Through the Looking Glass: Toxicity Identification Evaluations Past, Present and Future

Howard Bailey Ph.D., RPBio – Nautilus Environmental

Jeff Miller Ph.D., DABT – AQUA-Science

NAUTILUS ENVIRONMENTAL

Introduction

- This talk reflects over 30 years of conducting TIEs
  - Includes some of the technical insights and contributions published during that time
  - Reflects experience working with multiple industrial, municipal and agricultural sectors
- It is not a detailed review of different procedures that are available for use
- But does reflect some of the successes and failures that have occurred during that period
- And hopefully contributes to a better understanding of how to perform TIEs *and* evaluate the results

NAUTILUS ENVIRONMENTAL

What is a TIE?

- The process of identifying the cause of toxicity in a sample; typically water or sediment
- Generally use physico-chemical manipulations that affect toxicity associated with specific contaminant classes
- Can arrive at the correct conclusion via different pathways,
- But three main components must be included for an objective determination:
  - Characterization
  - Identification
  - Validation/confirmation (independent lines of evidence)

NAUTILUS ENVIRONMENTAL

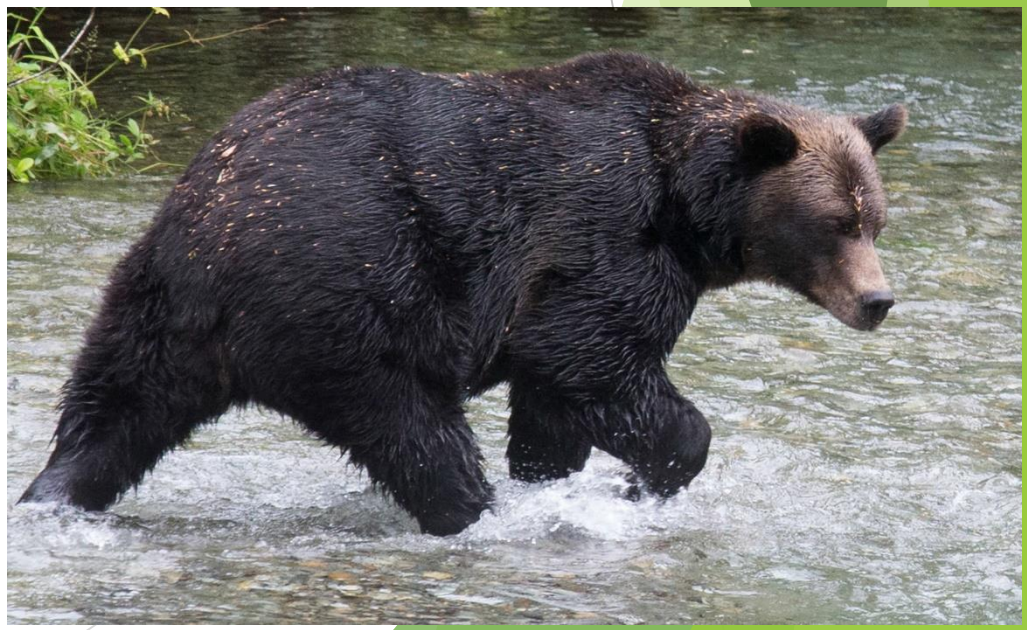
Who is involved?

- Dischargers, regulators, site owners, lawyers
  - Need answers
- Consultants/Laboratories
  - Provide a service ($$)
- Skill sets (primarily related to study design and data interpretation)
  - Chemist
  - Toxicologist
  - Statistician
- Anyone can run a TIE—EPA guidance documents have been available for 30 yrs
- Level of qualifications required with increase with complexity of sample
  - Ammonia, chlorine, copper pretty simple;
  - Multiple toxicants, interactions and unusual toxicants require additional insight

NAUTILUS ENVIRONMENTAL

Biggest Problems

- Not understanding the technical limitations of the different treatments
- Lack of clarity in study design
  - The more treatments you have, the more chances for false positives or negatives
  - Many treatments affect more than one class of toxicant, potentially leading to conflicting conclusions
- Lack of rigorous validation of results
  - Possible mis-identification
  - Doesn't account for other sources of toxicity



NAUTILUS ENVIRONMENTAL

Why does it matter?

