Understanding and Quantifying Nanomaterial Exposure and Dosimetry in Aquatic Hazard Testing - The Link Between Hazard, Exposure, and Risk Assessment

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QEEN Workshop
July 7-8, 2015
Rosslyn, VA, USA

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NANOSAFE INC

ERDC

RISK = EXPOSURE X TOXICITY

TOXICITY = EXPOSURE X TIME

EXPOSURE
varied concentrations

TIME = 48h, 96h, 7d, 10d, …
(acute, chronic, life-cycle,…)

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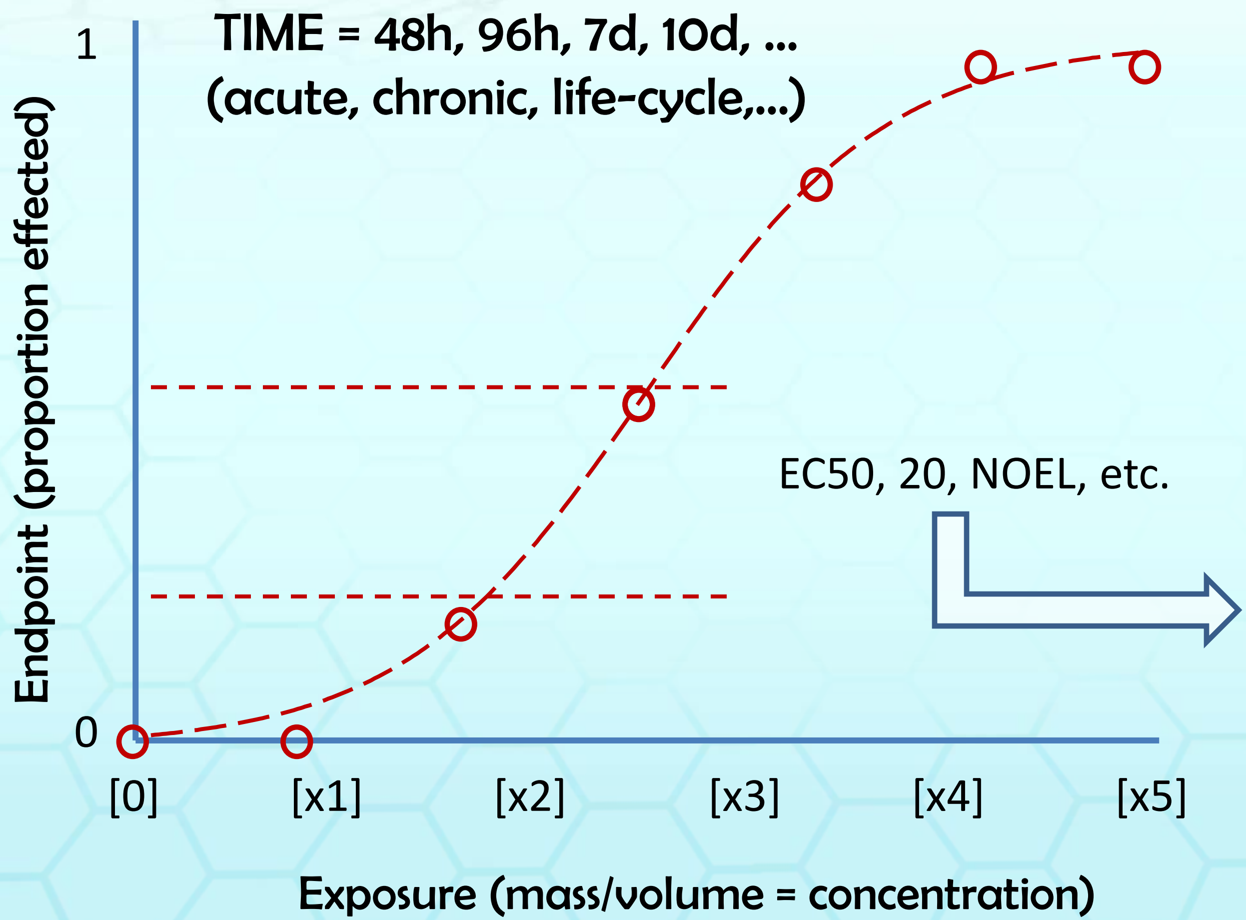


Effect levels are compared to expected field exposures

Almost exclusively soluble chemicals...

Formal Test guidelines: no colloids, particles, limits on variation in exposure ("20% rule")

Possible exceptions:

Petroleum: Testing of water accommodated fractions

Sediment dredging: Elutriate testing (toxic constituents)

Formal Test Guidelines lack any reference to testing of particles!

Do test approaches for soluble substances work for nanomaterials?

Testing Soluble Substances - Exposure

- known or predictable behavior
- exposure and effects are exclusively concentration-based
- nominal test values are often adequate
- established methods to address difficulties
  - OECD "Difficult Substances" guidance document
  - Water Accommodated Fraction methods
  - Sediment Dredging deposition testing
- < 20% losses typically obtainable
- continual renewal is often feasible

Testing Nanomaterials - Exposure

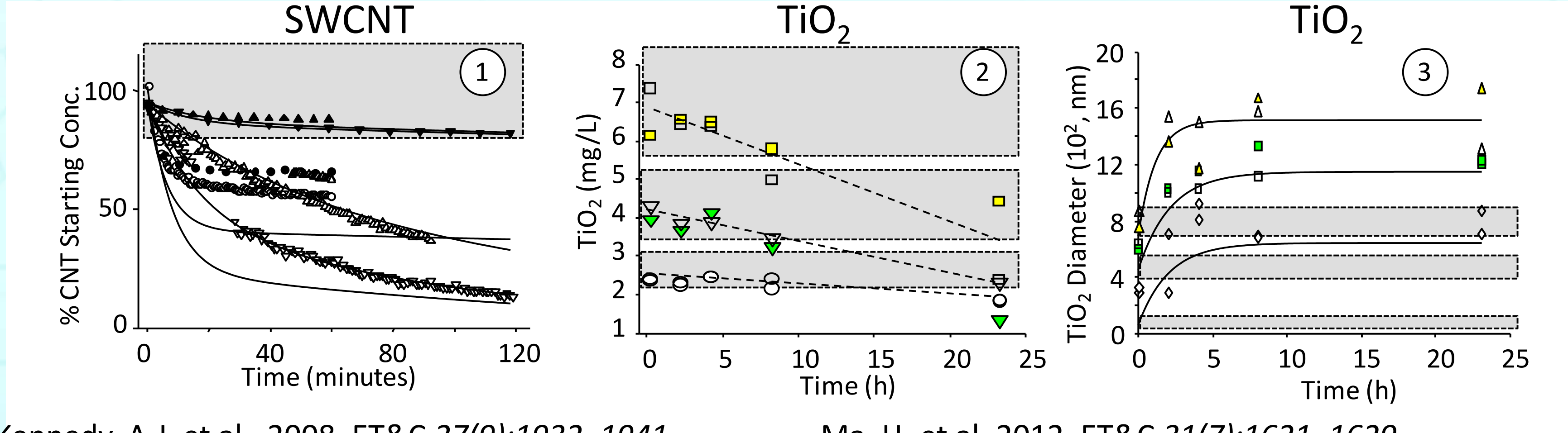
- unknown or unpredictable behavior
- exposure and effects typically concentration-based
- nominal test values typically reported
- methods to address difficulties?
- adherence to "20% rule" - **RARELY**
- continual renewal is problematic

So, what does a typical nanoparticle exposure look like?

