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TTI-160 Incident: Zinc Aquatic Risk Assessment (Ver. 1.2)

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Zinc is a moderately- to highly toxic trace element to aquatic organisms (see appendix). The EPA freshwater national water quality criteria for zinc is 120 ppb (0.12 ppm) acute and 110 ppb (0.11ppm) chronic. Data in EcoTox as processed in CAFÉ, a NOAA Database-Model in development, suggest that these concentrations are extremely protective for fish and very protective for aquatic crustacea. Below the toxicity of zinc to crustacea (including cladocera, water fleas) and in the context to a broader range of species (namely fish) are evaluated.

Fish

Shown below (Figure 1) are data and species sensitivity distributions (SSD's) for fish, freshwater and marine combined, derived from NOAA's CAFÉ/EPA Ecotox Database. Both marine and freshwater fish are included (we cannot separate in the current database). By inspection, the median fish "community" LC50 concentrations are roughly 10,000 ppb (10 ppm) at 24 hours, 8000 ppb (8 ppm) for 48 hours and 6000 to 7000 ppb (6-7 ppm) for 96 hours. Corresponding concentrations at 5% (95% species protection) are roughly 900 ppb at 24 hours, declining to about 100 to 200 ppb at 96 hours.

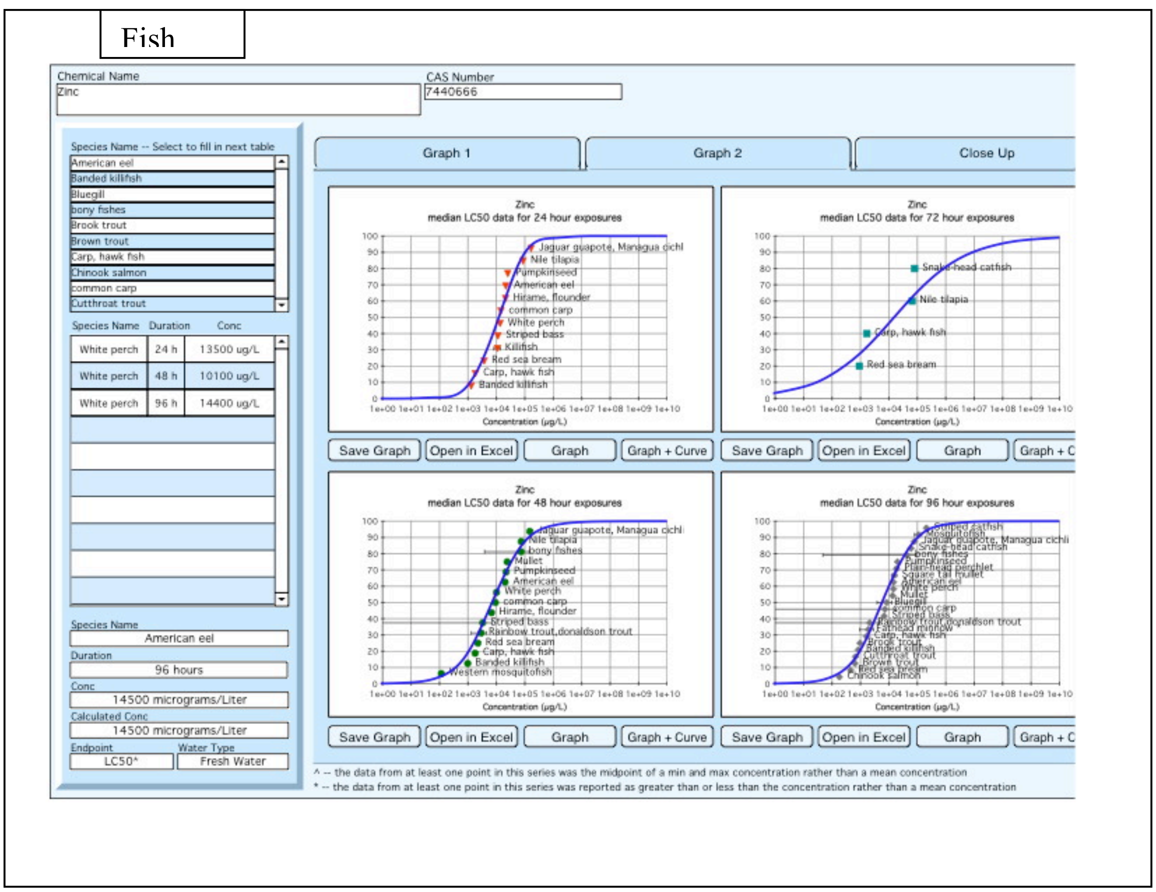

Figure 1. CAFÉ/EPA Ecotox Database for Fish

Crustaceans

Aquatic crustaceans are more sensitive than fish to zinc. Figure 2 is the data from the CAFÉ/EPA Exotox data base. By inspection, the median (50%) community LC50 concentrations are roughly 6000 ppb (6 ppm) at 24 hours, 3000 ppb (3 ppm) for 48 hours and 1000 ppb (1 ppm) for 96 hours. Corresponding concentrations at 5% (95% species protection) are roughly 500 ppb (0.5 ppm) at 24 hours, declining to about 40 ppb at 96 hours.

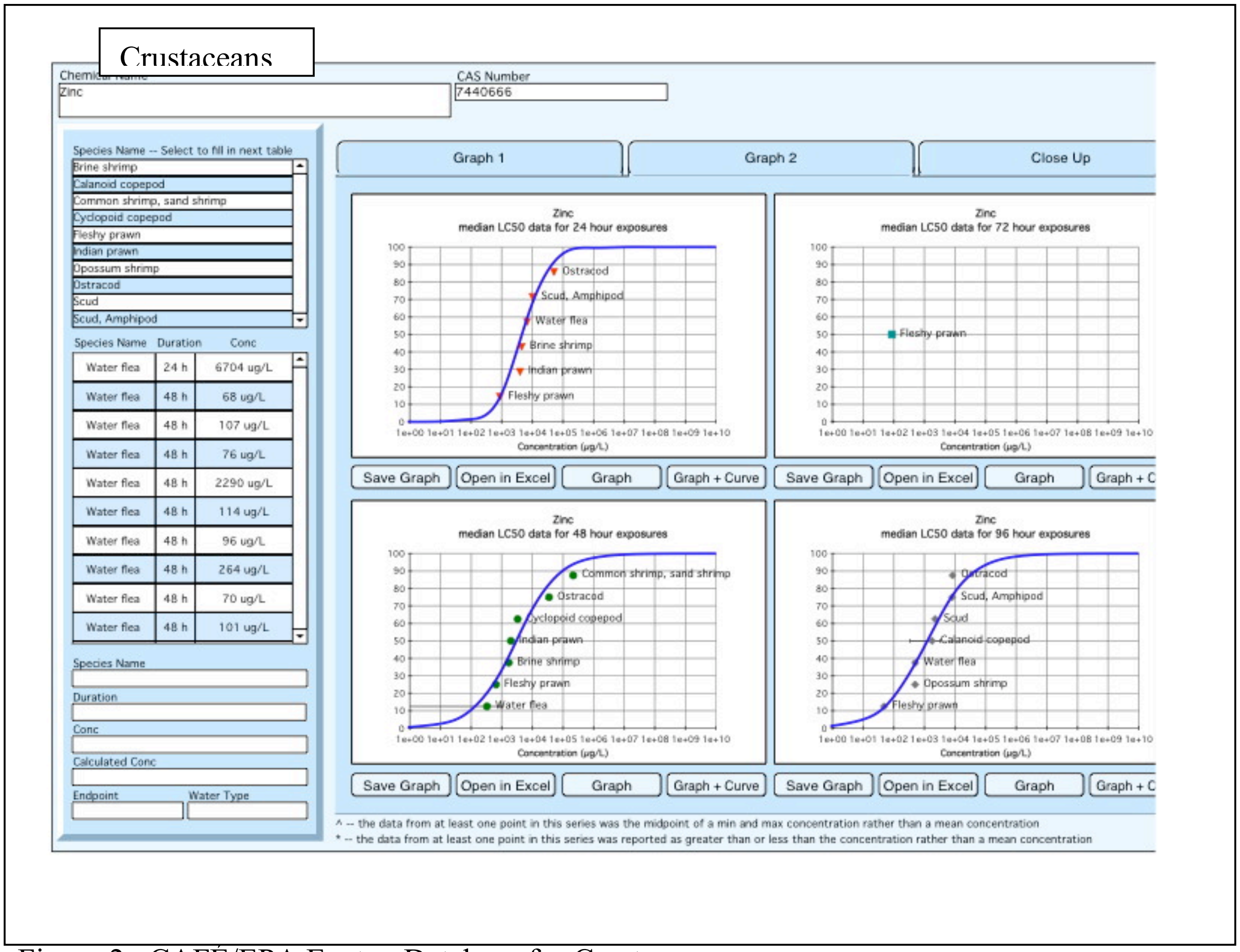

Figure 2. CAFÉ/EPA Ecotox Database for Crustaceans.

