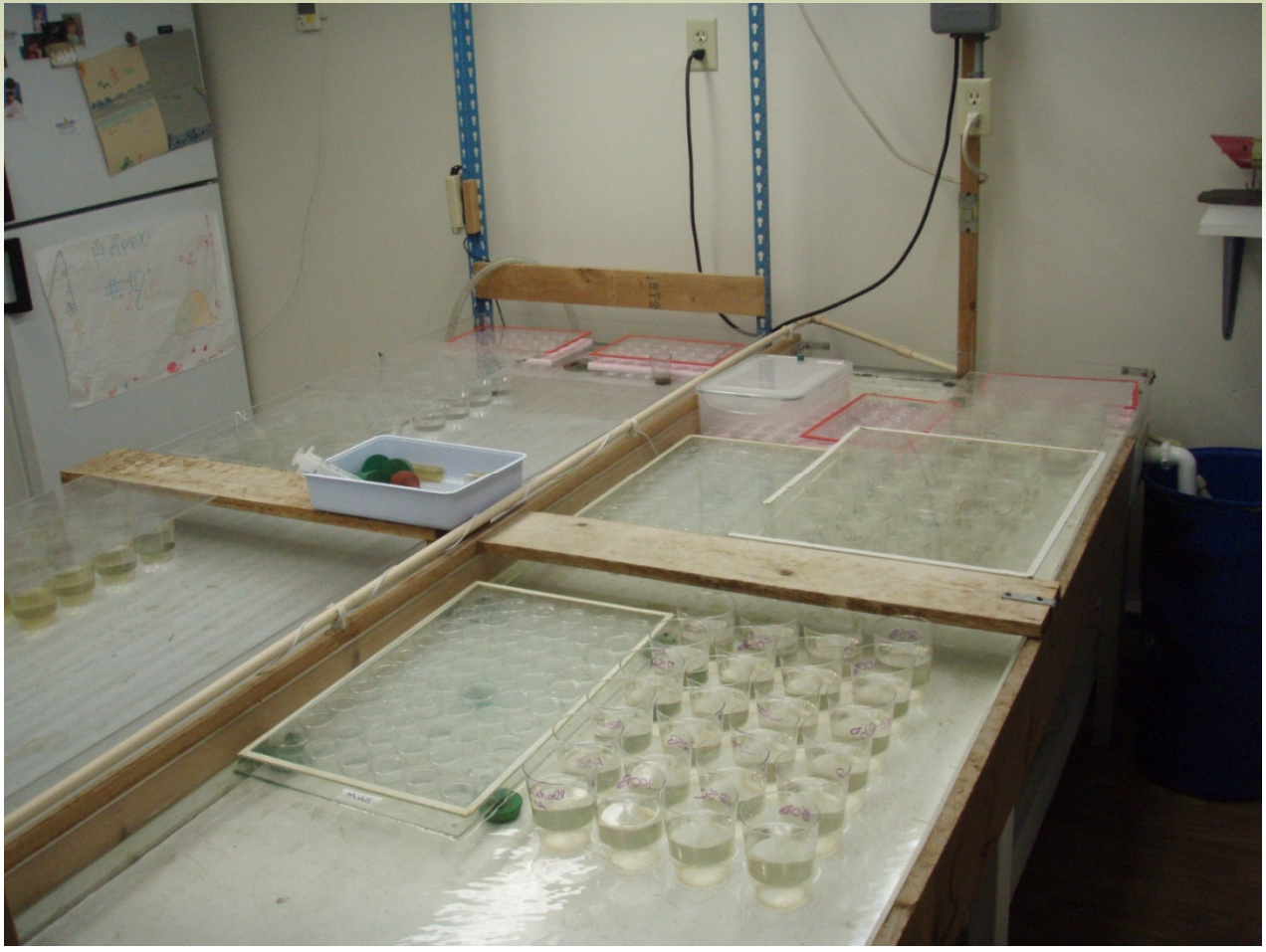
Determining the Aquatic Toxicity of Deicing Materials

- Laboratory-based study to evaluate the aquatic toxicity of liquid deicing chemicals
- Acute and "chronic" tests
- Test species
  - *Ceriodaphnia dubia*
    - Water flea, zooplankton
  - *Pimephales promelas*
    - Fish, fathead minnow
  - *Selenastrum capricornutum*
    - Algae

The Laboratory



Study Design

- Acute and chronic toxic effects
- Acute
  - 48 to 96 hour test
  - Measure survival
- Chronic
  - 7 day test (C. dubia, fathead)
  - 4 day test (algae)
  - Measure growth, reproduction, and survival
- Measureable outcome-endpoints

Study Design
endpoints

- LC50
  - Concentration at which there is a 50% reduction in survival...
- IC25
  - Concentration at which there is a 25% reduction in young production, growth...
- IC50
  - Concentration at which there is a 50% reduction in young production, growth...
- NOEC
  - Highest concentration at which there is no toxicity...