Variation in Exposure During Toxicity Assays

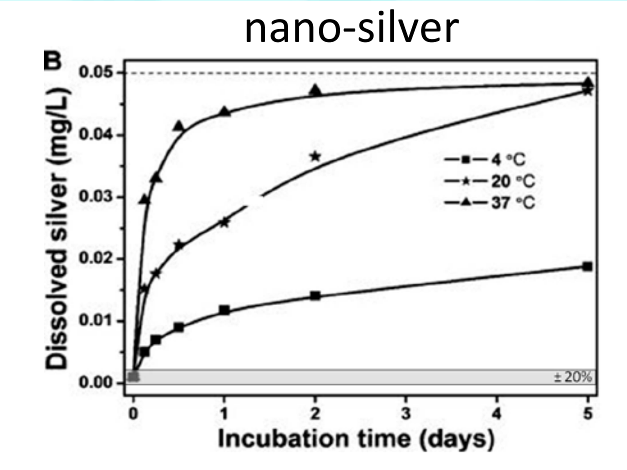
Varying mass concentration

Varying agglomerate size



Kennedy, A.J. et al., 2008. ET&C *27(9):1932–1941.*

Ma, H.,et al. 2012. ET&C *31(7):1621–1629.*

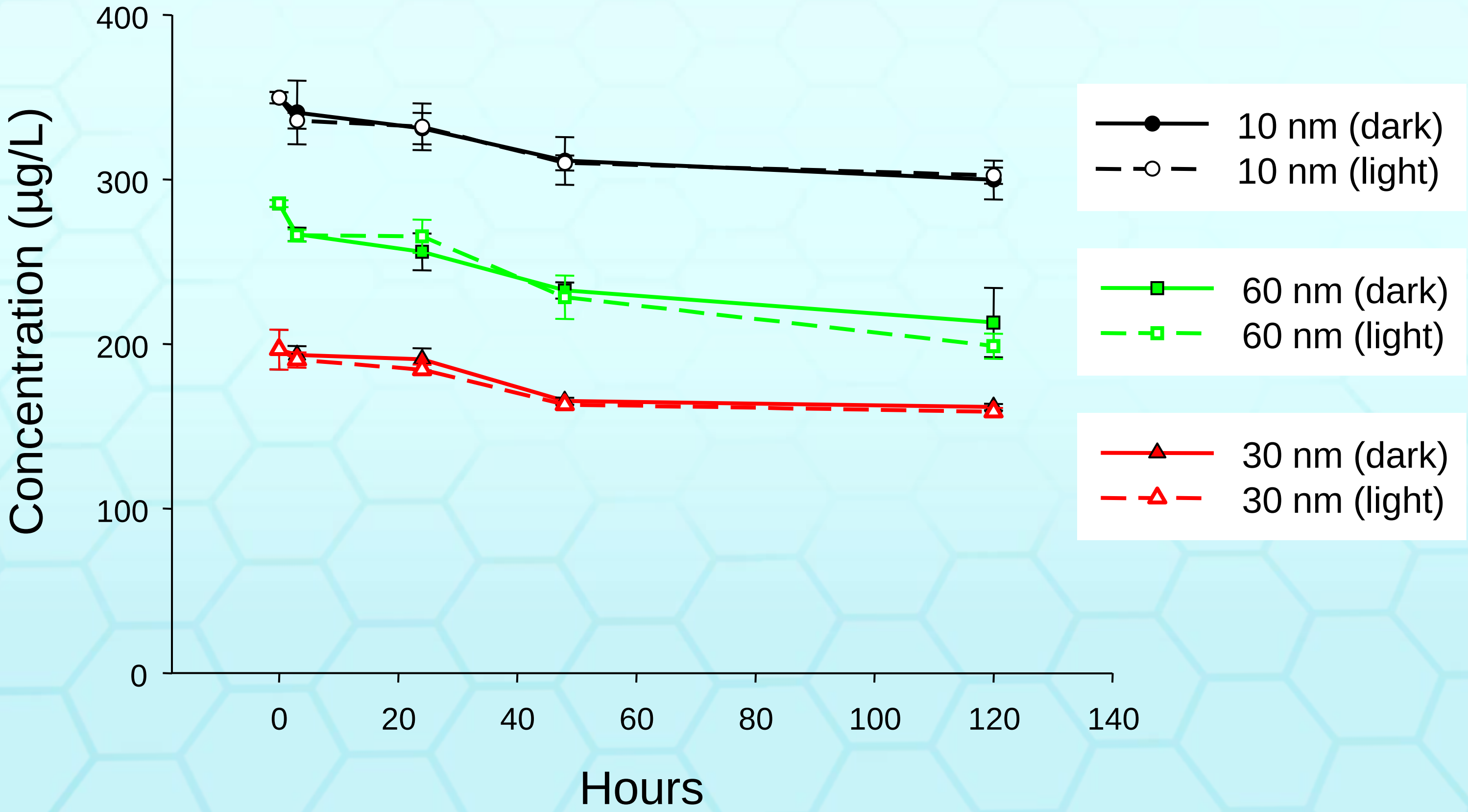


Liu, J. & Hurt, R.H., 2010. *ES&T 44(6):2169–2175.*

How to address variability:

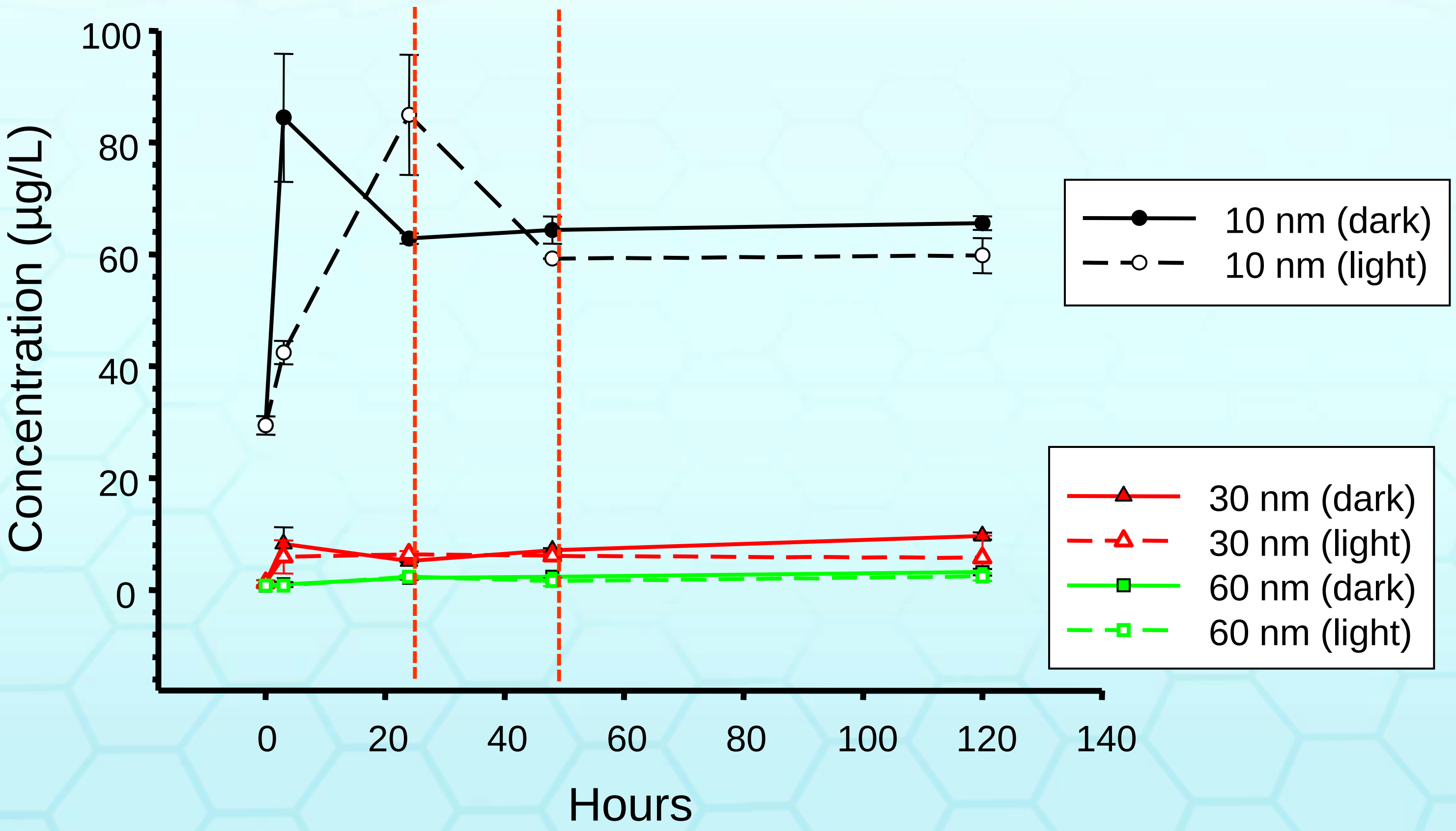
- Monitor exposure at intervals adequate for quantifying and modeling exposure
- Manipulate media, renewal intervals, add energy, add stabilizers
- Test only sediments

Citrate nAg (total)