Extrapolating Such Data to Very Short Term Exposures.

LC50 concentrations typically decrease with increasing exposure time, and visa versa. The data on toxicity of zinc to crustaceans may be sufficient to suggest concentrations of concern for time periods shorter than 24 hours. The following figure shows the data in the previous figure but plotted by time intervals. A non-statistical, line-of-sight curve is drawn across the data at points that appear to be the central tendency of LC50 data for each time period (except for 72 hours where data is sparse). Again, at 96 hours the data center around community median LC50's of about 1000 ppb (1 ppm), about 3000 ppb (3 ppm) at 48 hours, and about 6000 ppb (6 ppm) at 24 hours. Extrapolating to the left on the graph (shorter exposure periods) suggests the median community LC50's might be expected to be around 20,000 ppb (20 ppm) with only 12 hours exposure and 70,000 ppb (70 ppm) approaching 1 hour or less exposure. Since these are LC50s, the line indicates concentrations killing half the populations. A second, dashed, curve, is superimposed about one-order of magnitude below the solid line, indicating the lowest toxicities at each time period and extrapolating backwards (to the left) to zero time. This line approximates concentrations at each time period that are about one order of magnitude lower than the LC50 median or central-tendency values noted above. This line would suggest that the 12-hour and less-than-one hour most sensitive species concentrations might be on the order of 2000 ppb (2 ppm) and 7,000 ppb (7 ppm) respectively. Again, this is a visual, not a statistical treatment of this information, but does suggest that these crustaceans might survive very short-term exposures (hours or minutes) at concentrations of zinc well above 1 ppm, and possibly higher.

Figure 3.

Application to Drifting Organisms

Organisms (such as plankton animals) entrained in the plume will experience a spike and then declining concentrations of zinc with time. Using the 95% protection concentrations, estimated above, would produce not a single level of concern but rather a curve of declining concentrations of concern; such an approach is also used in dispersant risk assessments (Mearns et al, 2001).

The figure below (Figure 4) shows these values over a 96 hour time period for organisms exposed in a zinc plume. When the curve is superimposed on the plume concentration curve, it will be possible to determine by inspection if the entrained organisms are exposed to concentrations of concern, or not, and if so, when during their transit in the plume.

