integration of Decision Science**

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# Case Study Narrative

### Prepared for the 2014 Advancing Alternatives Analysis Workshop

This semi-fictional case involves the search for alternatives to copper-based anti-fouling paint for recreational boats. It is designed as background for the *Advancing Alternatives Analysis* workshop, providing context for discussion regarding alternatives analysis. Following a brief introduction to the problems presented by copper-based anti-fouling paint, it identifies a set of potential alternatives and sets out selected data (and data gaps) relevant to the issues to be covered during the workshop. (The paper assumes a basic knowledge of AA; for more information on AA see the *Background Paper on Alternatives Analysis*.)

In reading and using this case study during the workshop, it is important to remember that our goal in the workshop is not to actually complete an alternatives analysis (AA) or select a preferred alternative paint. Rather the case study and selected data it includes are meant to frame particular types of issues that are central to the workshop. For example, with respect to the integration of predictive toxicology into AA, the case study provides several examples of uncertain data and of data gaps for selected health or environmental criteria such as endocrine disruption or carcinogenicity. Likewise, regarding the role of decision analysis in AA, the case study highlights certain thorny trade-offs presented by the alternatives. Our goal is to use these and other concrete examples to explore how predictive toxicology and decision analysis might advance AA.

#### INTRODUCTION: THE PROBLEM CONTEXT

The case study centers on the City of Beachside's Downtown Marina which has slips for 1764 slips for recreational boaters. Beachside officials are facing difficult choices regarding the use of anti-fouling paint on boats at the Marina. Recent studies have concluded that copper levels in the marina exceed standards established by EPA and that the elevated levels are largely caused by leaching of copper from boats kept in the marina.

Marine organisms can attach themselves ("fouling") to boat bottoms, possibly damaging the boat's structure, reducing the boat's speed and maneuverability, and reducing its fuel

efficiency. Boats can also carry invasive fouling organisms to other harbors. Anti-fouling paint can be applied to boat hulls to prevent or reduce the attachment of marine organisms to boats. Many of these paints contain copper as a biocide, an active ingredient intended to kill barnacles,

<sup>&</sup>lt;sup>1</sup> EPA, Protecting Boats and Water Quality (last updated Dec. 20, 2013),http://www.epa.gov/region9/waste/features/safe-paint/index.html; U.S. EPA, NP00946501-4, Safer Alternatives to Copper Antifouling Paints for Marine Vessels FINAL REPORT (Jan. 2011).

algae, and other marine organisms. While copper effectively reduces fouling on boat hulls, it also enters the marine environment through leaching and during hull cleaning.

Beachside joins a growing list of governments moving away from copper-based anti-fouling paint. The Los Angeles Regional Water Quality Control Board recently required the reduction of copper loading in Marina del Rey Harbor, an action that essentially will phase out conventional copper-based anti-fouling paint. Washington State banned copper-based bottom paint on recreational boats (to come into effect in 2018). Other state and local governments are likewise considering the phase out of copper in such paints. Beachside officials will be conducting an alternatives analysis to determine whether there are viable alternatives to the use of copper-based bottom paint on recreational boats in the harbor. In doing so, they will evaluate the health/safety, environmental effects, technical performance, and economic impacts of each alternative paint. In addition to the quality of the alternatives analysis, Beachside officials are also concerned about issues regarding transparency, stakeholder input, and resource constraints.

The alternatives analysis will be used to assist decision-makers in determining whether copper should be phased out of use. However, it will also serve the dual purpose of assisting the public in choosing which paint to apply to their boat (regardless of whether copper is phased out). The information will also be made available to industry representatives who are trying to make various decisions throughout the value chain (i.e., selection of materials to be included in their product, etc.).

#### DESCRIPTION OF BASELINE PAINT AND ALTERNATIVE PAINTS

Officials have identified the six candidate alternatives, and collected reasonably available data regarding the alternatives' respective performance in terms of health/safety, environmental effects, technical performance and economic impact.

