

EDGEWOOD  
RESEARCH,  
DEVELOPMENT &  
ENGINEERING  
CENTER

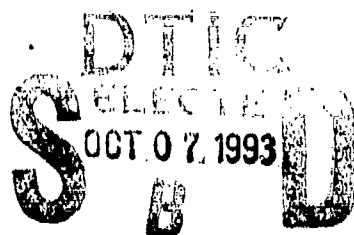
AD-A270 185



22

ERDEC-TR-094

**TOXICITY AND FATE COMPARISON  
BETWEEN SEVERAL BRASS AND  
TITANIUM DIOXIDE POWDERS**



Mark V. Haley  
Carl W. Kurnas

RESEARCH AND TECHNOLOGY DIRECTORATE

July 1993

Approved for public release; distribution is unlimited.

U.S. ARMY  
CHEMICAL  
AND BIOLOGICAL  
DEFENSE AGENCY



Aberdeen Proving Ground, Maryland 21010-5423

93-23583



5380

00 10 15 18 21 24 27 30 33 36 39 42 45 48 51 54 57 60 63 66 69 72 75 78 81 84 87 90 93 96 99

**Disclaimer**

**The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.**

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1993 July	3. REPORT TYPE AND DATES COVERED Final, 91 Jun - 91 Dec	
4. TITLE AND SUBTITLE  Toxicity and Fate Comparison Between Several Brass and Titanium Dioxide Powders			5. FUNDING NUMBERS  PR-1-84-09-7350-M76	
6. AUTHOR(S)  Haley, Mark V., and Kurnas, Carl W.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  DIR, ERDEC,* ATTN: SCBRD-RTL, APG, MD 21010-5423			8. PERFORMING ORGANIZATION REPORT NUMBER  ERDEC-TR-094	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES  *When this work was performed, ERDEC was known as the U.S. Army Chemical Research, Development and Engineering Center, and the authors were assigned to the Research Directorate.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Brass flakes (MD Both Industries, Ashland, MA), SF-150 Rich Gold, and four brands of titanium dioxide were tested to determine their toxicities to <i>Daphnia magna</i> (water flea), <i>Ankistrodesmus falcatus</i> (green algae), and <i>Selenastrum capricornutum</i> (green algae). The toxicity of the brass materials were ranked high, having EC <sub>50</sub> s below 1 mg/L for daphnia and algae. The fate of the brass materials were determined in fresh water of varying hardness, in synthetic marine salt water (30 ppt), and in physiological saline solution (9 ppt). The titanium dioxide materials were nontoxic to daphnia up to 1000 mg/L. Daphnia were able to ingest titanium dioxide and pack the entire gut without showing any apparent effects.				
14. SUBJECT TERMS  Daphnia      Algae      EC <sub>50</sub> Aquatic toxicity			15. NUMBER OF PAGES 27	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

Blank

## PREFACE

The work described in this report was authorized under Project No. 1-84-09-7350-M76, Smoke/Obscurant Munitions. This work was started in June 1991 and completed in December 1991.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for release to the public. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

**Blank**

## CONTENTS

	Page
1. INTRODUCTION .....	7
2. METHODS AND MATERIALS .....	7
2.1 Daphnia Assays .....	8
2.2 Algal Growth Inhibition Assays .....	8
2.3 Chemical Fate of the Brass Materials .....	9
3. RESULTS .....	9
4. DISCUSSION .....	10
5. CONCLUSION .....	11
LITERATURE CITED .....	21
APPENDIXES	
A. LIST OF MANUFACTURERS OF THE MATERIALS USED IN THIS REPORT .....	23
B. DESCRIPTION OF THE TEST MATERIALS AND SOME CHARACTERISTICS .....	25
C. LIST OF POLLUTANTS MONITORED IN THE WELL WATER EVERY FOUR MONTHS .....	27

## LIST OF FIGURES

1	Dissolved Copper and Zinc from Brass Material (MD Both Industries) in Fresh Water of Varying Hardness . . . . .	13
2	Dissolved Copper and Zinc in Marine Salt Mix and 9 ppt Saline Solution . . . . .	14

## LIST OF TABLES

1	List of Chemicals Used to Raise Distilled Water to the Desired Hardness . . . .	15
2	Toxicity Comparison Between Brass Materials and the Titanium Dioxide Materials . . . . .	16
3	Toxicity Comparison Between Brass, Titanium Dioxide, and Several Other Particulate Materials . . . . .	17
4	Dissolved Copper and Zinc in Fresh Water of Varying Hardness . . . . .	18
5	Dissolved Copper and Zinc in Full Salt Water Versus 9 ppt Physiological Saline Solution . . . . .	19



# TOXICITY AND FATE COMPARISON BETWEEN SEVERAL BRASS AND TITANIUM DIOXIDE POWDERS

## 1. INTRODUCTION

Extensive literature exists on the aquatic toxicity of trace metals (1). Traditionally the toxicant is introduced into the environment as a metal salt in solution and rarely in combination with other metals. Often overlooked is that many metals are released into the environment as alloys in the form of particles or filings. The constituents of the alloys may leach into the environment at various rates and cause interactions between metals that can alter the ecosystem. The brass powders examined in this report exhibit the same properties as described above. Commercially, brass powder is used in paints and pigments. The Army is considering using brass as an infrared smoke screen for troop and vehicle movement.