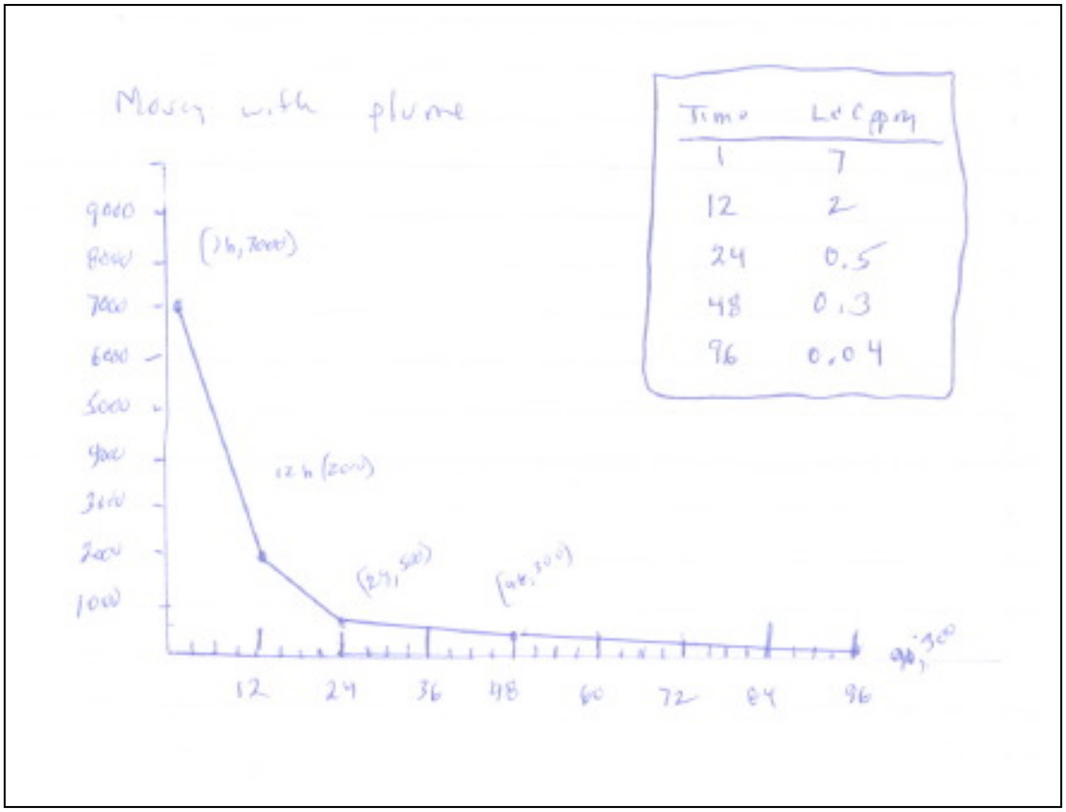

Figure 4.

Note, this information was produced as part of the NOAA Scientific Support during the TTI-160 response and has not been reviewed outside our scientific team. It is based on scientific information and best professional judgment of one of our Senior Scientist in context with the response information available.
Charlie Henry
NOAA Scientific Support Coordinator

Additional Independent Supporting Data
(Also Provided by Dr. Alan Mearns, NOAA)

Species Sensitivity Distribution variability
Bossuyt et al (2005) conducted zinc toxicity tests on whole cladoceran communities. Their reported generic species sensitivity distribution (SSD) resulted in a 95% protection concentration of 559 ppb (range 275 to 843 ppb).

Further testing by them, using various cladoceran species and water from five water bodies differing in chemical properties (pH, alkalinity, etc), resulted in "mean community sensitivities" (geometric mean of 48Hr EC50's) ranging from 0.973 to 1.808 ppm Zn with 95% protection ranging between 0.194 and 1.341 ppm, depending on the geographic location and species mix of the tested of the tested. The variability in these numbers was thought to be due to both variability in water quality parameters (which were measured for five sites) and/or different community species compositions.

The graph below is taken directly from their published paper. Added to it is a dashed line approximately representing the US EPA NWQC (120 ppb) plus the approximate location of their "generic" 95% species protection concentration (559 ppb).

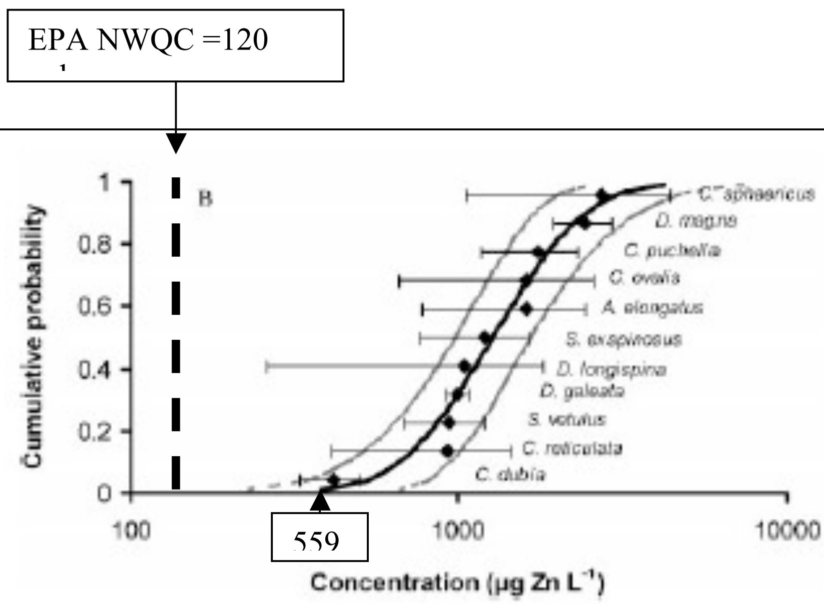

Fig. 1. Generic species sensitivity distribution (log-normal distribution) based on field-collected cladoceran species tested in standard medium for copper (A) and zinc (B) with 90% uncertainty limits. ♦ = Acute toxicity data points with standard deviation. Refer to Table 2 for names of species.