...compared to the controls

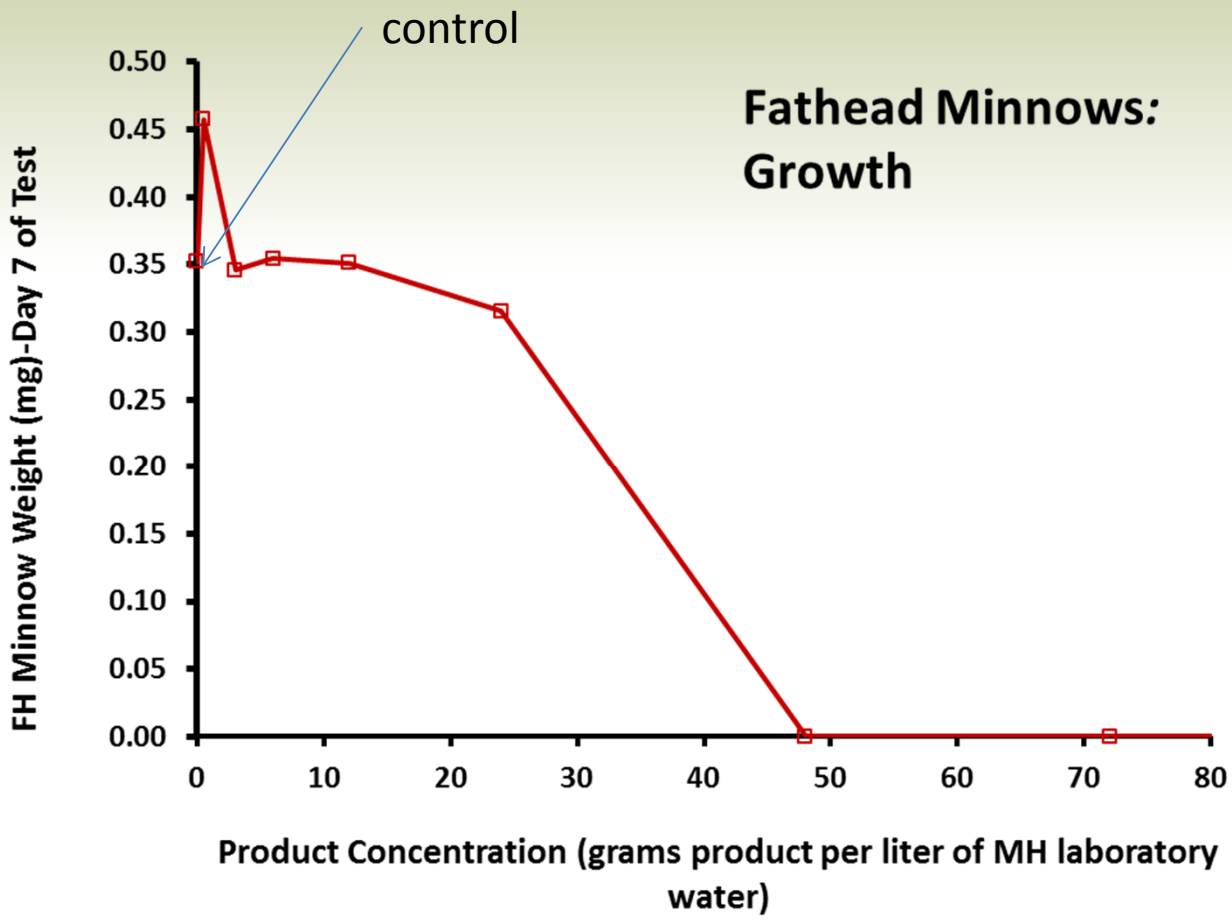
Study Design

- Dose-response
  - Add a range of volumes of deicing chemical to water
  - Get a range of responses from the test organisms
  - Result is a curve showing how the organism responds

Products Evaluated

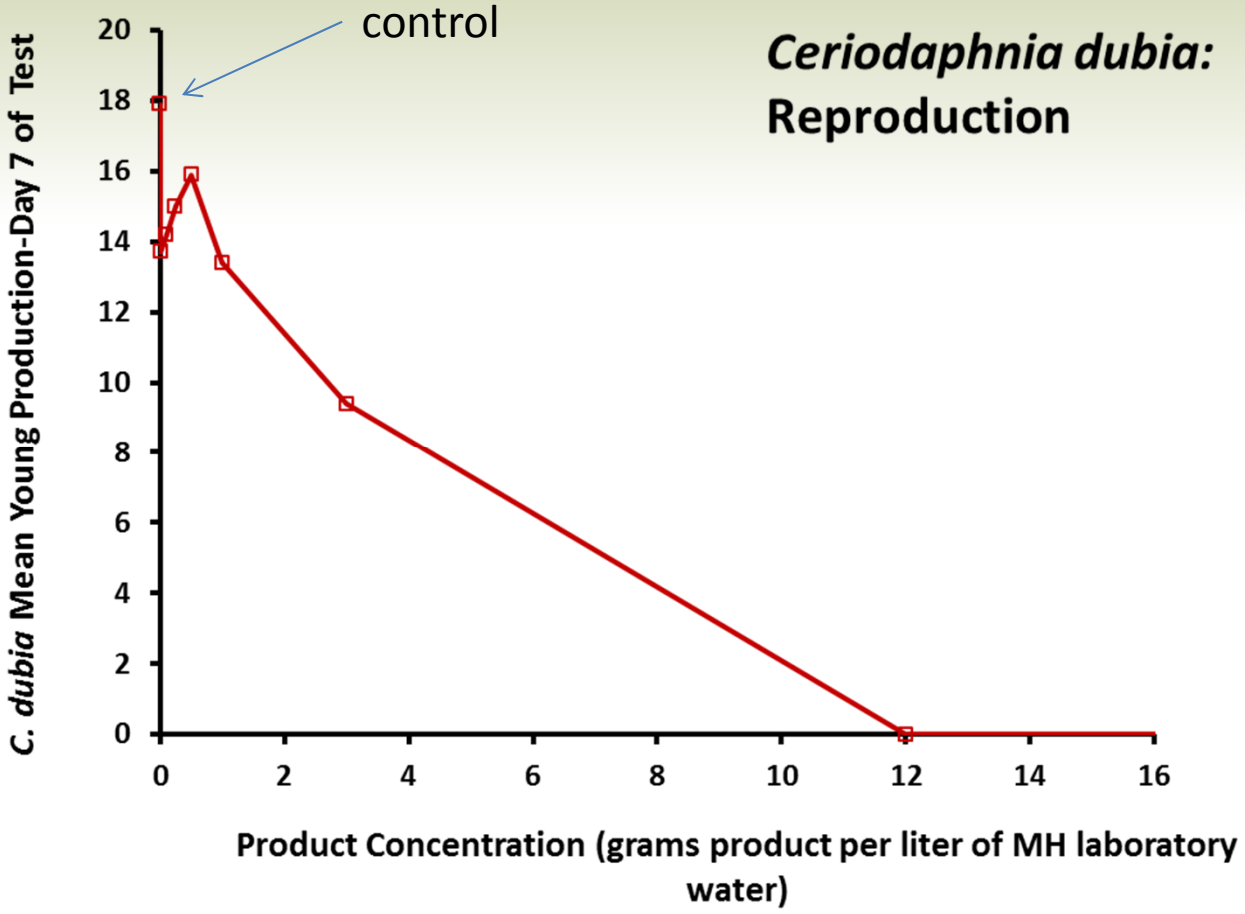
1. Watershed Cl inhibitor with sodium chloride salt brine
2. Beet 55 inhibitor with sodium chloride salt brine
3. FreezGard CI Plus inhibitor-magnesium chloride
4. Meltdown Apex inhibitor-magnesium chloride
5. Road Guard Plus inhibitor-calcium chloride
6. Boost inhibitor-calcium chloride
7. CF-7 inhibitor-potassium acetate
8. Apogee-glycerol