Few studies exist on the aquatic toxicity and fate of titanium dioxide in the environment (2,3). Titanium dioxide is widely used commercially in paints, cosmetics, dental materials, sun screens, and some experimental use in lenses. The Army is also considering using titanium dioxide as a smoke screen for troop and vehicle movement in the Army's Smoke/Obscurant program.

In this study, the acute aquatic toxicities of two brass and several titanium dioxide powders are examined. During field use, potential exists for dissemination into wetlands, fresh and marine ecosystems. This study is one of a series of studies investigating the toxicity of brass and titanium dioxide to aquatic organisms.

The fate of the brass powders were examined in fresh (using varied hardness) and marine waters. The dissociation of the brass powders into copper and zinc was monitored for 21 days.

The purpose of this study is to examine the differences in toxicity between the brass and titanium powders manufactured by different companies. In order to estimate the potential impact that these materials have on the environment, *Daphnia magna* (water flea) and *Selenastrum capricornutum* (a unicellular green algae) were used in 48 hr acute (daphnia) and 96 hr growth inhibition (algae) bioassays. These widely used, short term bioassays have well documented test procedures utilizing organisms easily maintained in the laboratory.

## 2. METHODS AND MATERIALS

This study was conducted under Good Laboratory Practices (GLP). All testing conformed to current Environmental Protection Agency (EPA) (4) and American Society for Testing and Material (ASTM) (5) guidelines.

The brass and titanium dioxide powders were obtained from several manufacturers. Appendix 1 includes the manufacturer and trade names of the materials used in this study. Appendix 2 describes some of the physical characteristics of each material.

Due to the extreme electrostatic nature and size of the brass particles, the brass material was added to a polycarbonate test tube, filled with the appropriate media to yield a concentration of 1 mg/ml. The test tube was immersed into a ultrasonic water bath to suspend the dust uniformly throughout the water column. While the particles were still in complete suspension, samples were withdrawn and added to volumetric flasks for serial dilution.

The titanium dioxide was added directly into the volumetric flasks. No ultrasonic water baths were necessary to suspend the compound.

## 2.1 DAPHNIA ASSAYS

*D. magna* were obtained from Dr. Freida Taub at the University of Washington in Seattle and cultured using methods described by Goulden, *et al.* [6]. Daphnia stock cultures were fed a mixture of vitamin enriched *Ankistrodesmus falcatus*, *Selenastrum capricornutum* and *Chlamydomonas reinhardtii* 90. Daphnia culture media was supplied from well water which was passed through a treatment system containing limestone pH adjustment, Zeata Sol iron removal, carbon filtration and UV sterilization. The well water is monitored for 92 commonly found ground water pollutants every four months by Watercheck National Testing Laboratories, Inc. located in Ypsilanti, MI. Appendix 3 lists the compounds and parameters measured.

The test beakers were placed into a temperature controlled room at 20°C with a light-dark cycle of 16:8 hrs with 315 ft candles of light. Two replicates per concentration contained 10 daphnia, less than 24 hrs old, in a total of 100 mls of solution. The pH, conductivity and hardness measurements were taken at the start of each test. Daphnia were gently touched with a pasteur pipet at 24 and 48 hrs. If the daphnia could not swim actively for 15 seconds immobilization was recorded. The EC<sub>50</sub> (the effective concentration at which 50 percent of the organisms were immobilized) values were computed using the probit analysis as prepared by Kessler [7]. The EC<sub>50</sub>s were also tabulated graphically using least square regression analyses which were used to verify all probit analyses.

## 2.2 ALGAL GROWTH INHIBITION ASSAYS

*Ankistrodesmus falcatus* and *Selenastrum capricornutum* were also obtained from Dr. Freida Taub, University of Washington, Seattle. Stock cultures of algae were maintained on 1.5% Difco-Bacto agar slants. Test algae were grown in a semi-flow through culture apparatus on T82MV(8) and taken during log phase growth for inoculation into the test flasks. Five hundred ml Erlenmeyer flasks with ground glass stoppers were used as test chambers. One hundred mls of T82MV were placed in each test chamber and inoculated with approximately  $4.0 \times 10^4$  algal cells per ml. The inoculated test chambers were placed in an incubator under the same conditions as described above for the daphnia 48 hr assays. Using a Newbauer Counting Chamber, cell densities were determined every 24 hrs for five consecutive days. The area under the growth curve (A) was calculated using the following equation:

$$A = \frac{(N_0 + N_1) - 2N_0}{2} \times (t_1) + \frac{(N_1 + N_2) - 2N_0}{2} \times (t_2 - t_1) + \frac{(N_{n-1} + N_n) - 2N_0}{2} \times (t_n - t_{n-1}) \quad (1)$$

where:

$N_0$  = number of cells at  $t_0$

$N_1$  = number of cells at  $t_1$

$N_n$  = number of cells at  $t_n$

$t_1$  = time of first measurement

$t_n$  = time of the nth measurement

The percent inhibition was calculated using the area under the growth curve. The following equation was used to calculate Percent inhibition (%In):

$$\%In = \frac{A_c - A_t}{A_c} \times 100 \quad (2)$$

where:

$A_c$  = area of control growth curve

$A_t$  = area of treatment growth curve

The %In values were plotted against the concentrations. A least square regression line was calculated and the IC<sub>50</sub> (the concentration at which algal growth was reduced to 50% of the control) was determined. ANOVA was run on the replicates to determine if any of the groups were significantly different. The Dunnett's test was conducted to determine which treatments groups were different from the control.