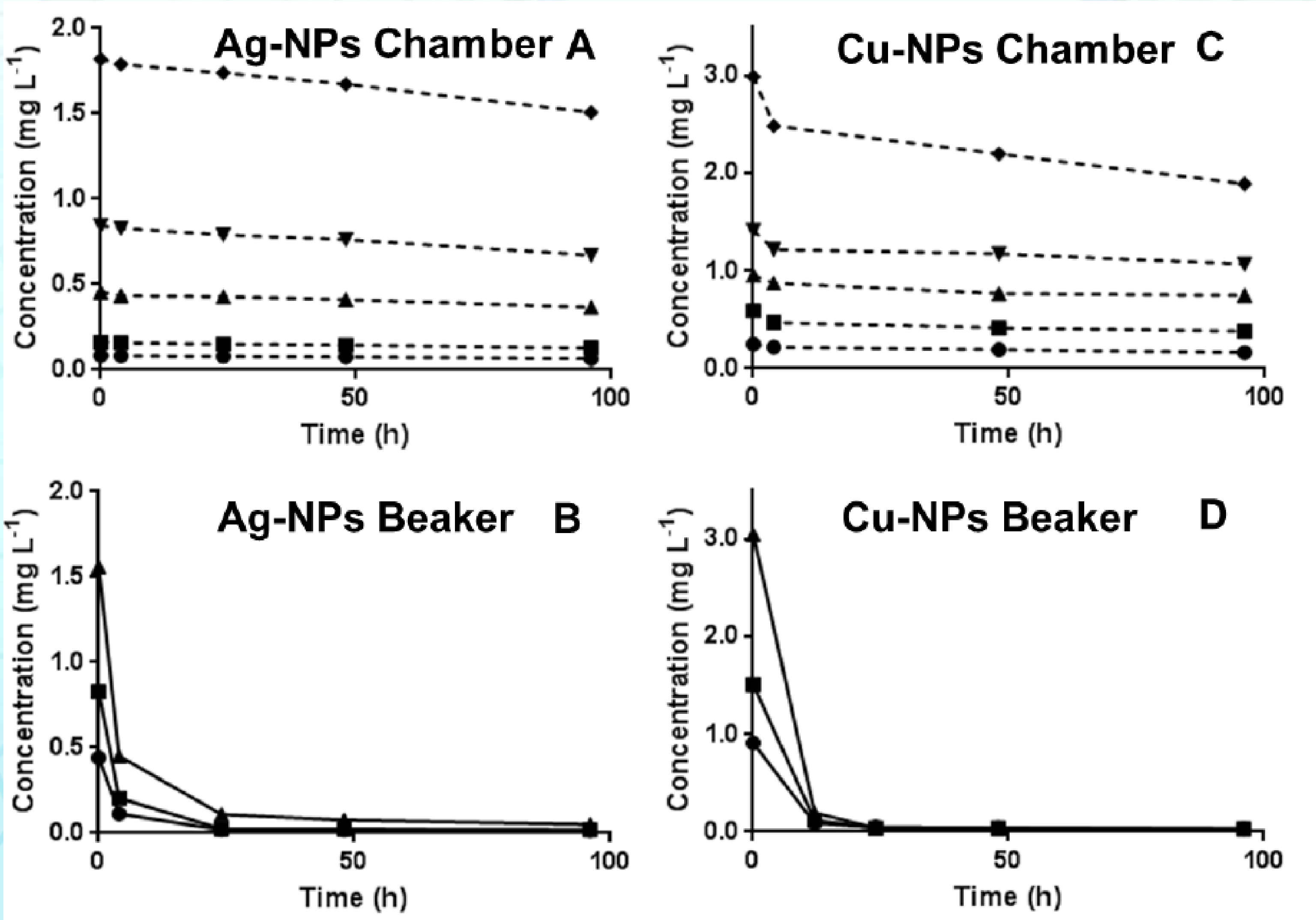


Kennedy, et al., unpublished

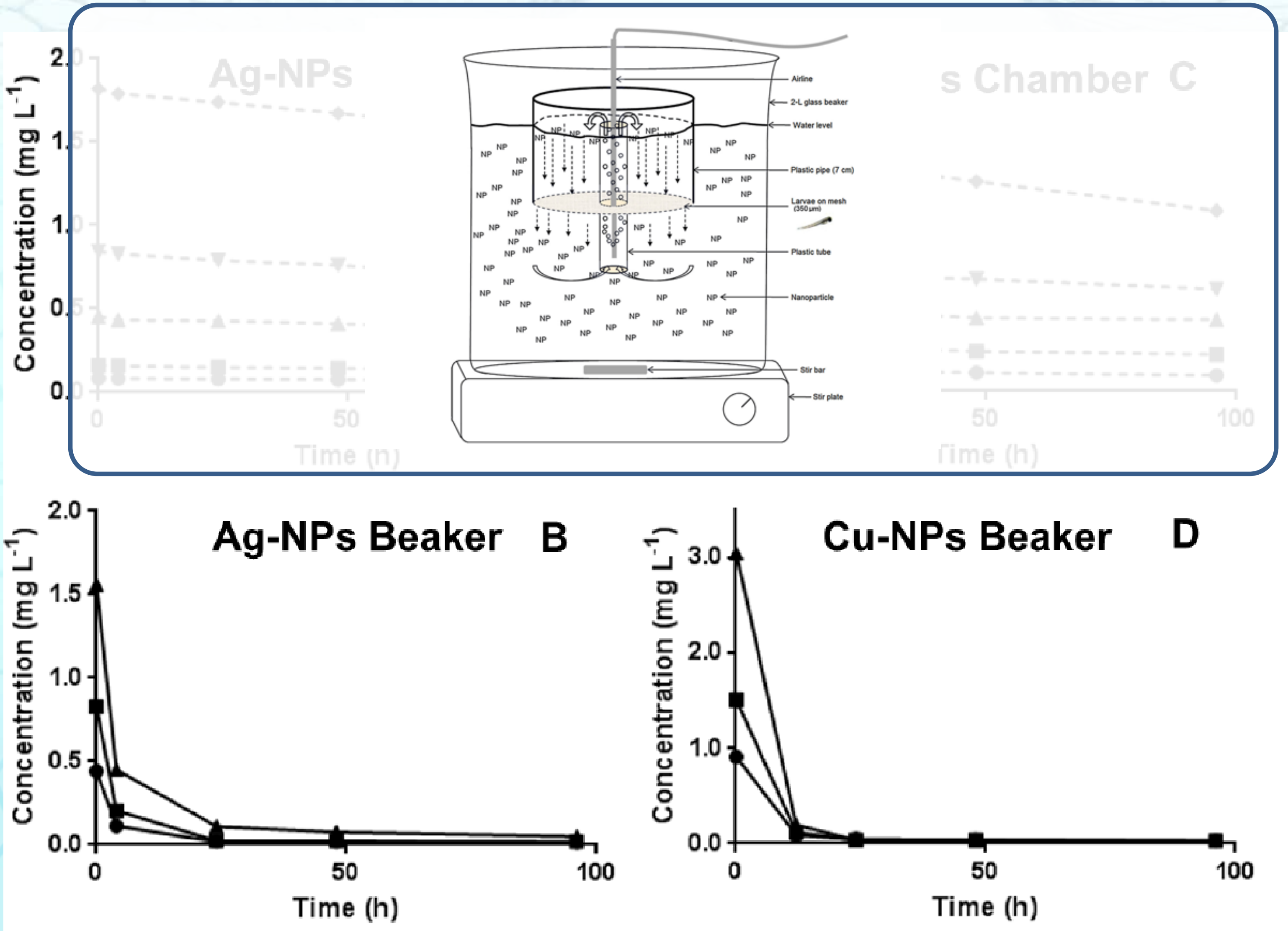
Citrate nAg (dissolved)



Kennedy, et al., unpublished

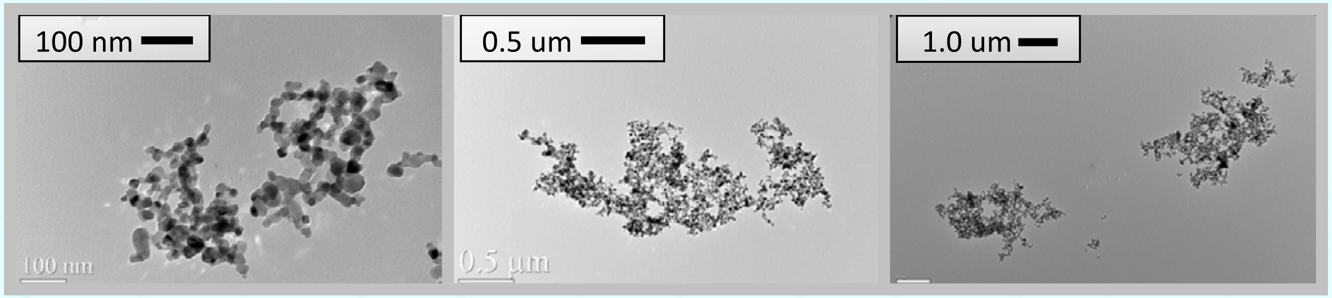


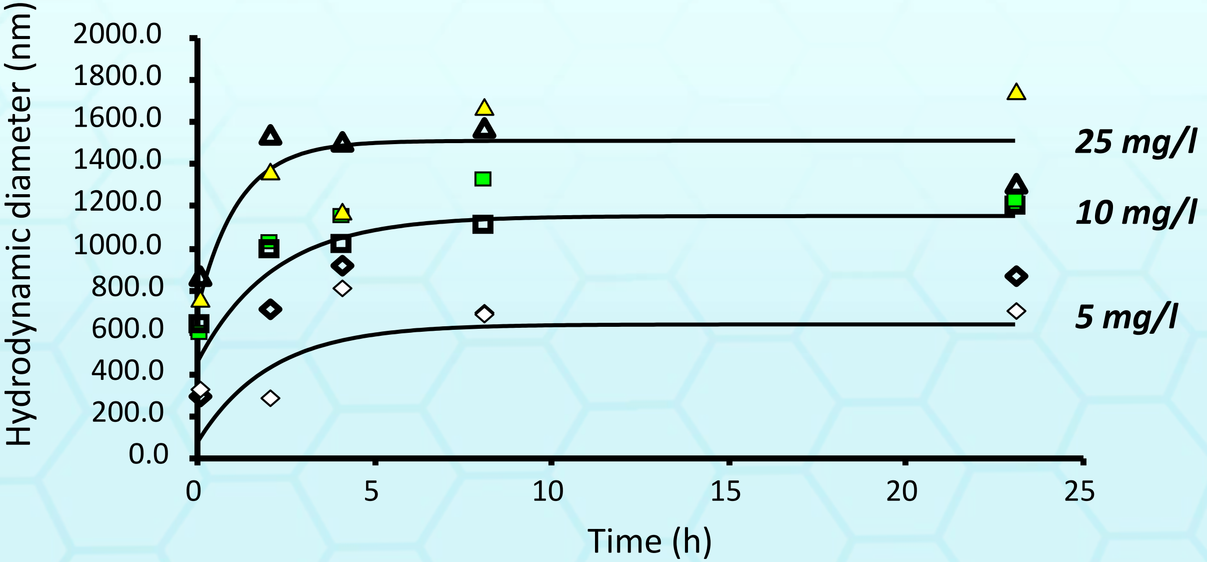
Boyle, D., Boran, H., Atfield, A.J., and Henry, T.B. 2015. ET&C 34:583–588.