Toxicity Test Dose-Response Example: Watershed CI



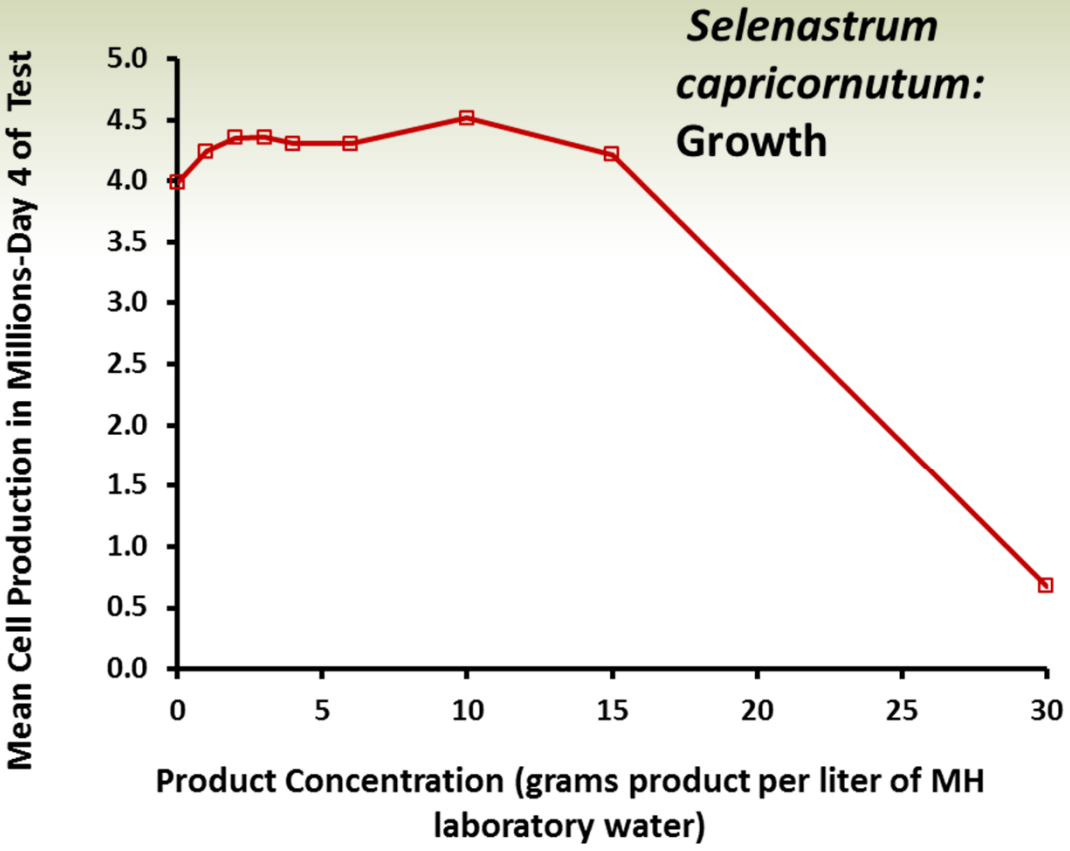
Toxicity Test Dose-Response Example: Watershed CI

chronic



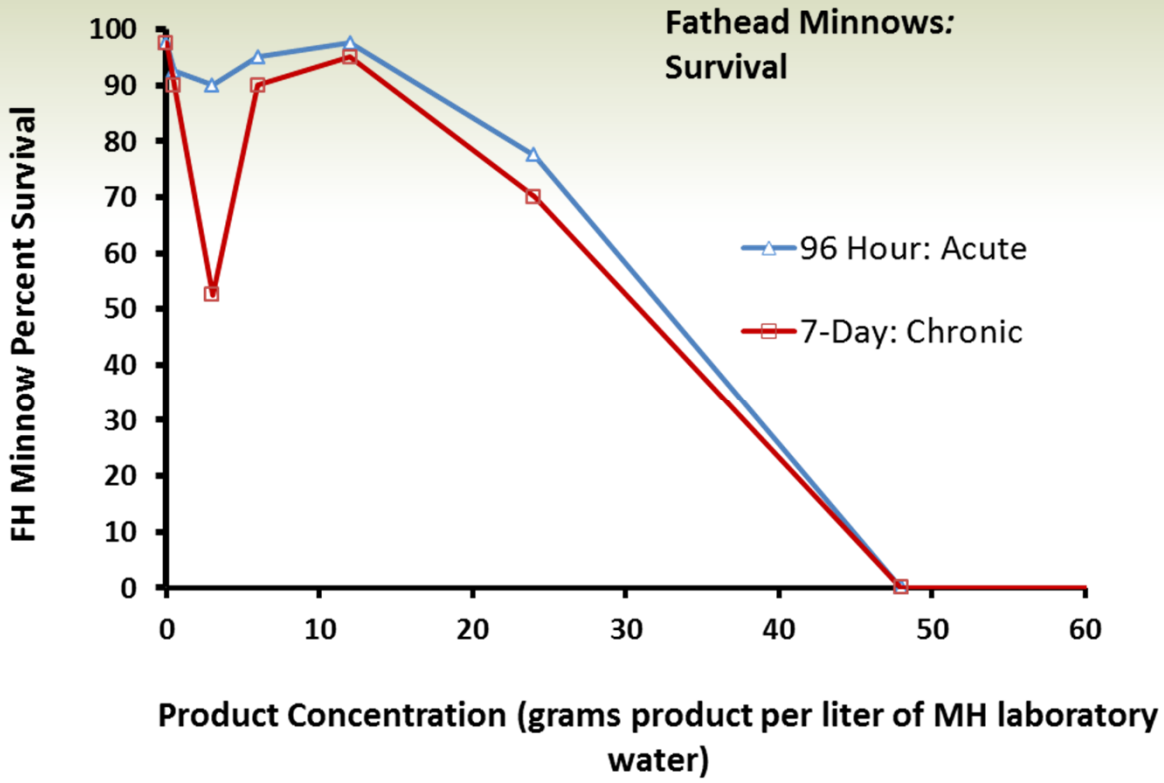
Toxicity Test Dose-Response Example: Watershed CI