### 2.3 CHEMICAL FATE OF THE BRASS MATERIALS

The dissociation of the brass materials into copper and zinc was monitored for 21 days in fresh water of various hardness, sea water (30 ppt, pH 8.2) and physiological saline solution (9 ppt, pH 5.8).

In the fresh water fate studies, distilled water and reagent grade salts were used to harden the water to desired levels. Table 1 list the chemicals used to bring distilled water to the desired hardness levels (9). The actual pH and hardness is also listed for each level at time 0. Forty Fathoms synthetic sea water manufactured by Marine Enterprises, Inc. (10) was prepared in distilled water and mixed to a final salinity of 30 ppt. The Physiological saline solution(sodium chloride injection) was purchased from Travenol Laboratories, Inc. This solution was used directly out of the bottle with no dilution.

Brass stock suspensions of 1 mg/ml were prepared as described above. Two ml of the stock solution were placed in 250 ml polycarbonate screw top flasks and filled with the appropriate media to yield a final volume of 200 ml with a concentration of 10 mg/L. There were six replicate flasks prepared for each water type. Each flask was randomly assigned to one sampling day (Day 0, 1, 3, 7, 14, or 21). Two 10 ml samples were withdrawn from the flasks (on the assigned day) and filtered through .45 micron filters. Samples were analyzed with atomic absorption (AA) spectroscopy for copper and zinc. Blanks of each water type were also run to monitor back ground concentrations of copper and zinc. Results were plotted against a standard curve and subjected to regression analysis to determine the levels of soluble copper and zinc in solution.

### 3. RESULTS

The titanium dioxide (TiO<sub>2</sub>) materials did not show any apparent toxic effects to daphnia up to 1000 mg/L. Microscopic examination (10x) of the daphnia following exposure to TiO<sub>2</sub>, showed that the organisms ingested the materials and passed it through the gut. Internal damage was not apparent in 48 hrs. After 24 hrs into the test all the TiO<sub>2</sub> had settled to the bottom of the test chambers except for the Kerr McGee (Tronox CRX). This material stayed in suspension, allowing ingestion to occur for the entire duration (48 hrs) of the test. The TiO<sub>2</sub> materials were ranked 0 (not

toxic), (based on a scale of 0-9, 9 being the most toxic) on the EPA Chemical Scoring System for Hazard and Exposure Identification (11). See table 2 for EC<sub>50</sub> results and 95% confidence limits.

The brass materials were also ingested (observed in the highest concentrations), however there was not enough time for the brass to pass through the gut before the daphnia had expired. The toxicity of the two brass materials (SF-150 Rich Gold, and MD Both Brass) were similar (see table 2 for EC<sub>50</sub> values and EPA rankings). Daphnia were the most sensitive to brass with EC<sub>50</sub>s ranging from .01 to .02 mg/L, followed by *S. capricornutum* and *A. falcatus* with EC<sub>50</sub>s ranging from .08 to 0.2 mg/L. Table 3 lists EC<sub>50</sub> comparisons between brass, TiO<sub>2</sub> and several other materials. Clearly the brass particulate is the most toxic to all the organisms tested.

The fate of the brass materials was monitored in salt and fresh waters for 21 days. In fresh water the soluble metal concentrations increased up to day one, then leveling to equilibrium at day three (figure 1). The highest concentration of soluble copper, after equilibrium, was reached in very hard (VH) water. The highest concentration of soluble zinc was in VH water for the MD Both brass, and very soft (VS) water for the SF-150 Rich Gold (equilibrium was never reached for SE-150). Table 4 presents copper and zinc concentrations in fresh waters of varying hardness. The behavior of soluble metals in salt water had several differences from fresh water. The copper levels at day 0 were very high, dropping down to equilibrium at day 1. The zinc followed similar trends as in fresh water (figure 2). The full marine salt mix liberated higher levels of copper than the saline solution. However the saline solution liberated higher levels of zinc.

#### 4. DISCUSSION

An extensive literature search was conducted to locate environmental data on titanium dioxide. Computer and library searches revealed no information on the aquatic toxicity and fate of titanium dioxide.

Aquatic ecosystems can be impacted in two ways; direct exposure to dissolved materials in solution and exposure through ingestion of particulate materials. The test organism used in this study (*D. magna*) is a filter feeder. Daphnia filter the surrounding water and ingest any particulate that is trapped in their filtering apparatus. They do not discriminate between particulate type. TiO<sub>2</sub> was clearly ingested by the daphnia and passed through the entire length of the gut within 24 hrs. After 24 hrs the particulates settled to the bottom of the test chamber becoming unavailable for the daphnia to ingest. The ability of the daphnia to clear the gut region and continue a normal life cycle was not determined. However, it is assumed that if the entire length of the gut becomes filled, the clearing mechanisms were not damaged and normal digestion would resume when the materials clear the water column.

The Kerr McGee TiO<sub>2</sub> (Tronox CRX) remained suspended in the water column throughout the 48 hrs of testing. This allowed the daphnia to filter this material for the entire duration of the test. The extended exposure did not show any apparent toxic effects.

Long term effects on aquatic organisms exposed to TiO<sub>2</sub> are not known. It is apparent that the TiO<sub>2</sub> is not toxic to daphnia (up to 1000 mg/L) on a short term basis (48 hrs). However, long term exposure may cause mechanical damage to body parts such as gill filaments and secondary antenna.