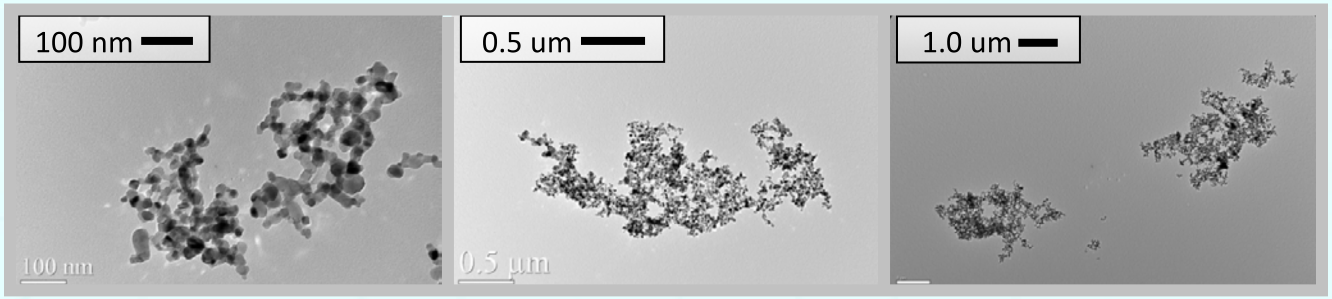
Boyle, D., Boran, H., Atfield, A.J., and Henry, T.B. 2015. ET&C 34:583–588.