- Failure to properly address liability issues (legacy contaminants, multiple dischargers)
- Failure to provide proper inputs into treatment or source control efforts
- Failure to provide constructive support for resolving plant upsets
- Most often a result of inadequate validation
  - Many TIEs start with the Phase 1 characterization, and progress to a desktop exercise (aka “risk assessment”) wherein a “best guess” is based on contaminant concentrations and response to the characterization treatments.
  - Deviations from expected usually attributed to unknown “matrix” effects that affect bioavailability

NAUTILUS ENVIRONMENTAL

Things to pay attention to…

- Key phrases
  - Matrix effects—usually invoked to explain unaccounted toxicity
  - TDS or ion imbalance—usually invoked when no treatment works
  - Surfactants—often applied when a number of treatments work, but not well
  - Directed or targeted TIE—not a bad thing, but if it involves a lot of treatments it probably isn't targeted…
- Incorrect explanations of why treatments are effective
- Incorrect applications of treatments
- More toxicants than Toxic Units
- Do lines of evidence converge?
- Are treatment blanks clean?

NAUTILUS ENVIRONMENTAL

TIEs are expensive…

- YES!
  - Chronic endpoints
  - Multiple toxicants
  - But….. Usually cost-effective on a per-sample/toxicant basis
- NO!
  - Acute endpoints
  - Single toxicants
- Cheap relative to engineers, lawyers
- Things that make it more expensive
  - Over management by plant operators, engineers or consultants
  - Delays, too many treatments, consulting time

NAUTILUS ENVIRONMENTAL

And some examples over the years…

- TIE conducted on algae
  - Among the Phase 1 treatments was PBO; first used as a biochemical inhibitor of enzymes that activate metabolically-activated organo-phosphorous pesticides (diazinon)
  - Bad in so many ways… algae lack the enzyme pathway for the process, as well as the neuronal system through which OPs exert toxicity

NAUTILUS ENVIRONMENTAL

More Toxicants than TUs

- Usually a function of over-interpretation of Phase 1 results; need to satisfy all perceived responses relative to expected response for candidate toxicants in EPA manual
  - Sample contained approximately 1 TU
  - Investigators concluded toxicity was a function of 3 “primary” toxicants, plus “a touch of silver”…
- Proper validation would have identified actual contributing toxicants, rather than qualitative explanation
- Doesn’t really help the engineers or source control specialists
- Really bad in sediment TIEs—lots of contaminants present > SQGs

NAUTILUS ENVIRONMENTAL

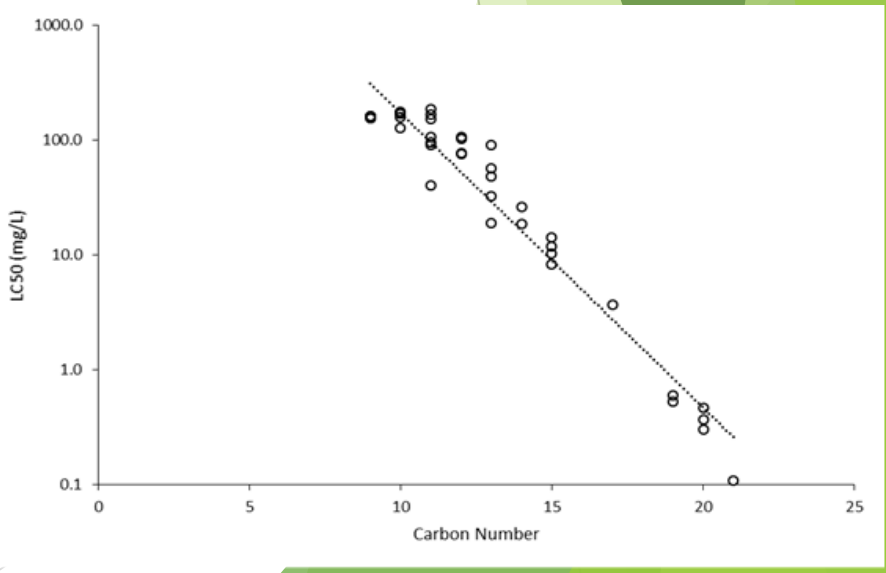
TIEs are obsolete!