The paints under consideration can be classified according to how they prevent fouling: copper biocide, organic biocide, organozinc biocode, and non-biocide. The "baseline" paints (Coppercoat and Cukote) are copper biocides. *Coppercoat* uses "copper powder" (metallic copper) as the active ingredient. *Cukote* contains cuprous oxide (Cu<sub>2</sub>O) as an active ingredient, and has been found to include nano-copper particles. Cukote also includes Igarol®, an organic biocide. *Pacifica Plus* uses an organic biocide (Econea®)<sup>2</sup> and an organozinc biocide (zinc omadine). *Seahawk Mission Bay* relies upon the organozinc biocide zinc omadine, and includes nano-zinc oxide particles. *Hempasil* is a silicone-based non-biocide that forms a slippery, low-friction surface to which organisms have trouble attaching. (See Table 1 for more information.).

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<sup>&</sup>lt;sup>2</sup> Also known as tralopyril.

Table 1
Candidate Paints

Paint Name	Туре	Active Ingred applicab	,	Other Relevant Ingredients
		Name	%	
Sea Hawk Premium Quality	Copper Biocide and Organic	Cuprous Oxide	47.57	Nano-copper
Cukote Biocide and Slime Resistant Antifouling Coating	Biocide	Irgarol®	2.00%	
CopperCoat	Copper Biocide	Copper Powder	99.7% <sup>3</sup>	
Pacifica Plus	Organic and Organozinc	Econea®	3.90%	
	Biocide	Zinc omadine <sup>4</sup>	4.12%	
Seahawk Mission Bay CSF Copper Free Antifouling Coating	Organozinc Biocide	Zinc omadine	4.02%	Nano-zinc Oxide: 20% Zinc Oxide: 5.4%
Hempasil X3 <sup>5</sup>	Non-biocide	N/A		Silicone hydrogel based; Includes xylene, ethylbenzene, and dibutyltin dilaurate

#### **AVAILABLE DATA**

Financial and staff resources prevented Beachside officials from generating site specific data regarding conditions at the marina, toxicity and fate and transport of ingredients in the paints, technical performance and economic aspects of the paints. Instead, officials conducted a literature review of information from the EPA, state agencies, and available industry information on the product and its potential impact on harbors. They have organized and presented the data in a "performance matrix," allowing for visual comparison of the paints across the relevant criteria (*e.g.*, physical chemical hazards, human health impacts, environmental and ecological impacts, economic feasibility, and technical feasibility).

<sup>&</sup>lt;sup>3</sup> Copper powder provided separately and mixed prior to application.

<sup>&</sup>lt;sup>4</sup> Also known as zinc pyrithione.

<sup>&</sup>lt;sup>5</sup> A Two-Component Paint (requires mixing of the base with a curing agent).

For purposes of our case study, we have selected a subset of criteria and associated data to highlight particular types of issues that typically arise in an AA. In particular, regarding the use of predictive toxicology approaches and methods, the selected data illustrates challenges created by data gaps and uncertainties. Regarding decision making approaches in AA, the selected criteria and data present tradeoffs within criteria (*i.e.*, between two types of human health impacts) and across criteria (*i.e.*, between human health impacts and ecological impacts). It also presents the challenge of how to deal with uncertainty in decision making. The performance data matrix excerpt itself will be provided separately.

### CONCLUSION: ADDRESSING CHALLENGES FOR AA ILLUSTRATED BY THE CASE STUDY

The case study raises a host of challenges presented by alternatives analysis. The workshop focuses on two major issues: potential integration of predictive toxicology approaches and methods into AA, and the potential role of decision analysis in AA. These issues (articulated in more detail below) will be raised through a set of challenge questions presented to three working groups during the workshop. (Clearly the case study raises other important issues, such as how an AA should deal with questions of exposure, or take account of hazards and exposures at each part of the product's lifecycle. While acknowledging the critical importance of these and other issues, for this workshop we put them largely to the side.)

With respect to predictive toxicology, two working groups will consider (1) whether and how existing and emerging approaches and methods could or should be used in AA, (2) how they may supplement, complement or replace conventional toxicology in AA, and (3) whether there is a hierarchy of predictive toxicology tools that should be used in AA. While the case study data is largely of the conventional sort, a variety of existing and emerging predictive approaches may be applicable to this case study. For example, mechanistic in vitro assays for endocrine activity are available and have already been used in a comparative analysis of potential water contaminants. Other forms of high content and high throughput screening of nano-copper have been demonstrated at the UC Center for Environmental Implications of nanotechnology for aquatic toxicity using zebrafish, and for a variety of cellular level impacts using bacteria. 9

With respect to decision analysis, one working group will consider a set of issues in the context of the case study: (1) the use of various decision analysis methods and tool to evaluate trade-offs particularly under conditions of uncertainty, (2) strategies for dealing with diverse types of data, and (3) whether and how to account for the relative importance of criteria (sometimes called "weighting" criteria.)