chronic



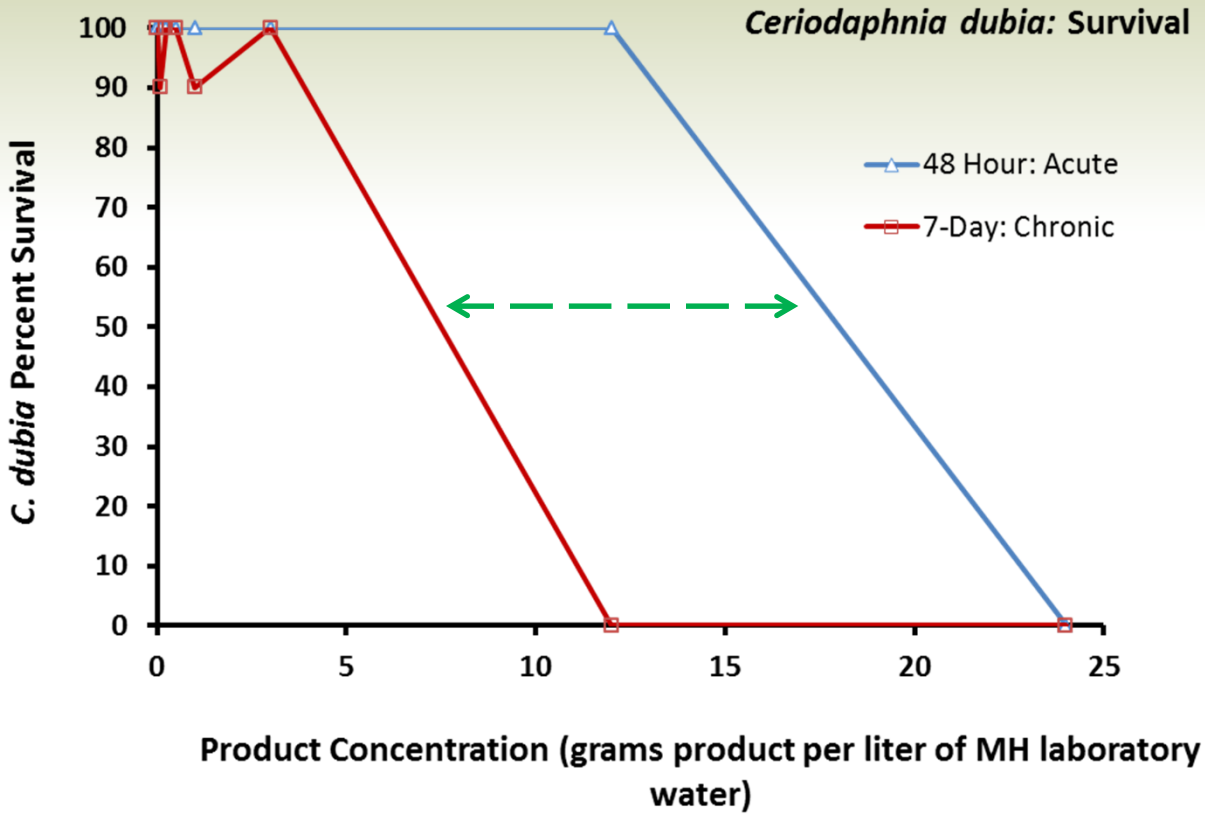
Toxicity Test Dose-Response Example: Watershed CI

Acute and Chronic



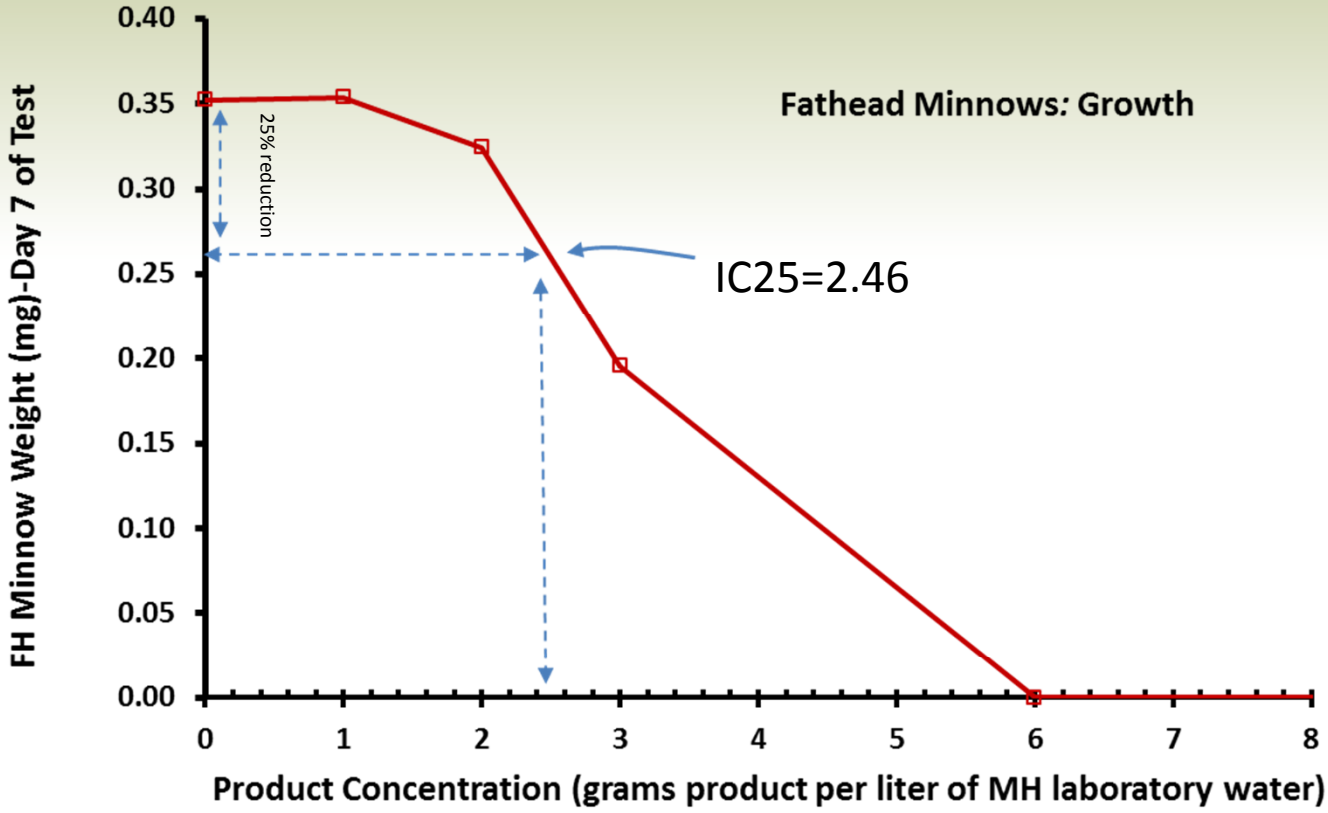
Toxicity Test Dose-Response Example: Watershed CI