- Not good news for practitioners… but it could be premature!
- Asked to troubleshoot a treatment plant (refinery) that was killing trout
- Plant was based on activated carbon, and designed by someone whose catch phrase was something like: “TIEs? We are way beyond that now…”
- Exploratory TIE work on the sample showed EDTA removed all toxicity
- The plant also received stormwater run-off…
- Review of original design documents showed that they started with a TRE approach, directly testing media that could be used in a treatment system, but never identifying the actual causes of toxicity and relative contributions
- Carbon will remove Zn, but is not an effective long-term solution.

NAUTILUS ENVIRONMENTAL

Case studies: OSPW

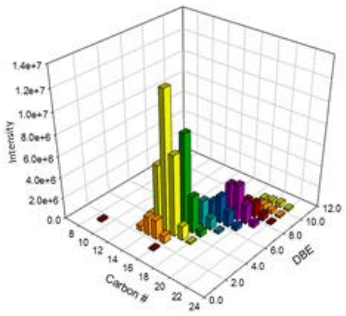
- Toxicity is potentially a function of >100 classes of compounds representing >500,000 compounds
- Industry has spent over 10 years and >$5M to identify cause
- We combined ultra-high resolution analytical support with multiple fractions representing a gradient of polarities and toxicity
- Statistical analysis eliminated compound classes of interest
- Toxicity of organics completely attributable to concentration *and potency* of classical NAs