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<sup>&</sup>lt;sup>6</sup> In addition, limited testing and data exist for the actual end use product. The selected data illustrates the challenges of relying on information for the main or active ingredient rather than product specific information.

<sup>&</sup>lt;sup>7</sup> For example while some of the human health data incorporates both hazard and risk in some measure of risk (such as MOE's for sub-chronic toxicity) much other data do not reflect issues of exposure or transformation chemicals in the environment.

<sup>&</sup>lt;sup>8</sup> Richard S. Judson, *Analysis of Eight Oil Spill Dispersants Using Rapid, In Vitro Tests for Endocrine and Other Biological Activity*, 44 Envt'l Sci. & Tech. 5979 (2010); Ki Chang Ahn, *et al.*, *In Vitro Biologic Activities of the Antimicrobials Triclocarban, Its Analogs, and Triclosan in Bioassay Screens: Receptor-Based Bioassay Screens*, 116 ENVT'L HEALTH PERSP. 1203 (2008).

<sup>&</sup>lt;sup>9</sup> See Sijie Lin, et al., Zebrafish High Throughput Screening to Study the Effects of Dissolvable Metal Oxide Nanoparticles on the Hatching Enzyme, ZHE<sub>1</sub>, 9 SMALL 1776 (2013).





# Anti-Fouling Paint Case Study Performance Matrix

Prepared for the 2014 Advancing Alternatives Analysis Workshop

A simplified performance matrix excerpt for the anti-fouling paint case study is attached for use during the A<sup>3</sup> Workshop. This matrix presents data regarding five human health criteria, five aquatic toxicity criteria, as well as technical performance criteria and economic criteria. An actual alternative analysis (AA) would typically also cover other criteria relevant to human health, ecological impacts, technical performance, economic impacts and other areas. Our performance matrix is limited in scope so as to make it more manageable in the context of the workshop, while including enough variety to illustrate the type of data gaps and tradeoffs that arise in AA.

The performance matrix excerpt includes the following human health criteria:

- Acute toxicity
- Sub-chronic toxicity
- Carcinogenicity
- Endocrine activity
- Reproductive toxicity

It also covers these aquatic toxicity criteria:

- Acute and chronic fish toxicity
- Acute and chronic invertebrate toxicity
- Estuarine/marine plant toxicity

For human health impacts and ecological impacts,

the matrix sets out the data for each active ingredient for each of the five alternative paints being evaluated in the AA. Thus, for example, for Pacifica Plus paint, the matrix includes information regarding both zinc omadine and tralopyril in two separate, respective columns. Where available, it also includes data regarding degradates of the active ingredients, *i.e.*, a chemical produced by the degradation or breakdown of the chemical in the environment. The matrix also identifies data gaps, which are highlighted in yellow. For technical performance and economic impacts, the data relates to the product as a whole rather than the active ingredients.

With respect to each of the decision criteria, the matrix identifies the metric that is used in assessing a paint's performance. Some metrics are quantitative while others are categorical. Acute fish toxicity is illustrative of the use of continuous, quantitative data: performance on that criterion is measured using lethal concentration 50 values (LC50) in parts per billion. For other of the criteria, the matrix uses categorical metrics. For example, acute toxicity for human health purposes is measured using EPA's Toxicity Categories for pesticide labeling, consisting of Category I (most toxic) through Category IV (least toxic). Materials are assigned to categories based upon the following table:

		(22)	2000	194/201
Hazard Indicators	1	Ш		IV
Oral LD <sub>50</sub>	Up to and including 50 mg/kg	>50 thru 500 mg/kg	>500 thru 5,000 mg/kg	>5,000 mg/kg
Dermal LD <sub>50</sub>	Up to and including 200 mg/kg	>200 thru 2000 mg/kg	>2000 thru 20,000 mg/ kg	>20,000 mg/kg
Inhalation LC <sub>50</sub>	Up to and including 0.2 mg/liter	>0.2 thru 2 mg/liter	>2 thru 20 mg/liter	>20 mg/liter
Eye irritation	Corrosive; corneal opacity not reversible within 7 days	Comeal opacity re- versible within 7 days; irritation per- sisting for 7 days	No corneal opacity; ir- ritation reversible within 7 days	No irritation
Skin irritation	Corrosive	Severe irritation at 72 hours	Moderate irritation at 72 hours	Mild or slight irritation at 72 hours

In our performance matrix, carcinogenicity is measured by reference to EPA's cancer classifications, which sort chemicals into five groups ranging from "A" (Human Carcinogen) to "E" (Evidence of Non-Carcinogenicity for Humans). Technical performance data regarding (1) cleaning effort required as part of boat maintenance and (2) amount of fouling observed are likewise categorical.

Some caveats and limitations are in order. The purpose of the attached performance matrix is to provide a concrete context for discussing the role of predictive toxicology and of decision analysis in AA. *It is not meant to be a comprehensive statement of the existing data regarding these paints, nor is it intended to provide a basis for actually performing an AA*. As such it is limited in several respects. Most notably, the matrix excerpt does not address issues of exposure or fate and transport (with limited exceptions). Clearly, for many analysts information about occupational, consumer and environmental exposure will be an important complement to the type of hazard information provided by the attached excerpt. However, the question of whether and how to integrate exposure assessment into the AA is beyond the scope of this workshop. For our purposes the information included in the matrix should be adequate to demonstrate the issues of data gaps, data integration and decision-making that arise in AA.

Also, the matrix is based primarily upon a relatively limited data set: documents generated by or for EPA as part of its administration of the federal pesticide and federal water pollution control regulations. This information was supplemented by publically available safety data sheets.

#### REFERENCES

Institute for Research and Technical Assistance, SAFER ALTERNATIVES TO COPPER ANTIFOULING PAINTS: NONBIOCIDE OPTIONS (2011)

San Diego Unified Port District and Institute for Research and Technical Assistance, SAFER ALTERNATIVES TO COPPER ANTIFOULING PAINTS FOR MARINE VESSELS: FINAL REPORT (2011)

<sup>&</sup>lt;sup>1</sup> For those who are interested, we will make additional information regarding environmental fate and transport available.

EPA, ZINC PYRITHIONE (ZINC OMADINE®): AD PRELIMINARY RISK ASSESSMENT FOR THE REGISTRATION ELIGIBILITY DECISION DOCUMENT (April 21, 2004)

EPA, Summary of Product Chemistry, Environmental Fate, and Ecotoxicity Data for the 1,3,5-Triazine-2,4-Diamine, N-Cyclopropyl-N-(1,1-Dimethylethyl)-6-(Methylthio)-Registration Review Document Decision (March 29, 2010)

EPA, REGISTRATION ELIGIBILITY DECISION (RED) FOR COPPERS (May 2009)

EPA, TRALOPYRIL (ECONEA) FINAL WORK PLAN (December 2013)