The authors proceeded to look at cladoceran SSD’s for five specific water bodies (in the Netherlands) and report EC50 values. The site-to-site variability of the species sensitivity curves for the five water bodies studied by Bossuyt et al (2005) are shown below together with my dashed lines approximating the acute NWQC (120 ppb). There is moderate variability among sites. At four of these specific sites (A, B, C and E) the species sensitivities are well above, and do not overlap, the NWQC value; at one site (D) they do. Thus in four out of five cases cladoceran communities were protected (95% species) at 48 Hr zinc concentrations well above the NWQC and at concentrations approaching or exceeding 1000 ppb (1 ppm). At the fifth site (D) the 48 hr EC50 95% protection converges on the NWQC concentration of 120 ppb

Use of field-collected crustacean populations in SSD *Environ. Toxicol. Chem.* 24, 2005 475

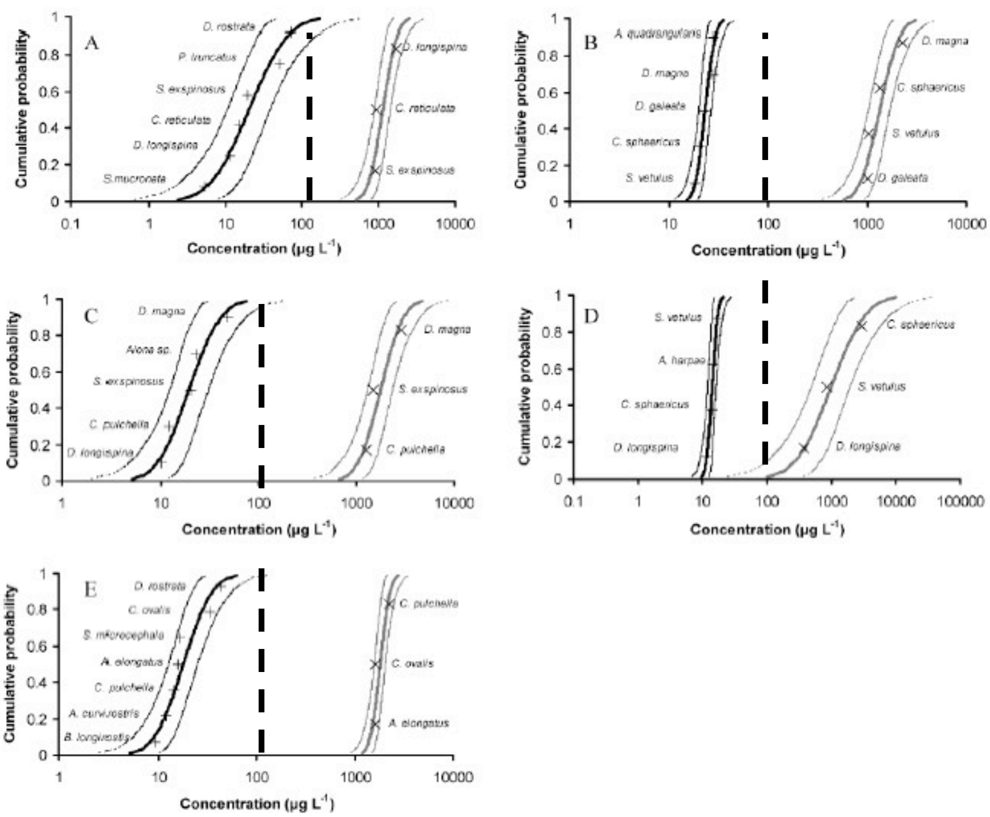

Fig. 2. Site-specific species sensitivity distributions (log-normal) based on field-collected cladoceran species for copper (black lines) and zinc (grey lines), with 90% uncertainty limits. Acute toxicity data points for copper (+) and zinc (×) obtained in standard medium. Sites: (A) Ankeveen; (B) Leuven; (C) Markermeer; (D) Oberkirchen; (E) Teut. Refer to Table 2 for names of species.

Pulse Exposure Paper
In another relevant study Diamond et al (2006) exposed juvenile minnows and adult cladocerans to one or more pulse exposures of zinc. The pulses were 24 hours long at maximum concentrations of 400 ppb (0.4 ppm) and were followed by 24 hours or more of recovery injections of clean water. There were unpredictable delayed effects (on survival or growth) in about half the tests for both species. However, they also presented shorter-term exposure data which they did not explore in their text. The following exposures (concentration vs time) resulted in no measurable effects for the cladoceran (Daphnia):

2500 ppb (2.5 ppm) for 3 hours
1000 ppb (1.0 ppm) for 6 hours

But, 750 ppb (0.75 ppm) for 12 hours did result in a significant increase in mortality. Unfortunately, they did not subject the fish to the same short-term exposures or high concentrations.