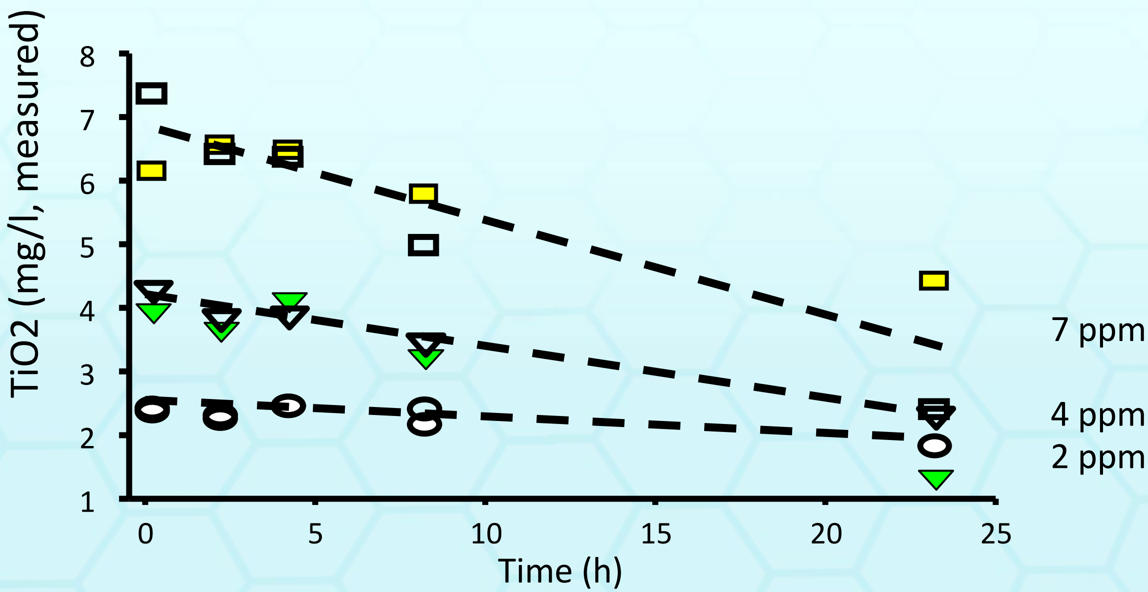
TiO2 Exposures



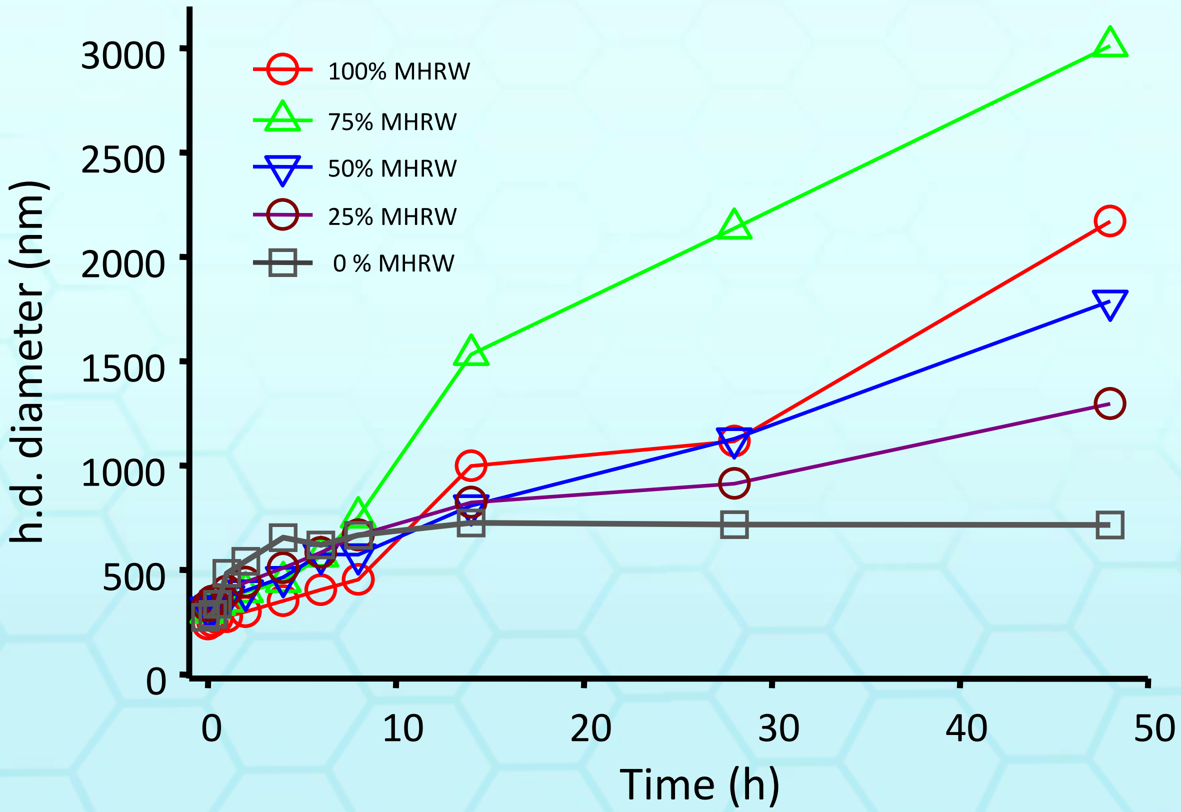


TiO2 Exposures



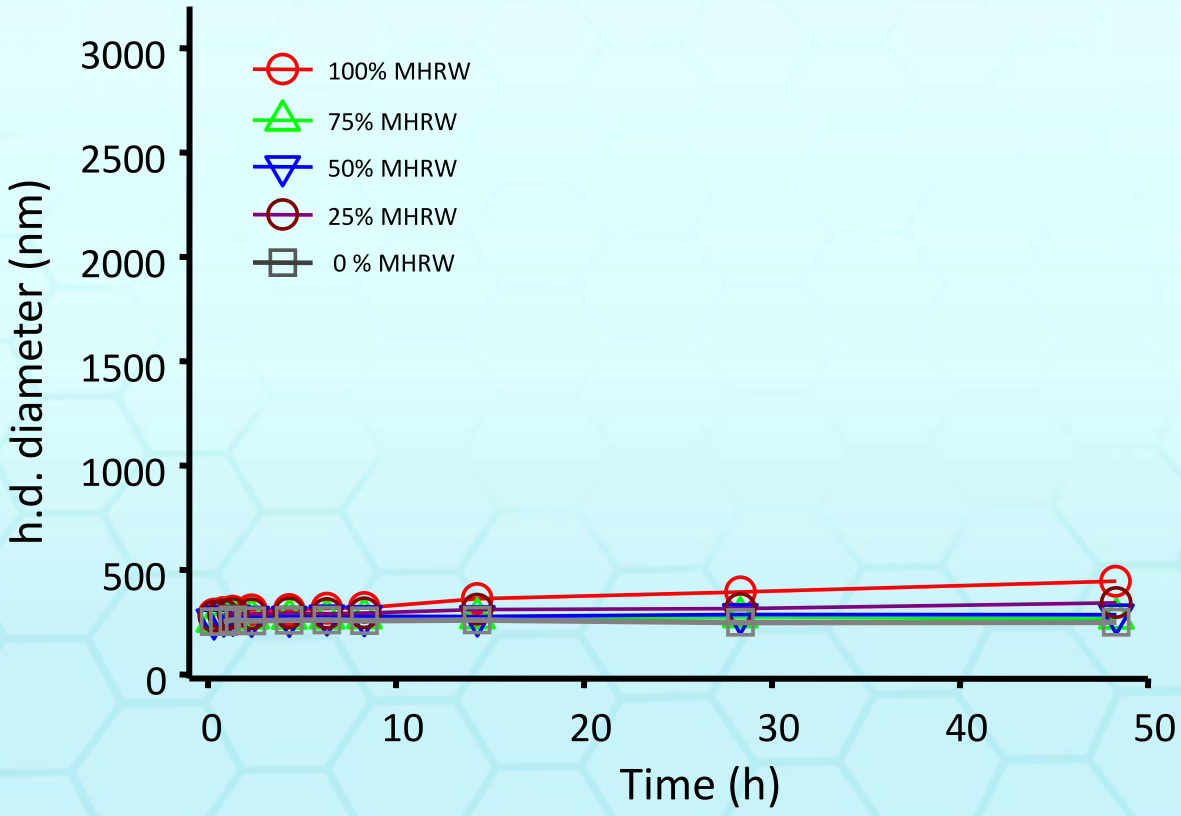


Ionic Strength and TiO2 Agglomeration



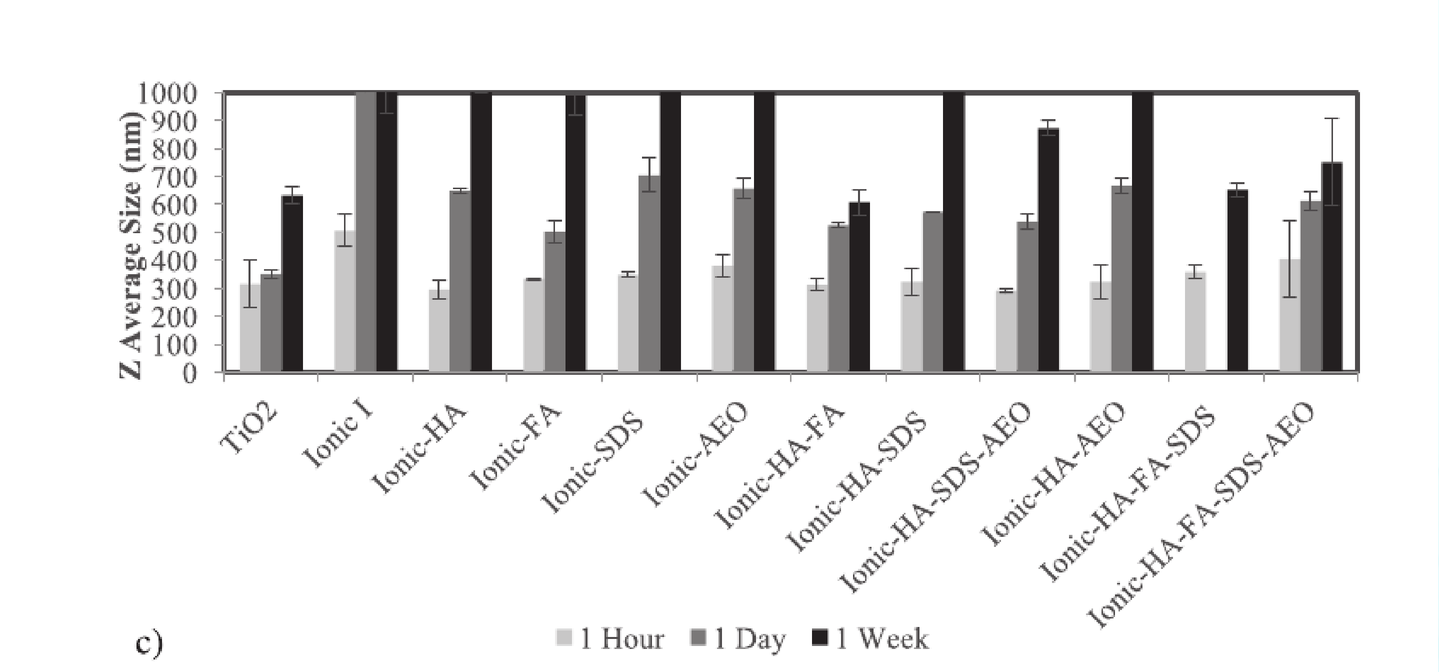
Diamond et al, unpublished

Ionic Strength and TiO2 Agglomeration
-- Adding 5 mg Carbon/L as DOC --



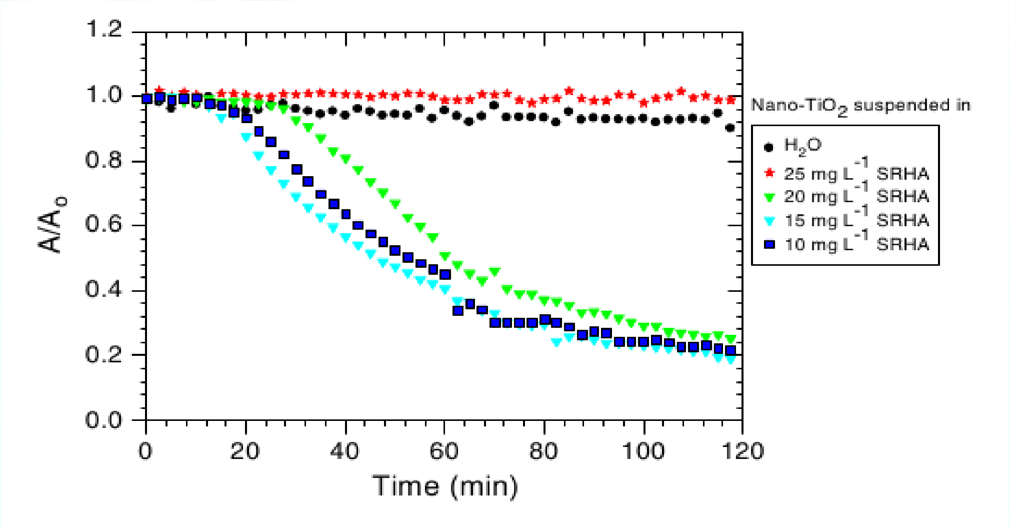
Diamond et al, unpublished

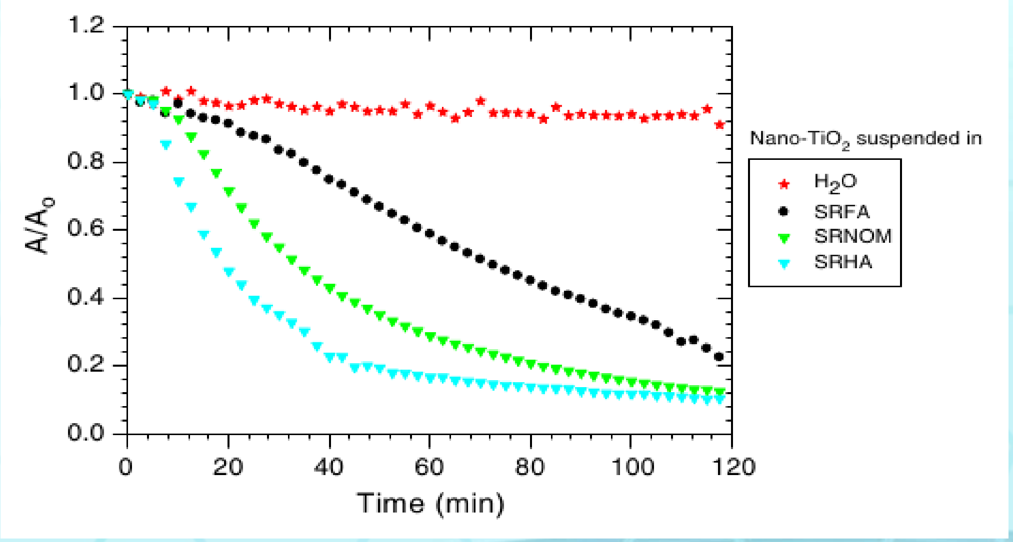
TiO2, ionic strength, NOM



Topuz, E., Sigg, L., and Talinli, I. 2014. Environmental Pollution 193:37–44.

NOM Type and Concentration: TiO2





Erhayem, M., and Sohn, M. 2014. Science of The Total Environment 468:249–257.