Acute and Chronic



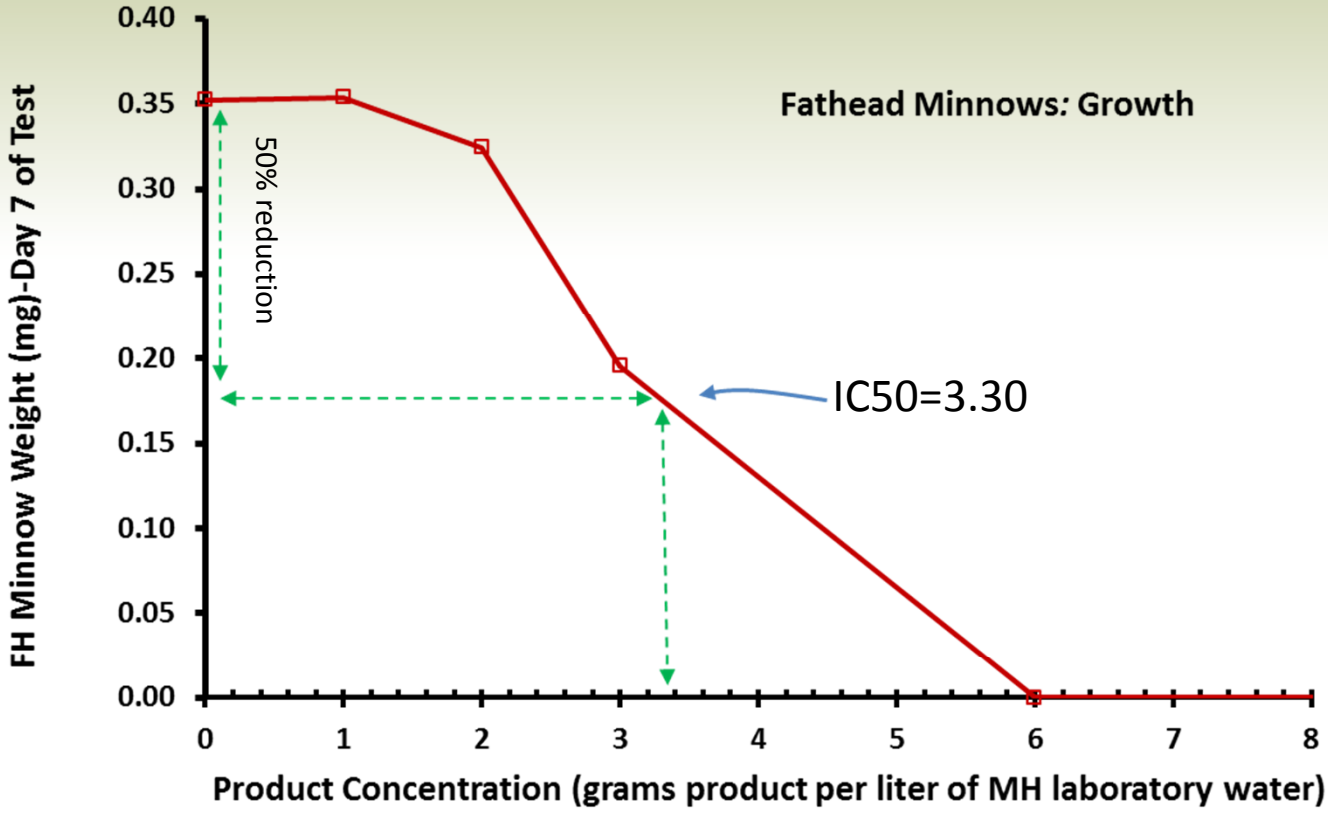
Endpoints example
RoadGard Plus

chronic



Endpoints example
RoadGard Plus

chronic



Endpoint Tables
mass based

Ceriodaphnia dubia

Product	Toxicological Endpoint as Product (grams product/liter of diluent)						
	Acute NOEC (survival)	Acute LC50 (survival)	Chronic NOEC (survival)	Chronic LC50 (survival)	Chronic NOEC (young production)	Chronic IC25 (young production)	Chronic IC50 (young production)
Watershed Cl: Inhibitor + Salt (NaCl)	12.0	17.0	3.00	4.81	1.00	0.990	3.43

Mass of Product/Volume of Diluent = Mass of liquid product diluted in runoff and the receiving water body

Endpoint Tables
volume based

Ceriodaphnia dubia

Product	Toxicological Endpoint as Product (milliliters of product/liter of diluent)(1)						
	Acute NOEC (survival)	Acute LC50 (survival)	Chronic NOEC (survival)	Chronic LC50 (survival)	Chronic NOEC (young production)	Chronic IC25 (young production)	Chronic IC50 (young production)
Watershed Cl : Inhibitor + Salt (NaCl)	9.4	13.3	2.3	3.8	0.8	0.8	2.7

Volume of Product/Volume of Diluent = volume of liquid product diluted in runoff and the receiving water body

For the practitioner!

Endpoint Tables
salt content based

Ceriodaphnia dubia

Product	Chemical Used for Endpoint Calculation	Stock Concentration (grams salt / liter of product)[2]	Toxicological Endpoint as Primary Salt (milligrams salt/liter of diluent)[1]						
			Acute NOEC (survival)	Acute LC50 (survival)	Chronic NOEC (survival)	Chronic LC50 (survival)	Chronic NOEC (young production)	Chronic IC25 (young production)	Chronic IC50 (young production)
Watershed Cl : Inhibitor + Salt (NaCl)	Na + Cl	288	2705	3826	676	1084	225	223	773
Beet 55: Inhibitor + Salt (NaCl)	Na + Cl	224	1760	2782	17.6	102	1.76	12.4	64.8

Mass of salt per volume of product/volume of diluent = mass of salt diluted in runoff and the receiving water body

To normalize products based upon salt mass per unit volume and to promote comparison

Which inhibitor is more chronically toxic?