Most of the open literature dealing with metal toxicity involve metal salts, overlooking metals introduced into the environment as particulates and alloys such as brass, pewter, solders and stainless steel. The constituents of alloys may leach into

the environment at various rates and the interactions between the metals may alter the toxic response of a biological community [14].

The toxicity of metals to aquatic organisms are influenced by pH, hardness, conductivity, humic matter and suspended sediments. Low pH, and/or low hardness will increase metal toxicity to aquatic organisms. However, if the hardness of the water is high and the pH near neutral, the toxicity from metals is reduced. In part, this is due to the competition between the trace metal and the hardness metal (Ca and Mg) for the active sites on the cell membrane [15]. Excess trace metals on the membranes alter the effectiveness of gas exchange and the organisms die from respiratory complications [15]. However, in natural waters trace metals typically form stable hydroxy or carbonate complexes and only a small fraction of the total concentration remains in solution. Humic materials and suspended clays will reduce the effects of metals on aquatic organisms. These materials will complex the metals reducing their ability to bind to active sites in the cell membrane. In most cases trace metals will be deposited into bottom sediments rendering them relatively harmless to pelagic organisms. However, bottom and sub-surface dwellers may be subjected to toxic insult through ingestion and dermal contact.

The brass materials used in this study consist of a mixture of copper, zinc, and aluminium (see appendix 2). When suspended in water the brass dissociates into the water column and reaches equilibrium within three days. Dissolved copper and zinc from the brass particulate was highly toxic to daphnia and algae (Table 2.). There were no major differences in toxicity between the two brass materials to the test organisms used in this study.

Copper and zinc concentrations, between the two type of brass materials in the waters of varying hardness, were similar (Figure 1) except for the concentration of zinc from the SF-150 Brass in very soft water (Table 3). The zinc levels did not reach equilibrium after 21 days. The highest levels of copper occurred in the very hard water which was not expected since the pH of the water was above 7.0. The pH and hardness of the water drastically effects the amount of dissolved metals in solution [17].

The dissociation of the brass materials in salt water exhibit a markedly different trend than in fresh water (figure 1 & 2). At day 0 the copper levels were elevated then dropped to equilibrium levels, compared to the fresh water levels which started out with low copper concentrations increasing to equilibrium. It is hypothesized that the corrosive nature of the salt water dissolve the constituents in the brass much quicker than in fresh water. Since the test chambers were constructed of polycarbonate, adsorption to the container has been ruled out. It is possible that free copper ions were binding with the chloride in the media to form a precipitate which gets filtered out before AA analysis.

The MD Both brass has approximately 6 % more copper contained in the material than SF-150 Brass. This is not evident in the AA analysis of any of the water types (fresh or salt).

Brass suspended in the Marine salt mix at equilibrium had a copper ion concentration one order of magnitude higher than the brass suspended in the saline solution, which was not expected. Due to the low pH (5.8) the saline solution was expected to have higher levels of dissolved metals than the marine salt mix.

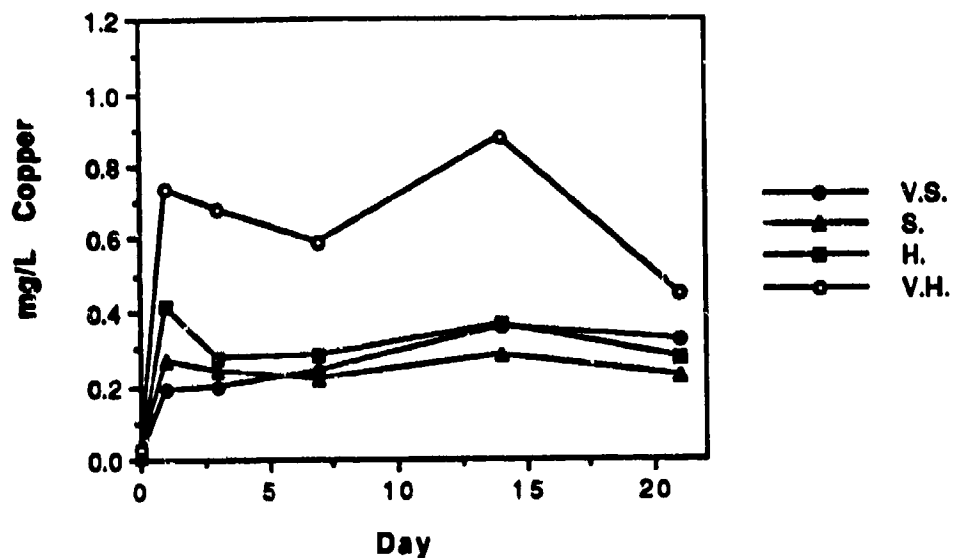
## 5. CONCLUSION

1. The  $\text{TiO}_2$  did not show any toxic effect to daphnia after 48 hrs of exposure. The titanium was ingested by the daphnia and still no apparent toxic effects were observed.

2. The brass dust (SF-150 Brass and MD Both) were extremely toxic to daphnia and two species of algae and there was no significant difference in toxicity between the two types of brass.