					SEA HAWK PREMIUM QUA SLIME RESIS. ANTIFOUL. C		CopperCoat	Pacifica Plus		Seahawk Mission Bay CSF Cop Coating	per Free Antifouling	Hempasil X3 (87500)
"Group" Criteria	Sub-Criteria	Sub-Criteria	Metric	Min/Max	Cuprous Oxide (bulk and nano-size forms)	Igarol	Copper Powder	Zinc Omadine/Zinc Pythrione	Tralopyril	Zinc Omadine/Zinc Pythrione	Nano-zinc (non-active ingredient)	Silicone based material
	acute toxicity	oral	Toxicity Category	Maximize (Tox Cat IV most preferred)		Tox Cat III	Tox Cat III	Tox Cat II	Tox Cat I	Tox Cat II	Data Gap	Data Gap
		inhalation	Toxicity Category	Maximize (Tox Cat IV most preferred)		Tox Cat III	Tox Cat III	Tox Cat III	Tox Cat II	Tox Cat III	Data Gap	Data Gap
		dermal	Toxicity Category	Maximize (Tox Cat IV most preferred)		Tox Cat III	Tox Cat III	Tox Cat III	Tox Cat III	Tox Cat III	Data Gap	Data Gap
Human Health Impacts		Oral	NOAEL in mg/kg/day	Maximize (Higher NOAEL preferred)	Data Gap	8.2	Data Gap	3	5.2 (LOAELNo NOAEL)	3	Data Gap	Data Gap
	Sub-chronic toxicity	Inhalation	NOAEL in mg/kg/day	Maximize (Higher NOAEL preferred)	Data Gap	Data Gap	Data Gap	0.13	5.7 (LOAELNo NOAEL)	0.13	Data Gap	Data Gap
		Dermal	NOAEL in mg/kg/day	Maximize (Higher NOAEL preferred)	Data Gap	>1000	Data Gap	100	100	100	Data Gap	Data Gap
	carcinogenicity		EPA Cancer Catergory		Group D (not classifiable as to carcinogenicity)	Data Gap	Group D (not classifiable as to carcinogenicity)	Data Gap: Analog sodium pyrithione (a structurally related chemical) was classified as a Group D (not classifiable as to carcinogenicity)		Data Gap: Analog sodium pyrithione (a structurally related chemical) was classified as a Group D (not classifiable as to carcinogenicity)	Data Gap	Data Gap
	Endocrine Activity		Catergory		identified data gap	Conflicting Data	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap
	Reproductive toxicity		NOAEL in mg/kg/day	Maximize (Higher NOAEL preferred)	Data Gap	55 (reproductive effects); 9.5 (maternal effects)	Data Gap	Data Gap: The level for sodium pyrithione (a structurally related chemical) is 1.5	Data Gap	Data Gap: The level for sodium pyrithione (a structurally related chemical) is 1.5	Data Gap	Data Gap
		Acute-fish	LC50 in ppb	Maximize (Higher LC50 preferred)	12.66	.66		Data Gap	Data Gap			
Ecological Impacts		Chronic-fish	NOAEC in ppb	Maximize (Higher NOAEC preferred)	Data Gap	170 (Igarol) (NOEL)	Data Gap	1.22 (ZO); 10 (Degradates	) 4.3 (Tralopyril); 240 (Degradates)	1.22 (ZO); 10 (Degradates)	Data Gap	Data Gap
		Acute- invertebrates	LC50/EC50 in ppb	Maximize (Higher LC50/EC50 preferred)	6.49	400 (Igarol); 1500 (Degradate)	6.49	4.7 (ZO); >70,000 (Degradates)	.64 (Tralopyril); 310 (Degradates)	4.7 (ZO); >70,000 (Degradates)	Data Gap	Data Gap
		Chronic- invertebrates	NOAEC in ppb	Maximize (Higher NOAEC preferred)	Data Gap	110 (NOEL)	Data Gap	2.82 (ZO)	2.28 (Tralopyril); 82 (Degradates)	2.82 (ZO)	Data Gap	Data Gap
		Marine plants (diatom)	LC50/EC50/IC50 in ppb	Maximize (Higher LC50/EC50/IC50 preferred)	250	0.45	250	Data Gap	2.7 (Tralopyril); 470 Degradates)	Data Gap	Data Gap	Data Gap

				SEA HAWK PREMIUM QUALITY CUKOTE BIOCIDE +	CopperCoat	Pacifica Plus	Seahawk Mission Bay CSF Copper Free Antifouling	Hempasil X3 (87500)
				SLIME RESIS. ANTIFOUL. COAT.			Coating	
	Cleaning Frequency	Interval in weeks	Maximize					
				3	4	3	3	3
	Cleaning effort	Good (1)/ Fair(2)/	Minimize					
Performance		Poor (3)						
				1	1	3	2	2
	Amount of Fouling	Good (1) /Fair(2) /						
		Poor(3)	Minimize	1	1	1	1	2
	Longevity	Years	Maximize	2	2	1.5	1.5	7.5
	Application Cost	Dollars	Minimize	1038	1038	1448	1404	3858
	Annual Cleaning Cost	Dollars	Minimize	593	593	730	730	653
	Total Annualized Cost							
	Over Life of Paint	Dollars	Minimize	1133	1133	1734	1703	1188