TiO2/Graphene composite

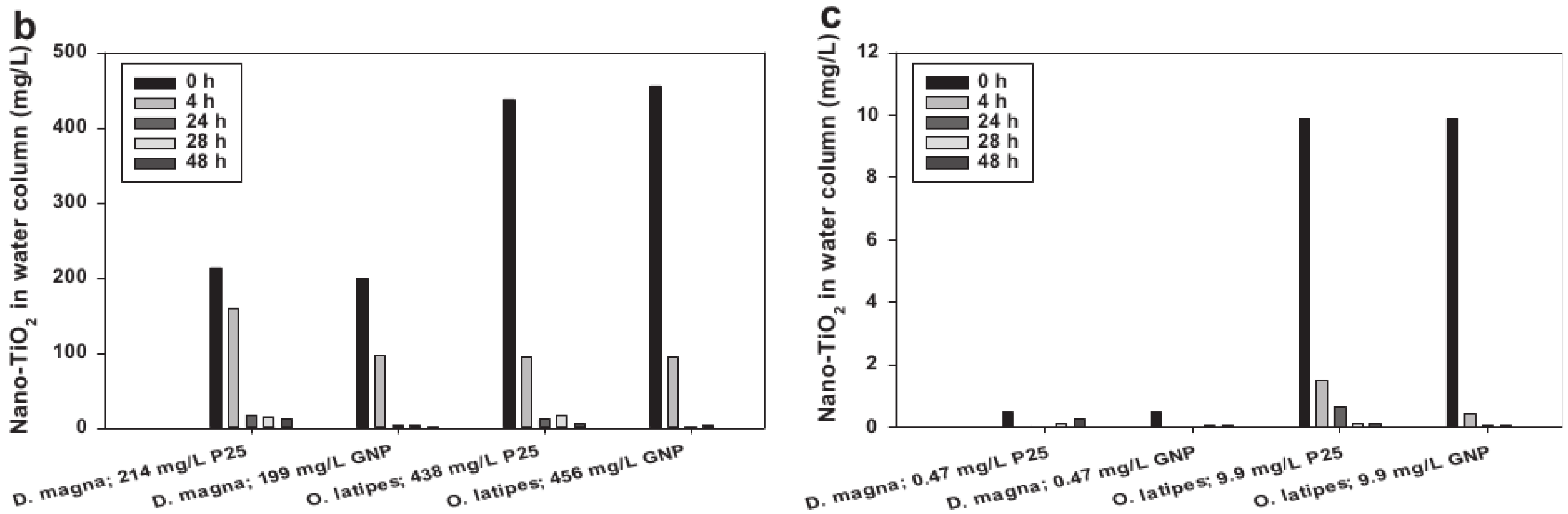
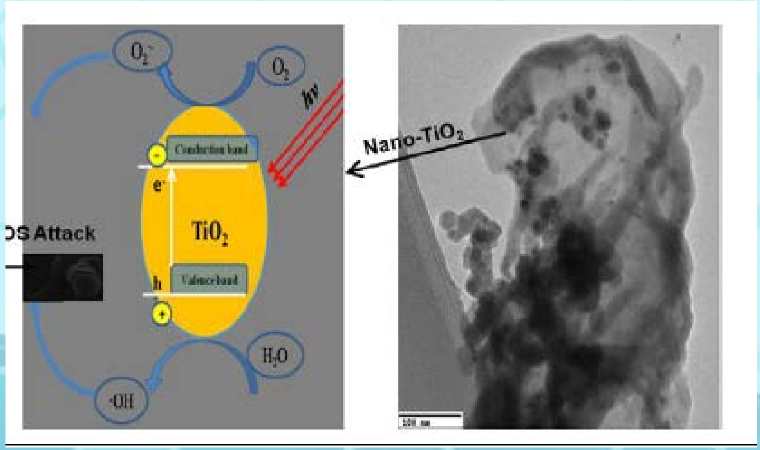
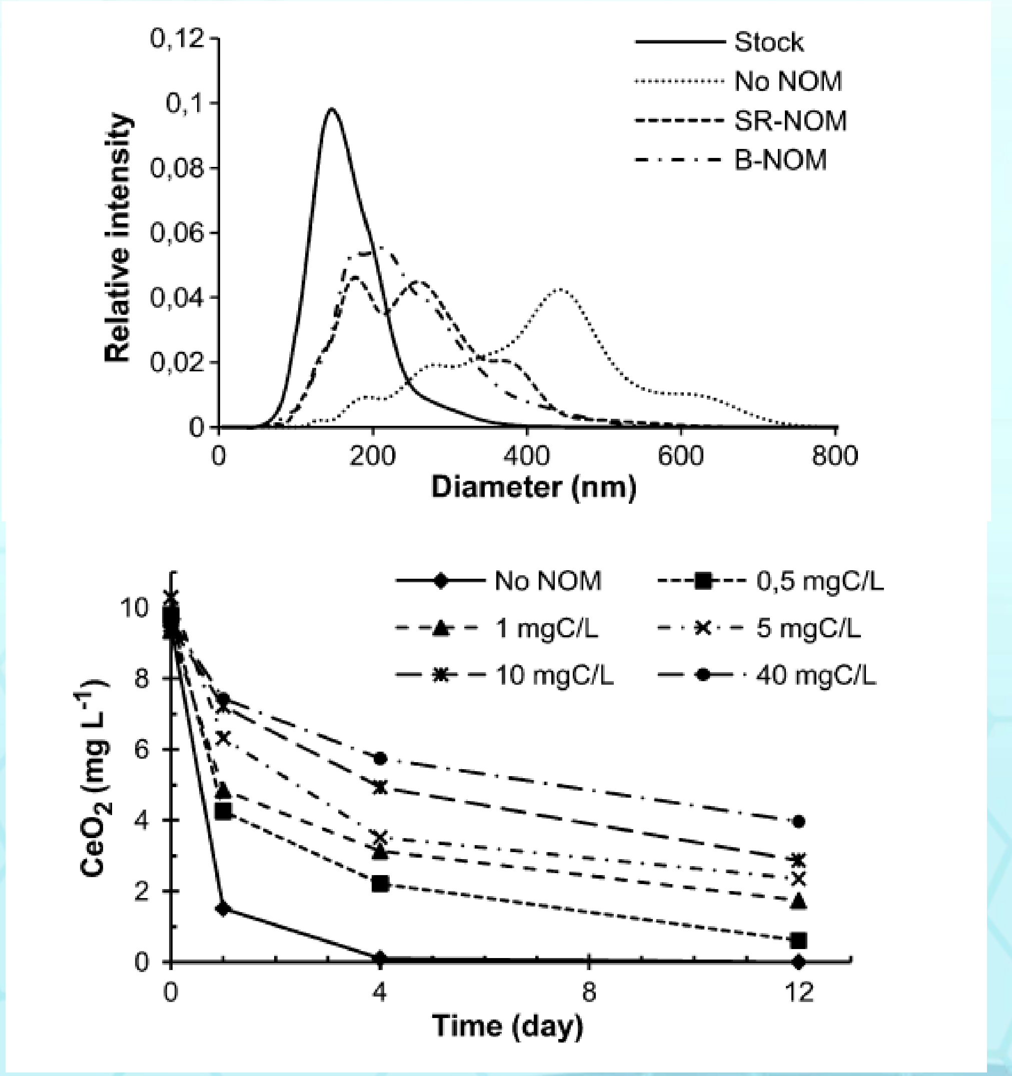


Fig. 2. Agglomerate size (a) of particles and mass of nano-TiO_2 (b, dark; and c, SSR) in water columns during the 48-h bioassay.



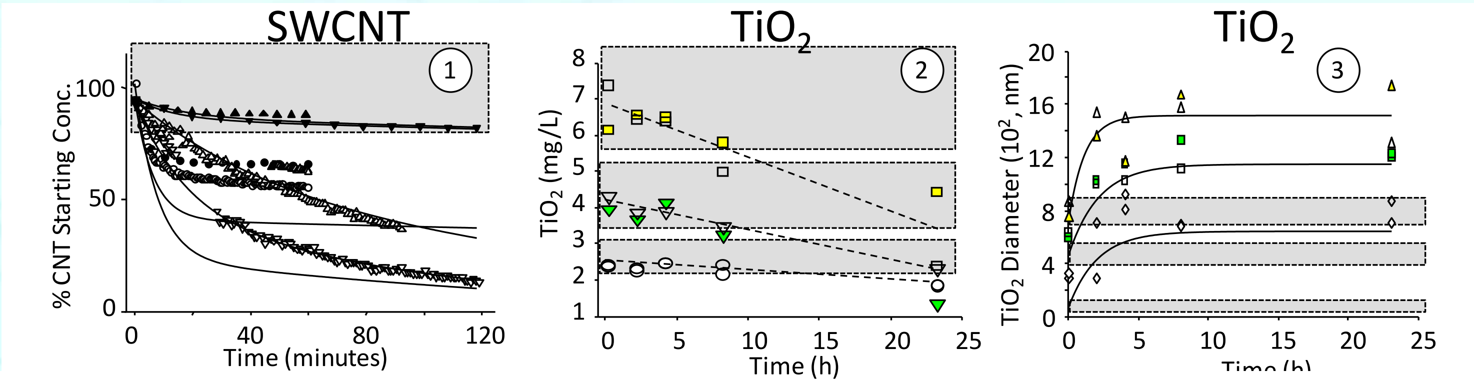
Li, S., et al., 2014. Chemosphere 112:62–69.

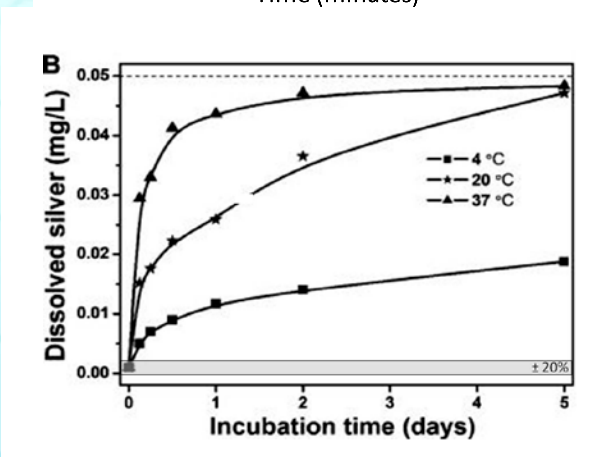
NOM Type and Concentration: Cerium

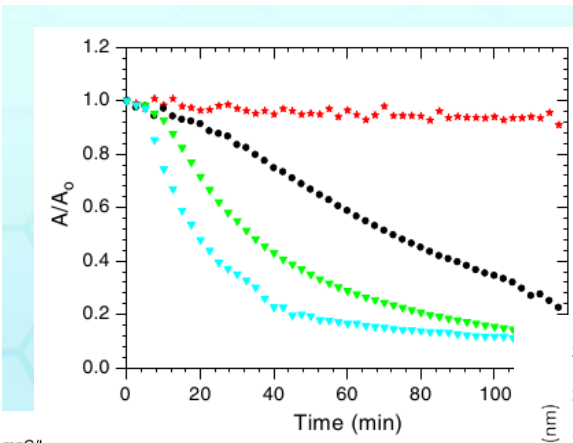


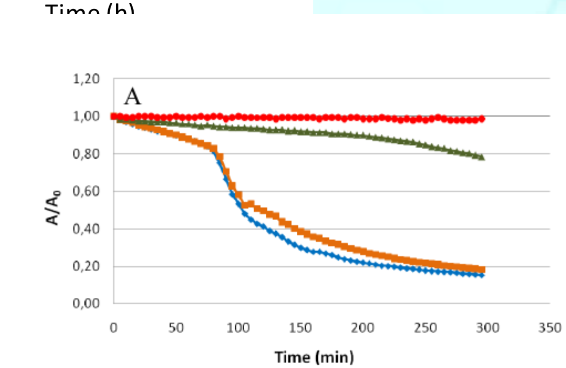
Quik, J.T.K., et al. 2010.Chemosphere.2010.07.062.