3. At time zero the salt water media had much higher levels of copper than was found in any of the fresh water media.

### COPPER CONCENTRATIONS FROM MD BOTH BRASS



### ZINC CONCENTRATIONS FROM MD BOTH BRASS

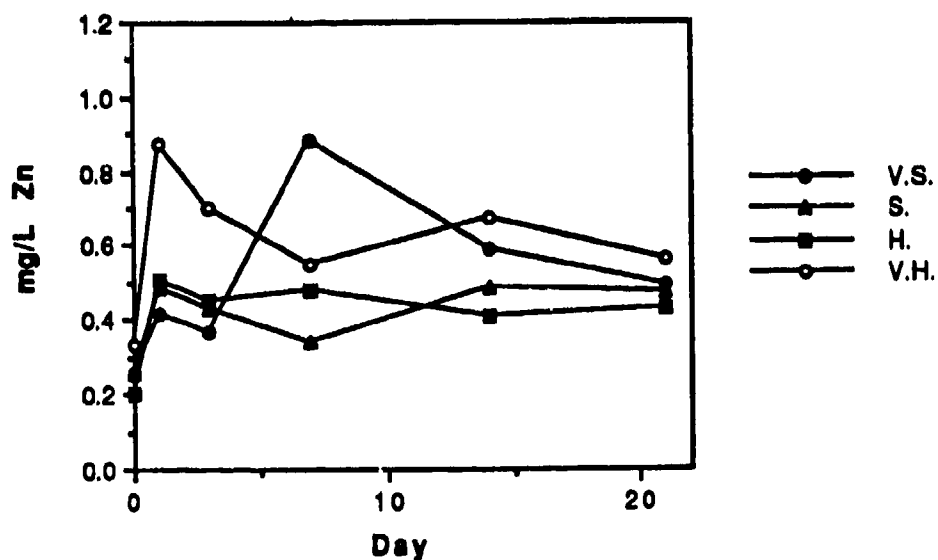
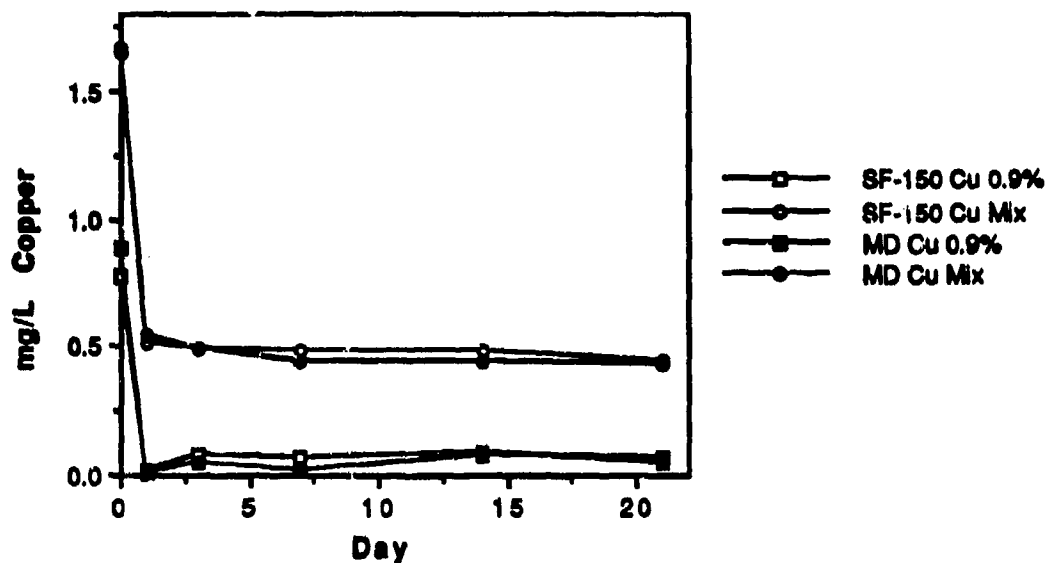


Figure 1. Dissolved copper and zinc from brass material (MD Both Industries) in fresh water of varying hardness.

## COPPER CONCENTRATIONS FROM BRASS IN SALT WATER



## ZINC CONCENTRATIONS FROM BRASS IN SALT WATER

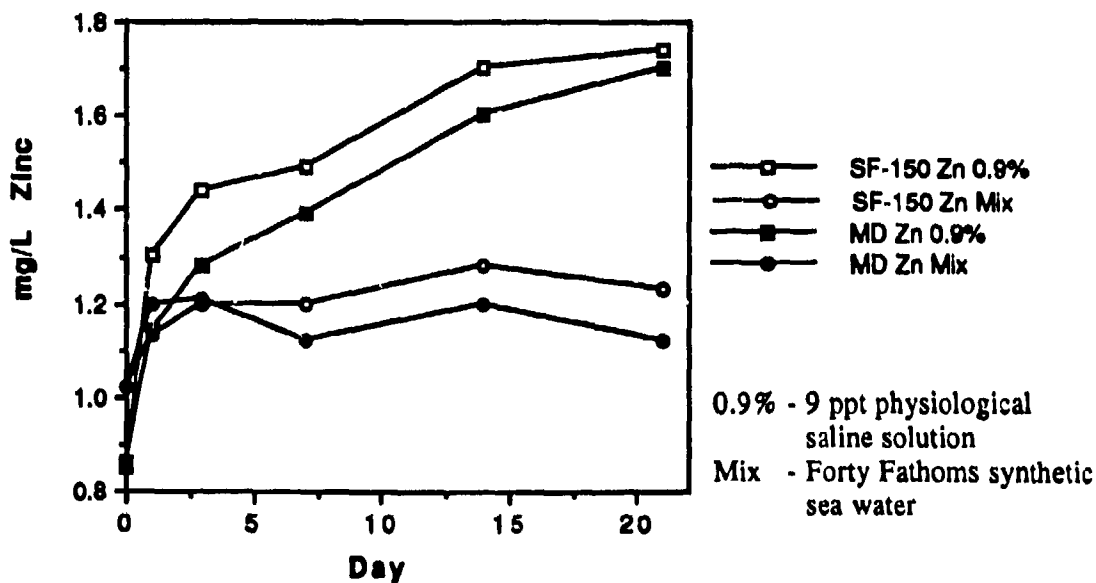


Figure 2. Dissolved copper and zinc in marine salt mix and 9 ppt saline solution. Definition of the legend is as follows: 0.9% - is the 9 ppt physiological saline solution, Mix - is the synthetic marine salt mix media, MD - is MD Both Industries brass, SF-150 - is Obron Corporation brass.