Detection and Avoidance
Jones (1964) reported flume experiments in which stickleback (a freshwater fish) were observed for their ability to react to sudden exposures to zinc sulfate at concentrations of 1300, 98, 9.8 and 3.3 ppm, levels much higher than discussed above. At 9.8 ppm and higher the fish reacted to the zinc contaminated water by darting about and eventually finding their way into the zinc-free flume. At 3.3 ppm (and presumably below) the fish did not react. Further, survival times (the old way of reporting toxicity!) were 85 minutes at 1300 ppm, 190 minutes at 98 ppm, 7 hours at 9.8 ppm and 15 hours at 3.3 ppm.

Conclusion: Exposures of Concern
The two kinds of exposure of concern are (1) plume entrained organisms such as plankton and fish eggs and (2) relatively fixed or immobile organisms that will briefly experience a passing plume.

If concentrations in the plume remain above the concentrations shown in Figure 4 (shown earlier) one would expect the entrained organisms to be irreversibly injured or killed within the area and volume of the plume. Organisms entrained in the plume, after the concentrations have deceased below these, presumably down river many miles, will not be affected and the plume footprint will be quickly be recolonized by new viable organisms. The worst time to release the zinc in such a situation would be during the most productive planktonic and fish spawning period, presumably mid spring through summer. Relative to then, a better time would be now.

Relatively fixed organisms will be able to tolerate high concentrations for short periods of time. The data we have investigated suggests that 1 to 5 PPM at exposure times less that an hour or two should not significantly affect these organisms.

References

Bossuyt, B.T.A., B.T.A. Muyssen and C.R. Janssen. 2005. Relevance of generic and site-specific species sensitivity distributions in the current risk assessment procedures for copper and zinc. Environ. Toxicol. Chem. 24(2):470-478.

Diamond, J.M., S.J. Klaine and J.B. Buthcher. 2006. Implications of pulsed chemical exposures for aquaqtic life criteria and wastewater permit levels. Environ. Sci. Technol. 40:5232-38.

Jones, J.R.E. 1964. Fish and River Pollution. Buttersworth, London.

Mearns et al. 2001. (CalCOFI dispersant paper).

Appendix:
Ecological Risk Assessment 101

Ecological Risk Assessment is a formal EPA procedure for evaluating effects of pollution releases into the environment. The focus is on ecolical health, not human health. Ecological Risk Assessment involves several steps: Problem Formulation, Hazard Assessment, Exposure Assessment and Ris Assessment.

Hazard
Hazard Assessment includes an evaluation of the potency of the contaminants of concern. Kamrin (1997) proposed the following classification, in ug/L or parts per billion (ppb) for estimating the acute potency, based on LC50's, of pollutants to marine and aquatic life:

CATEGORY	LC50, ug/L (PPB)
Very Highly Toxic	< 100
Highly Toxic	100 – 1000
Moderately Toxic	1,000 – 10,000
Slightly Toxic	10,000 – 100,000
Not Acutely Toxic	>100,000

96 Hr studies with zinc on aquatic organisms produce LC50's in the range of 100 to 10,000 ppb. Thus, from an aquatic hazard point of view, **zinc** may be considered a **moderately-to-highly toxic substance** in marine and aquatic environments. (By comparison, dissolved **copper** yields many LC50's in the <100 ppb range, and would be considered a very highly toxic substance to marine and aquatic organisms whereas **sodium** (as salt, sodium chloride) yields freshwater fish LC50's on the order of 10,000 ppb and would be classified as **slightly toxic**.).

Exposure Assessment

Once the hazard of a chemical is defined the next step involves Exposure Assessment. The first step in assessing exposure is developing **Expected Environmental Concentrations (EEC's)** from a pollutant released into the water. This will be done by modeling, taking into account contaminant dilution, fate, transport and scale.

The EEC's are then compared to data on aquatic organisms that may be exposed to the EEC's. One way of doing this is to compare the toxicity (LC50's) at various exposure times with the EEC's. Where there is overlap in time and space injury can be expected. In practice, LC50's from a wide range of species at risk (crustaceans, mollusks, fish, etc) are assembled into **Species Sensitivity Distributions (SSD'**s) so that the risk assessors can evaluate threats to the entire aquatic ecosystem and also focus on the highest EEC's that produce the least risk to the aquatic community.

Risk Assessment

In screening level risk assessment, the risk of injury is defined as the overlap in probabilities between the EEC's and the SSD's.