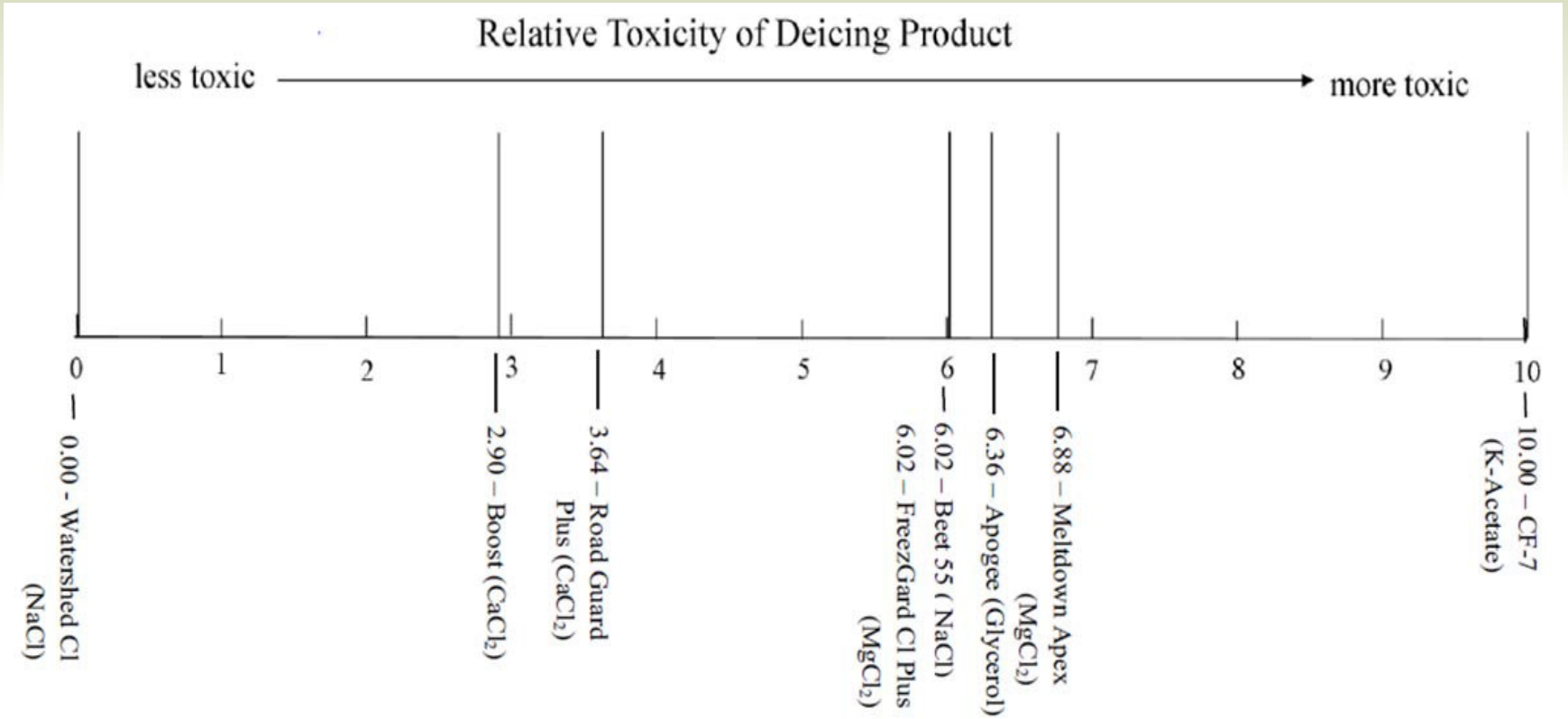
Ranking

Ranking by Total Product Mass

Product	Relative Toxicological Rank
Watershed Cl: Inhibitor + Salt (NaCl)	1
Boost (CaCl2)	2
Road Guard Plus (CaCl2)	3
Beet 55: Inhibitor + Salt (NaCl)	4
FreezGard Cl Plus (MgCl2)	5
Apogee (Glycerol)	6
Meltdown Apex (MgCl2)	7
CF-7 (K-Acetate)	8

Ranking by Salt Mass

Product	Relative Toxicological Rank
Watershed Cl: Inhibitor + Salt (NaCl)	1
Boost (CaCl2)	2
Road Guard Plus (CaCl2)	3
FreezGard Cl Plus (MgCl2)	4
Meltdown Apex (MgCl2)	5
Beet 55: Inhibitor + Salt (NaCl)	6
CF-7 (K-Acetate)	7


Relative Toxicity of Deicing Product
less toxic
more toxic
0
1
2
3
4
5
6
7
8
9
10
0.00 - Watershed Cl (NaCl)
2.90 – Boost ($CaCl_2$)
3.64 – Road Guard Plus ($CaCl_2$)
6.02 – FreezGard Cl Plus ($MgCl_2$)
6.02 – Beet 55 (NaCl)
6.36 – Apogee (Glycerol)
6.88 – Meltdown Apex ($MgCl_2$)
10.00 – CF-7 (K-Acetate)

Ranking by Salt Type

For this current study (from most to least toxic):

K-Acetate > $MgCl_2$ > $CaCl_2$ > NaCl

Salt only toxicity from the literature:

K-Acetate > $MgCl_2$ > $CaCl_2$ = NaCl

Other Observations
dissolved oxygen

Dissolved Oxygen Measured During The Test

Product	*C. dubia*		Fathead Minnow		*Selenastrum Capricornutum*
	Dissolved Oxygen (mg/L)				
	At Acute LC50	At Chronic IC50	At Acute LC50	At Chronic IC50	At IC50
Watershed CI : Inhibitor + Salt (NaCl)	7.91	8.09	5.1	6.54	9.49
Beet 55: Inhibitor + Salt (NaCl)	4.26	7.69	1.70	6.24	9.64
FreezGard CI Plus ($MgCl_2$)	7.96	8.04	4.70	7.09	9.53
Meltdown Apex ($MgCl_2$)	8.07	8.19	7.20	7.38	8.14
Road Guard Plus ($CaCl_2$)	7.24	7.74	4.24	4.60	8.16
Boost ($CaCl_2$)	5.54	7.33	3.28	3.97	9.01
CF-7 (K-Acetate)	7.29	7.98	4.64	6.50	9.05
Apogee (Glycerol)	7.16	7.70	4.54	5.58	9.78

Reminder: Daily Renewals

Dissolved oxygen effects still possible in the receiving water body

Other Observations
species sensitivity to products

Acute Toxicity:

more sensitive.....less sensitive

fathead minnow > *Ceriodaphnia dubia*

(96 hour test) (48 hour test)

Chronic Toxicity:

more sensitive.....less sensitive

Ceriodaphnia dubia >>> Selenastrum > fathead minnow

(7 day test) (4 day test) (7 day test)

Conclusions

- Testing provided high-quality data set for a selected number of liquid deicing products
- Testing results can be used to make estimates of potential toxicological impact on receiving waters, recognizing that:
  - Receiving water may have different chemistry than the laboratory water used in this study
  - Some of the product may be retained in soils and this will need to be considered in any impact assessment.
- Acute or chronic data use
  - Depends upon typical storm length for given region of country
  - Depends upon the receiving water body, e.g.
    - Large river = acute
    - Lake = chronic

Conclusions: potential future work

- Temperature
  - Need to determine if these products are more or less toxic at low temperatures
- Longer term dissolved oxygen loss and effects on toxicity
- Product retention and decay
- Study effects with exposure periods representative of storm events

PACIFIC NORTHWEST SNOWFIGHTERS (PNS) SNOW AND ICE CONTROL CHEMICAL AND INHIBITOR PRODUCTS SPECIFICATIONS

PRESENTED BY:

RON WRIGHT

CENTRAL LABORATORY MANAGER

IDAHO TRANSPORTATION DEPARTMENT

SPECIFICATION GOALS

- PRODUCT PERFORMANCE
- ENVIRONMENTAL IMPACT
- BUDGET

SPECIFICATION OVERVIEW

- GENERAL SPECIFICATIONS
- BID PROCESS
- PRODUCT DELIVERY
- FIELD INSPECTION, UNLOADING, SAMPLING AND TESTING
- CHEMICAL PRODUCT CATEGORIES
- TEST METHODS