Table 1. List of chemicals used to raise distilled water to the desired hardness.

Water Type	NaHCO <sub>3</sub>	CaSO <sub>4</sub> (2H <sub>2</sub> O) (Required Salts, mg/L)	MgSO <sub>4</sub>	KCl	pH*	Hardness* (mg/L CaCO <sub>3</sub> )
Very Soft	12.0	7.5	7.5	0.5	7.3	10.0
Soft	48.0	30.0	30.0	2.0	7.8	28.0
Hard	192.0	120.0	120.0	8.0	8.4	125.0
Very Hard	384.0	240.0	240.0	16.0	8.4	190.0

\* The pH and hardness was measured at time 0 before the addition of brass.

Table 2. Toxicity comparison between brass materials and the titanium dioxide materials.

TEST MATERIAL	TEST SPECIES	EC <sub>50</sub> (mg/L) (95% Confidence Limits)	EPA* Ranking
SF-150 B	<i>D. magna</i>	0.021 (0.160 - 0.026)	9 (12)
	<i>A. falcatus</i>	0.242 (0.120 - 0.470)	9 (13)
	<i>S. capricornutum</i>	0.087 (0.070 - 0.110)	9
MJ Both Brass	<i>D. magna</i>	0.012 (0.009 - 0.015)	9
	<i>A. falcatus</i>	0.160 (0.140 - 0.190)	9
	<i>S. capricornutum</i>	0.110 (0.090 - 0.150)	9
Titanox 1000 (TiO <sub>2</sub> )	<i>D. magna</i>	>1000.0	0
Tronox CRX (TiO <sub>2</sub> )	<i>D. magna</i>	>1000.0	0
Tioxide R-PC6 (TiO <sub>2</sub> )	<i>D. magna</i>	>1000.0	0
Tiona RCL-69 (TiO <sub>2</sub> )	<i>D. magna</i>	>1000.0	0

\* Toxicity ranking based on the EPA chemical scoring system for hazard and exposure identification. Scoring is based on a scale of 0 - 9, 9 being the most toxic. The authors have ratted the scale with the following potency levels: 0 - 3 (not toxic - low toxicity), 4 - 5 (moderate toxicity), and 6 - 9 (high toxicity).

\*\* All *D. Magna* EC<sub>50</sub> results are 48hrs in duration.

\*\*\* All *A. falcatus* and *S. capricornutum* EC<sub>50</sub> results are 96hrs in duration.

Table 3. Toxicity comparison between brass, titanium dioxide, and several other particulate materials.

TEST MATERIAL	TEST SPECIES	EC <sub>50</sub> (mg/L)	EPA* Ranking
SF-150 Brass	<i>Daphnia magna</i>	0.021	9
	<i>Ankistrodesmus falcatus</i>	0.242	9
	<i>Selenastrum capricornutum</i>	0.087	9
MD Both Brass	<i>Daphnia magna</i>	0.012	9
	<i>Ankistrodesmus falcatus</i>	0.160	9
	<i>Selenastrum capricornutum</i>	0.110	9
Micro 260 (Graphite)	<i>Daphnia magna</i>	80.6	4
	<i>Ankistrodesmus falcatus</i>	>100.0	4
Jet-A (Jet Fuel)	<i>Daphnia magna</i>	3.1	7
	<i>Selenastrum capricornutum</i>	4.2	7
Fibers (Graphite )	<i>Daphnia magna</i>	>100.0	4
Fibers (Nickel Graphite)	<i>Daphnia magna</i>	>100.0	4
Silica	<i>Daphnia magna</i>	>1000.0	0
Titanox 1000 (TiO <sub>2</sub> )	<i>Daphnia magna</i>	>1000.0	0
Tronox CRX (TiO <sub>2</sub> )	<i>Daphnia magna</i>	>1000.0	0
Tioxide R-FC6 (TiO <sub>2</sub> )	<i>Daphnia magna</i>	>1000.0	0
Tiona RCL-69 (TiO <sub>2</sub> )	<i>Daphnia magna</i>	>1000.0	0
Teflon	<i>Daphnia magna</i>	> 1000.0	0
Stainless Steel (304)	<i>Daphnia magna</i>	>5000.0	0
Celion Carbon Fibers (C-6-S)	<i>Daphnia magna</i>	713.4	3
	<i>Ankistrodesmus falcatus</i>	>2000.0	0
Celion Carbon Fibers (burned sample)	<i>Daphnia magna</i>	>1000.0	0
	<i>Ankistrodesmus falcatus</i>	>2000.0	0
Polycrystalline Iron Wickers	<i>Daphnia magna</i>	>100.0	4

\* Toxicity ranking based on the EPA chemical scoring for hazardous and exposure identification.