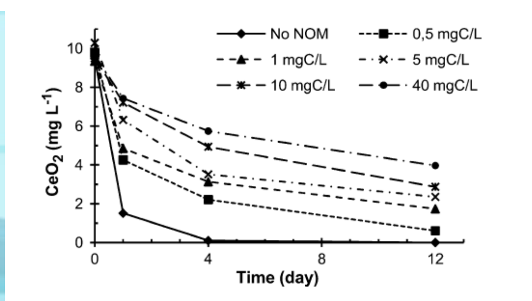
A Collage of Exposure Variability...

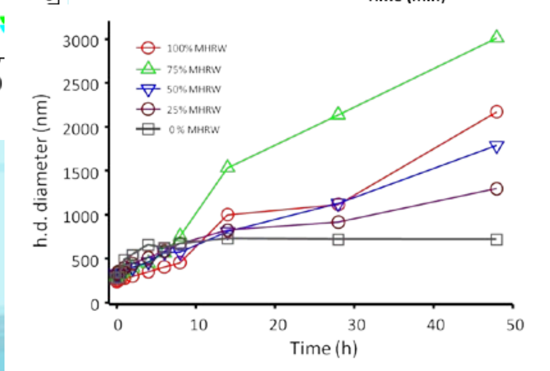










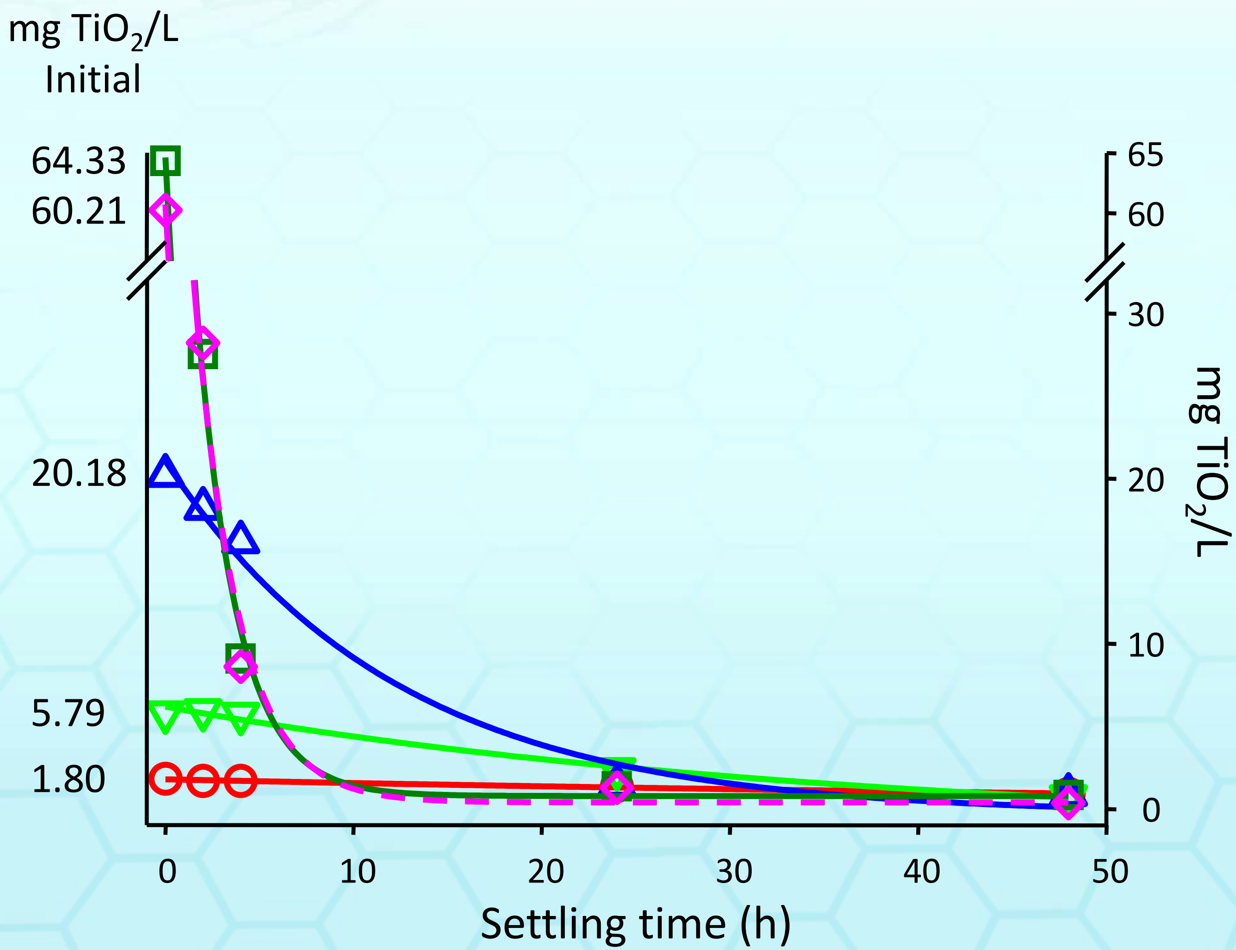


Very few hazard studies document exposure...

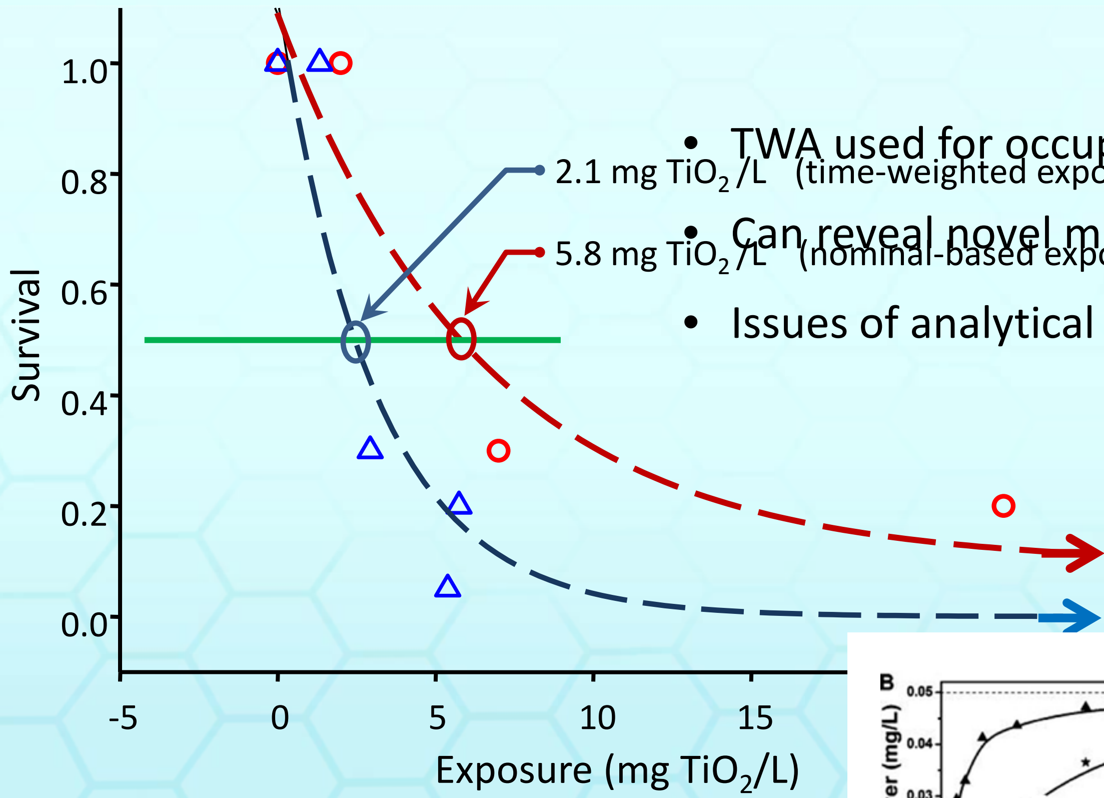
"Setting aside questions of dose metrics, significant and substantial reduction in concentration over exposure period suggests that literature data are in the main improperly interpreted and nanoparticles are likely to have far greater biological effects than suggested thus far by poorly controlled exposures."

Römer, I., White, T.A., Baalousha, M., Chipman, K., Viant, M.R., and Lead, J.R. 2011. Aggregation and dispersion of silver nanoparticles in exposure media for aquatic toxicity tests. Journal of Chromatography A 1218: 4226–4233. Elsevier.