OVERVIEW - CONTINUED

- PRICE ADJUSTMENTS
- BID EVALUATIONS / AWARD
- QUALIFIED PRODUCTS LIST

GENERAL SPECIFICATIONS

CONSTITUENT LIMITS LIST

- ARSENIC
- BARIUM
- CADMIUM
- CHROMIUM
- COPPER
- LEAD
- MERCURY
- SELENIUM
- ZINC
- CYANIDE
- PHOSPHORUS

GENERAL SPECIFICATIONS

- CORROSION INHIBITED
- CONTAMINATION ISSUES
- DAMAGE TO EQUIPMENT OR STORAGE FACILITIES
- ACCEPT/REJECT - PUBLIC SAFETY
- VENDOR NOTIFICATION OF TEST RESULTS

ADDITIONAL PARAMETERS

- NITROGEN
- AMMONIA
- BIOLOGICAL OXYGEN DEMAND
- CHEMICAL OXYGEN DEMAND
- TOXICITY
- FRICTION

BID PROCESS

- SUBMIT SAMPLES
- PRODUCT CHECK LIST
  - CATEGORY
  - MANUFACTURER
  - PERCENT CONCENTRATION
  - pH : ORGANIC COMPOUND OR ORGANIC MATTER
  - ANALYTICAL RESULTS
  - CORROSION TEST DATA
  - IDENTIFY THE CORROSION INHIBITOR

BID PROCESS

- SPECIFIC GRAVITY TABLE
- PROPRIETARY INFORMATION
- MATERIAL SAFETY DATA SHEETS

- FIELD APPLICATION TESTING AND EFFECTIVENESS OF PRODUCT
- DATA USED TO CONSTRUCT A FINGERPRINT OF THE PRODUCT

PRODUCT DELIVERY

- BILL OF LADING
  - NAME OF PRODUCT
  - SUPPLIER AND MANUFACTURER
  - DESTINATION
  - QUANTITY
  - LOT NUMBER
  - TRANSPORTER INFORMATION
  - LIQUIDS - %CONC AND SP. GRAVITY

PRODUCT DELIVERY

- INVOICE
  - UNIT MEASURE - TONS, LITERS, GALS.
  - UNIT PRICE
  - TOTAL PRICE
- TRANSFER EQUIPMENT
- MSDS REQUIREMENTS
- ANTI-FOAM AGENT

PRODUCT DELIVERY

- PLACING ORDERS
  - FAX/EMAIL ORDERS TO SUPPLIER
  - CONFIRMATION FAX/EMAIL BACK FROM SUPPLIER
- TIME LIMITS
- PRICE REDUCTION FOR TARDY DELIVERIES
- SPECIAL CONSIDERATIONS

FIELD INSPECTION, UNLOADING, SAMPLING, AND TESTING

- PRELIMINARY INSPECTION
  - DOCUMENTATION
  - VISUALLY INSPECT THE PRODUCT
- PRIOR TO UNLOADING
  - RECORD VOLUME IN STORAGE
  - FIELD TEST A GRAB SAMPLE
  - ACCEPT OR REJECT UNLOADING OF MATERIAL

FIELD INSPECTION, UNLOADING, SAMPLING, AND TESTING

- SAMPLING AND TESTING
  - COLLECT DURING UNLOADING
  - FIELD MEASUREMENTS
  - RECORD INFORMATION
  - SEND TO CENTRAL LABORATORY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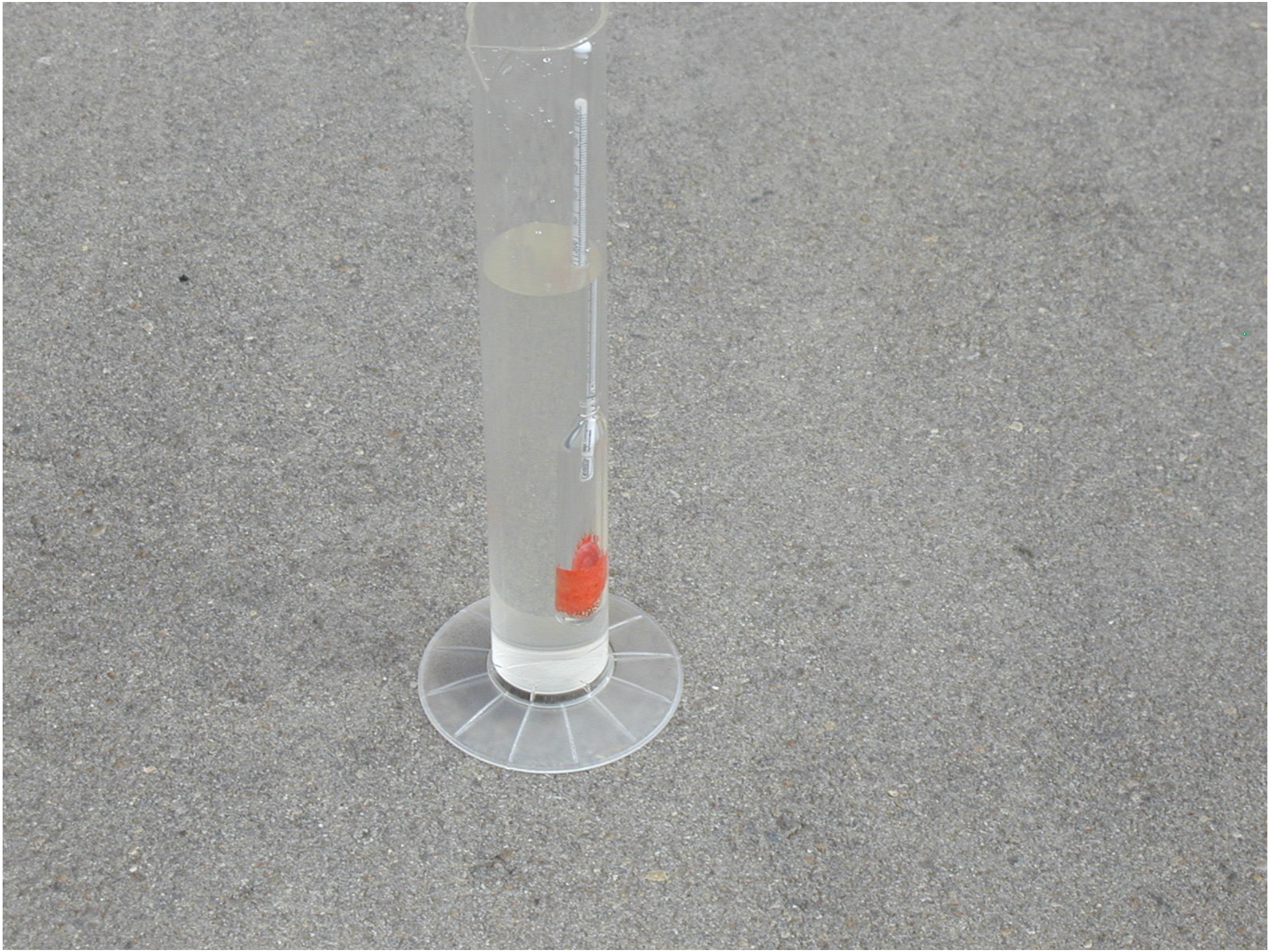
TRACEABLE® THERMOMETER
OFF
ON
17.8°C
-50 to 158°C
-58 to 302°F
°F
°C
97459741