Scoring is set on a scale of 1 - 9, 9 being the most toxic.

\*\* All *D. Magna* EC<sub>50</sub> results are 48hrs in duration.

\*\*\* All *A. falcatus* and *S. capricornutum* EC<sub>50</sub> results are 96hrs in duration.

**Table 4.** Dissolved copper and zinc in fresh water of varying hardness is presented below. The numbers listed below are the average amount of Cu and Zn in solution after equilibrium was reached. The percentage ionization is presented in parentheses.

		Freshwater Type*			
		VS	S	H	VH
<b>MD Both Brass</b>					
<b>Cu++</b>	0.27 mg/L (3.7%)	0.24 mg/L (3.2%)	0.29 mg/L (4.0%)	0.64 mg/L (8.7%)	
<b>Zn++</b>	0.58 mg/L (23.0%)	0.43 mg/L (17.0%)	0.44 mg/L (17.5%)	0.62 mg/L (24.6%)	
<b>SF-150 Brass (15)</b>					
<b>Cu++</b>	0.41 mg/L (5.9%)	0.33 mg/L (4.8%)	0.41 mg/L (5.9%)	0.53 mg/L (7.7%)	
<b>Zn++</b>	1.83 mg/L (66.6%)**	0.44 mg/L (16.0%)	0.37 mg/L (13.4%)	0.37 mg/L (13.4%)	

\* VS - very soft water, S - soft water, H - hard water, VH - very hard water.

\*\* Equilibrium not reached, therefore 21 day levels were used in this table.

**Table 5. Dissolved copper and zinc in full salt water versus 9 ppt physiological saline solution. The numbers listed below indicate an average amount of Cu and Zn in solution after equilibrium was reached. The percent ionization is presented in parentheses.**

	Marine Salt Mix	9 ppt Saline Solution
<b>MD Both Brass</b>		
Cu++	0.46 mg/L (6.8%)	0.04 mg/L (0.6%)
Zn++	1.16 mg/L (42.1%)	1.70 mg/L (61.8%)*
<b>SF-150 Brass</b>		
Cu++	0.48 mg/L (6.4%)	0.06 mg/L (0.8%)
Zn++	1.20 mg/L (47.8%)	1.74 mg/L (69.3%)*

\* Equilibrium was not reached, therefore day 21 levels were used in this table.

**Blank**

## LITERATURE CITED

1. Leland, H.V. and Kuwabara, J.S., in *Fundamentals of Aquatic Toxicology: Methods and Applications*, G.M.Rand and S.R.Petrocelli, Eds., Hemisphere Publishing Corp., Washington, DC, 1985, pp.374-415.
2. Haley, M.V., The comparative toxicity of grenade disseminated ironox titanium dioxide and EA-5999, Technical Report CRDEC-TR-245, January 1991.
3. Johnson, D.W., Haley, M.V., Hart, G.S., Muse, W.T., and Landis, W.G., Toxicity of brass particulate to *Daphnia magna*, Technical Report CRDC-TR-85006, November, 1985.
4. U.S.Environmental Protection Agency, Users guide: procedures for conducting *Daphnia magna* toxicity bioassays. EPA-660/8-87/011. March 1987
5. American Society for Testing and Materials. Standard E729, Guide for conducting acute toxicity tests with fishes, macroinvertebrates and amphibians, 1986
6. Goulden, C.E., R.M. Conotto, J.A. Hendrickson, Jr., L.L. Hornig and K.L. Johnson, Procedures and recommendations for the culture and use of *Daphnia magna* in bioassay studies. ASTM Special Technical Report Publication 766, p 139-160, 1982
7. Florence Kessler, Probit analysis, U.S. EPA, 26 West Martin Luther King Dr., Cincinnati, Ohio 45268.
8. Taub, F.B. and Read, P.L., Standardized aquatic microcosm protocol, Vol. II, Final Report Contract No. 223-80-2352, Food and Drug Administration, Washington, DC, 1983.
9. U.S.Environmental Protection Agency, Methods for acute toxicity tests with fish, macroinvertebrates and amphibians, EPA 660/3-75-009, 1975.
10. Marine Enterprises, Inc., 8755 Mylander Lane, Baltimore, Maryland, 21204.
11. O'Bryan, T. and R. Ross, Chemical scoring system for hazard and exposure assessments, Draft Report, Office of Toxic Substances, U.S.E.P.A.
12. Johnson, D.W., M.V. Haley, G.S. Hart, W.T. Muse and W.G. Landis, Acute toxicity of brass particles to *Daphnia magna*, *Journal of Applied Toxicology*, Vol.6(3), 225-228, 1986
13. Haley, M.V., D.W. Johnson, G.S. Hart, W.T. Muse and W.G. Landis, The toxicity of brass dust to the microalgae *Ankistrodesmus falcatus* and *Selenastrum capricornutum*, *Journal of Applied Toxicology*, Vol.6 (4), 281-285, 1986
14. Adams, T., and Sanders, J.R., The effects of pH on the release to solution of zinc, copper and nickel from metal-loaded sewage sludge, *Environmental Pollution, Series B*, Vol. 8, P85-99, 1984.
15. Wentzel, R.S., Muse, W.T. and Riley, E. P., The aquatic fate of brass powder, CRDEC-TR-86042, U.S.Army Chemical Research Development and Engineering Center, May 1986, pp 48 - 68.