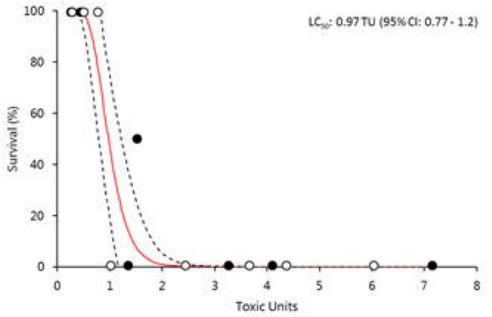
NAUTILUS ENVIRONMENTAL

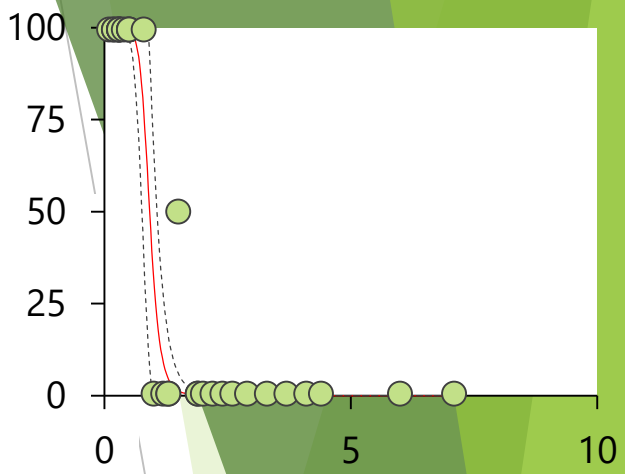
Flow Diagram

OSPW



+ $TU = \sum_i [O_2^-]_i \times e^{0.591i - 12.53}$



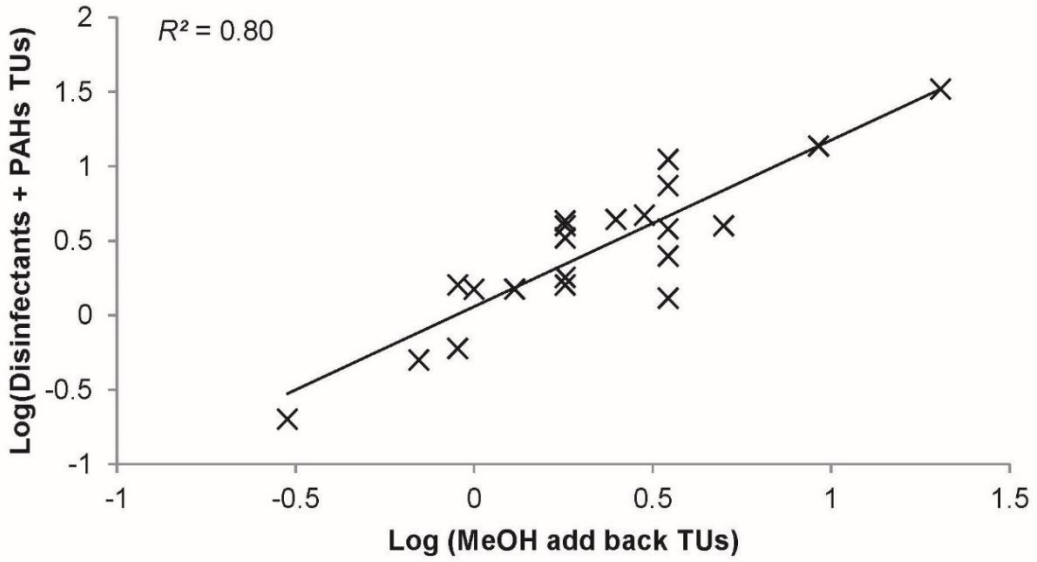


Toxic Units (TU)

NAUTILUS ENVIRONMENTAL

Case study: Contaminated sediment site

- Multiple historical and current users
- Current and legacy contamination
- Toxicity primarily a function of organics
- RAs focused on PAHs and PCBs based on analytical and toxicity results
- TIE showed disinfectants (CSOs) and PAHs caused toxicity across site
- Never would have been identified w/o TIE
- Expensive (?), but…



NAUTILUS ENVIRONMENTAL

Question the obvious…

- Toxic groundwater from Olympics site (Sydney); RAs focused on copper and zinc based on guideline exceedances.
  - **Implications for clean-up and treatment**
  - Turned out to be mostly ammonia, with a few locations driven by metals
- Se treatment plant in upset mode; dead fish downstream; HGs focused on nitrite based on concentration and methemoglobinemia (no TIE)
  - **Implications for clean up and treatment**
  - Ruled out nitrite based on transient dose-response and chloride
  - Turned out to be H_2S in spite of positive redox (also forms methemoglobinemia)
- Copper and zinc, diazinon and chlorpyrifos, pyrethroids
  - Often co-occur; no definitive conclusions until all TUs accounted for

NAUTILUS ENVIRONMENTAL

Emerging contaminants of concern

- Process chemicals—polymers, etc
- Unreacted by-products of treatment process
  - Greater throughput
  - Smaller footprints
  - Less opportunity for reactions to reach equilibrium
- New consumer products (e.g., health care and disinfection products)
- Pet and landscape products

NAUTILUS ENVIRONMENTAL

Other considerations

- Analytical support is a key component of process
  - Ammonia, nitrite easily done in house
  - More complex analyses done in outside labs
- Ability to work with unusual samples and matrices at low detection limits
- Very few research-level labs; most are specialists
- Speciation matters….
- Interactions with test parameters: temperature, pH, DO
  - Potential to confound or contribute to results
  - Partition or control for effects

NAUTILUS ENVIRONMENTAL

Acknowledgements

Many thanks and appreciation to all of the researchers that we collaborated with over the years….

NAUTILUS ENVIRONMENTAL