9-1831
Champ
Battery Tester
For all 6, 12, 24-volt
stem — shows battery
detects overcharge
Kansas 66111
SPECIFIC GRAVITY
1.300
1.275
1.250
1.225
1.210
1.150
GOOD
FAIR
HARGE

CHEMICAL PRODUCT CATEGORIES

- CI LIQUID MAGNESIUM CHLORIDE
- CI LIQUID CALCIUM CHLORIDE
- CI LIQUID CMA
- CI SOLID SODIUM CHLORIDE (2)
- CI SOLID NACL + 10%$MGCL_2$
- CI SOLID NACL + 20%$MGCL_2$
- SOLID CMA
- NON-CI SOLID NACL

CHEMICAL PRODUCT CATEGORIES

- CI LIQUID SODIUM CHLORIDE
- CI LIQUID SODIUM CHLORIDE PLUS CALCIUM CHLORIDE
- CI LIQUID CHLORIDE BLENDS
- EXPERIMENTAL PRODUCTS

INHIBITOR PRODUCT CATEGORIES

- CI SODIUM CHLORIDE
  - Minimum Concentration 21%
- CI SODIUM CHORIDE PLUS CALCIUM CHLORIDE
  - Minimum Concentration 15% NaCl and 2% $CaCl_2$
- CI SODIUM CHLORIDE
  - Minimum Concentration 15% NaCl and 15% corrosion inhibitor

INHIBITOR PRODUCT CATEGORIES

- Temperature Classifications for Storgage
  - Class 1: 10° F
  - Class 2: 0° F

TEST METHODS

- PERCENT CONCENTRATION OF ACTIVE INGREDIENT IN LIQUID
- SPECIFIC GRAVITY (WT/GAL)
- CORROSION INHIBITOR CONC.
- pH
- CORROSION RATE
  - 70% LESS CORROSIVE THAN NACL
  - AS PER CONTRACT


0
BL
2
1
500ml
KIMAX
500ml
KIMAX
500ml
KIMAX


7
453
500ml
KIMAX
USA
NO. 26650
STOPPER NO. 16
APPROXIMATE VOLUMES


BL
2
500ml
KIMAX
USA
NaCl
500ml
KIMAX
USA


7
460
500 mL
400
300
200
100
8
468
500 mL
PYREX


7
460
500
400
300
200
300
200

TEST METHODS

- PERCENT TOTAL SETTLEABLE SOLIDS AND PERCENT SOLIDS PASSING A NO. 10 SIEVE
- TOTAL PHOSPHORUS
- TOTAL CYANIDE
- TOTAL METALS
- MILLEQUIVALENTS OF UNREACTED BASE


50
40
30
20
10

TEST METHODS

- MOISTURE CONTENT OF SOLID CHEMICAL PRODUCTS
- GRADATION
- VISUAL INSPECTION AND FIELD OBSERVATIONS

TEST METHODS

- Toxicity Test
- Ammonia – Nitrogen
- Total Kjeldahl Nitrogen
- Nitrate and Nitrite – Nitrogen
- Biological Oxygen Demand (BOD)
- Chemical Oxygen Demand (COD)
- Frictional Analysis
- Insoluble Material
- Chloride

PRICE ADJUSTMENTS

- LIQUID CONCENTRATIONS
  - BIDDER QUOTED CONCENTRATION
  - BQC LESS 1% - NO PA
  - BQC LESS 1.1 % TO MINIMUM CONCENTATION LIMIT - $ PA
  - 24.9 TO 24.0 - $ PA
  - 23.9 TO 22.0 - $ PA
  - LESS THAN 21.9%-100%PA (OR REJECTION)

PRICE ADJUSTMENTS

- **SODIUM CHLORIDE**
  - **OUTSIDE GRADATION LIMITS – $ PA**
  - **PERCENT MOISTURE**
  - **PAY RATE (PR)**
  - **PR=100.5 X WET WT/100 + %MOISTURE**

    (For a product that has a limit of 0.50% moisture)

PRICE ADJUSTMENTS

- GENERAL ADJUSTMENTS
  - ALL OTHER REQUIREMENTS – BASED ON A PERCENT DEVIATION FROM THE SPECIFIED LIMIT - $ PA
  - TOTAL REJECTION
- TOTAL REJECTION
  - REPLACE REJECTED MATERIAL PLUS REPLACE ALL CONTAMINATED MATERIAL AT VENDORS COST

BID EVALUATION PROCESS

- BID PREFERENCE FOR HIGHER CONCENTRATIONS
- BEST BUY FACTOR
  - PRICE / PERCENT CONCENTRATION
  - $60.00 / 27% = 222.22
  - $65.00 / 30% = 216.67

BID EVALUATION PROCESS

BID PREFERENCE FOR SUPERIOR CORROSION INHIBITION

CI EFFECTIVENESS	VALUE ADDED
25.0 TO 30.0	0.00
20.0 TO 24.9	1.00
15.0 TO 19.9	3.00
10.0 TO 14.9	5.00
5.0 TO 9.0	7.00
4.9 AND LESS	10.00

BID EVALUATION PROCESS

- BID PREFERENCE FOR VALUE ADDED
- FINAL BEST BUY FACTOR
  - $60.00 / 27% = 222.22 - 10.00 = 212.00
  - $65.00 / 30% = 216.67 - 0.00 = 216.67

RECOMMENDATIONS

- BID PRODUCTS THAT ARE ON THE PNS QPL AT THE TIME OF THE BID LETTING
- GIVE EARLY NOTICE TO VENDORS THAT YOU PLAN TO DO THIS
- HELPS MAKE BIDS RUN SMOOTHER AND AGENCIES DO NOT HAVE TO DETERMINE IF PRODUCTS MEET PNS STANDARDS

PNS/CLEAR ROADS WEBSITES

http://pnsassociation.org/

http://clearroads.org/

Thank you