16. Pagenkopf, G.K., Gill surface interaction model for trace-metal toxicity to fishes: role of complexation, pH, and water hardness, Environmental Science and Technology, Vol. 17, No. 6, p 342-347, 1983.

17. Chakoumakos, C., Russo, R.C. and Thurston, R.V., toxicity of copper to cutthroat trout (*Salmo clarki*) under different conditions of alkalinity, pH and hardness, Envir. Sci. Technol., Vol. 13, pp 213-219, 1979.



## APPENDIX A

### LIST OF MANUFACTURERS OF THE MATERIALS USED IN THIS REPORT

Manufacturer	Address	Material	Trade Name
NL Chemicals	PO Box 700 Hightstown, NJ 08520	TiO <sub>2</sub>	Titanox 1000
Kerr-McGee Chemical Corp (Experimental)	Kerr-McGee Center Oklahoma City, OK 73125	TiO <sub>2</sub>	Tronox CRX
Tioxide American, Inc.	Suite 447 2000 Century Plaza Columbia, MD 21044	TiO <sub>2</sub>	Tioxide R-FC6
SCM Chemicals	7 St Paul Street Baltimore, MD 21202	TiO <sub>2</sub>	Tiona RCL-69
MD-Both Industries Brass	Box 506 Nickerson Rd Ashland, MASS 01721	Brass	MD-Both
Obron Corporation Gold	8 N. State Street Painesville, OH 44077	Brass	SF-150 Rich

Blank

## APPENDIX B

### DESCRIPTION OF THE TEST MATERIALS AND SOME CHARACTERISTICS

#### Trade Name

Titanox 1000 (TiO <sub>2</sub> )	Description:	white powder
	Density:	3.9 g/cm <sup>3</sup>
	Solubility:	insoluble
	Weight / Gallon:	32.5
	Composition:	98.5 % TiO <sub>2</sub>
Tronox CRX (Experimental) (TiO <sub>2</sub> )	Description:	white powder
	Density:	4.2 g/cm <sup>3</sup>
	Solubility:	insoluble
	Weight / Gallon:	39.9
	Composition:	97.0 % TiO <sub>2</sub>
Tioxide R-FC6 (TiO <sub>2</sub> )	Description:	white powder
	Density:	4.0 g/cm <sup>3</sup>
	Solubility:	insoluble
	Weight / Gallon:	9.6
	Composition:	97.0 % TiO <sub>2</sub>
Titan RCL-69 (TiO <sub>2</sub> )	Description:	white powder
	Density:	4.2 g/cm <sup>3</sup>
	Solubility:	insoluble
	Weight / Gallon:	
	Composition:	97 % TiO <sub>2</sub>
MD-Both Brass	Description:	bronze powder
	Composition:	74.3 % copper
		25.1 % zinc
		0.45 % aluminum
SF-150 Brass	Description:	bronze powder
	Composition:	68.5 % copper
		27.5 % zinc
		0.20 % aluminum

\* The Tronox CRX was an experimental formulation and the exact technical data are not available. The data above for Tronox CRX were obtained through personal communication with other researchers.

**Blank**

## APPENDIX C

### LIST OF POLLUTANTS MONITORED IN THE WELL WATER EVERY FOUR MONTHS

#### METALS

Arsenic  
Barium  
Cadmium  
Chromium  
Copper  
Iron  
Lead  
Manganese  
Mercury  
Selenium  
Silver  
Sodium  
Zinc

#### INORGANICS AND PHYSICAL PARAMETERS

Alkalinity  
Chloride  
Fluoride  
Nitrite  
Nitrate  
Hardness  
pH  
Total Dissolved Solid  
Turbidity

#### ORGANICS

Bromoform  
Bromodichloromethane  
Chloroform  
Dibromochloromethane  
Benzene  
Vinylchloride  
Carbontetrachloride  
1,2-Dichloroethene  
Trichloroethylene  
1,4-Dichlorobenzene  
1,1-Dichloroethylene  
1,1,1-Trichloroethane  
Bromobenzene  
Bromoethane  
Chlorobenzene  
Chloroethane

#### ORGANICS CONT'

Chloroethylvinyl ether  
Chloromethane  
O-Chlorotoluene  
P-Chlorotoluene  
Dibromochloropropane  
Dibromomethane  
1,2-Dichlorobenzene  
1,3-Dichlorobenzene  
Dichlorodifluoromethane  
1,1-Dichloroethane  
Trans-1,2-Dichloroethylene  
Cis-1,2-Dichloroethylene  
Dichloromethane  
1,2-Dichloropropane  
Trans 1,3-Dichloropropene  
Cis 1,3-Dichloropropene  
2,2-Dichloropropane  
1,1-Dichloropropene  
1,3-Dichloropropane  
Ethylbenzene  
Ethylenedibromide  
Styrene  
1,1,1,2-Tetrachloroethane  
1,1,2,2-Tetrachloroethane  
Tetrachloroethylene  
Trichlorobenzene  
1,1,2-Trichloroethane  
Trichlorofluoromethane  
1,2,3-Trichloropropane  
Toluene  
Xylene

#### ORGANICS (Pesticides)

Alachlor	Hexachloropentadiene
Atrazine	Lindane
Chlordane	Methoxychlor
Aldrin	PCBs
Dichloran	Pentachloronitrobenzene
Diieldren	Silvex 2,4,5-TP
Endrin	Simazine
Heptachlor	Toxaphene
Heptachlor Epoxide	Trifluralin
Hexachlorobenzene	2,4-D