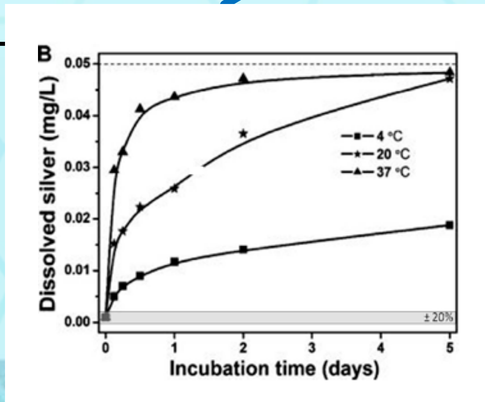
Exposure Variability: Example, Nano-TiO_2 in Mod-Hard Water



Exposure Variability: Example, Nano-TiO_2 in Mod-Hard Water
-- Exposure-Response Estimation --



- TWA used for occupational exposures
- Can reveal novel modes of actions
- Issues of analytical capability



What is nominal?

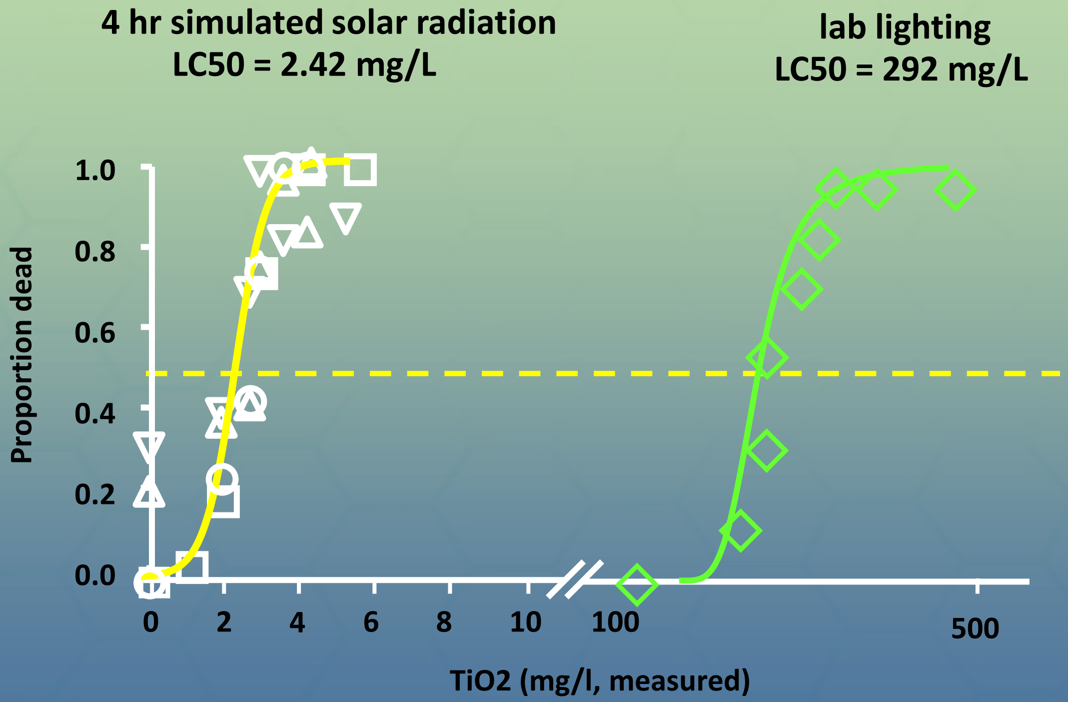
These examples are all pristine, as-produced materials...

- May not represent that enter commerce
- Not subject to fate, transport, and material modification
- Limited range of environmental modifying factors
- Product-based releases are likely to be complex
- Product-based releases remain largely unidentified
- Their complexity will exacerbate controlled exposure issues

An example: Nano-scale TiO2 in cement:

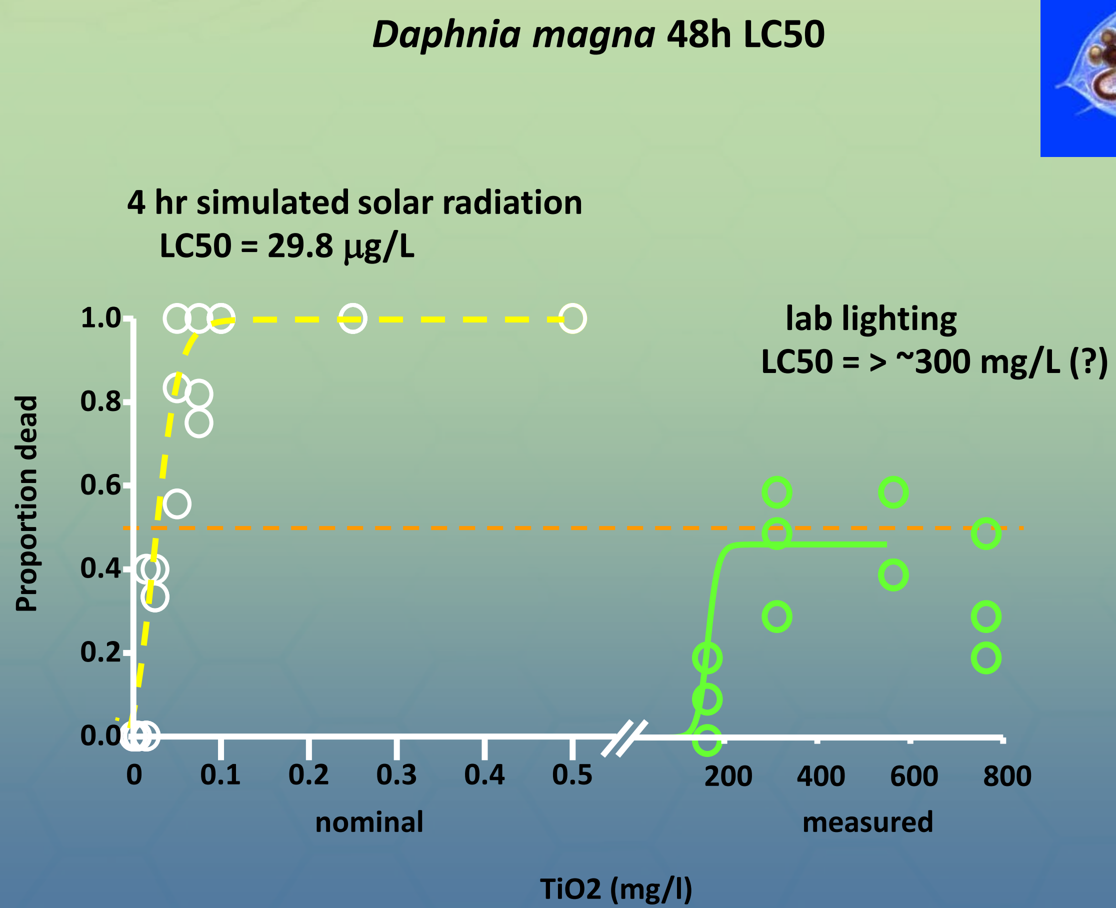
Photoreactivity: Phototoxicity - 96-h Japanese medaka assay

Japanese medaka 96h LC50



Ma, H., Brennan, A. & Diamond, S. a, 2012, *ET&C, 1621–9.*

Photoreactivity: Phototoxicity - 48-h *Daphnia magna* bioassay



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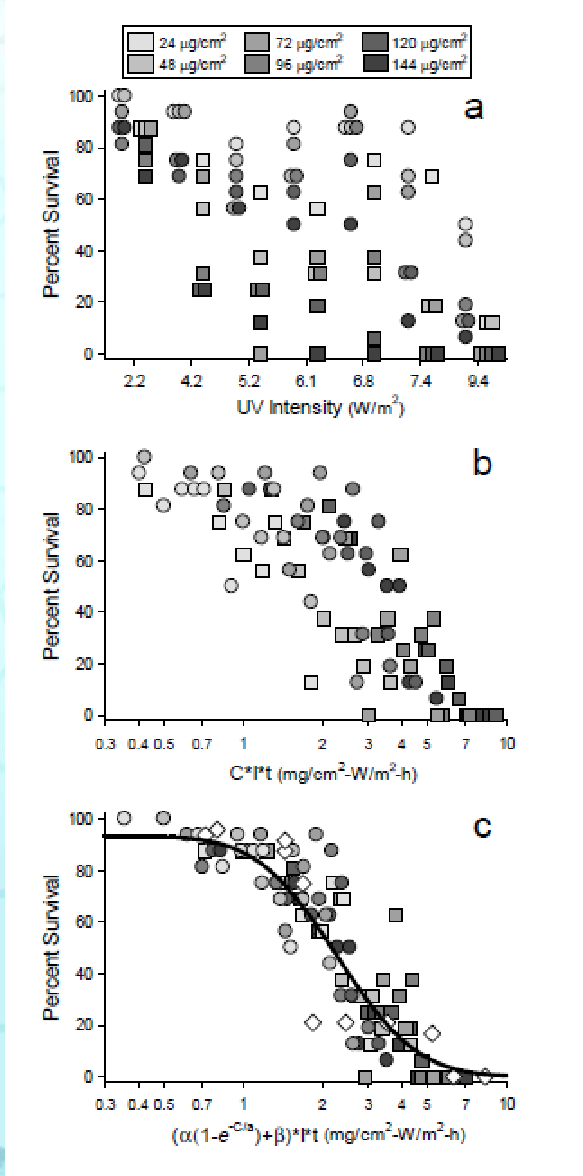


Phototoxicity Exposure

TiO2 Concentration
X
Sunlight Intensity
X
Exposure Duration

(mg/L-Wh/m^2)

"Full" exposure model is the basis for environmental risk assessment.

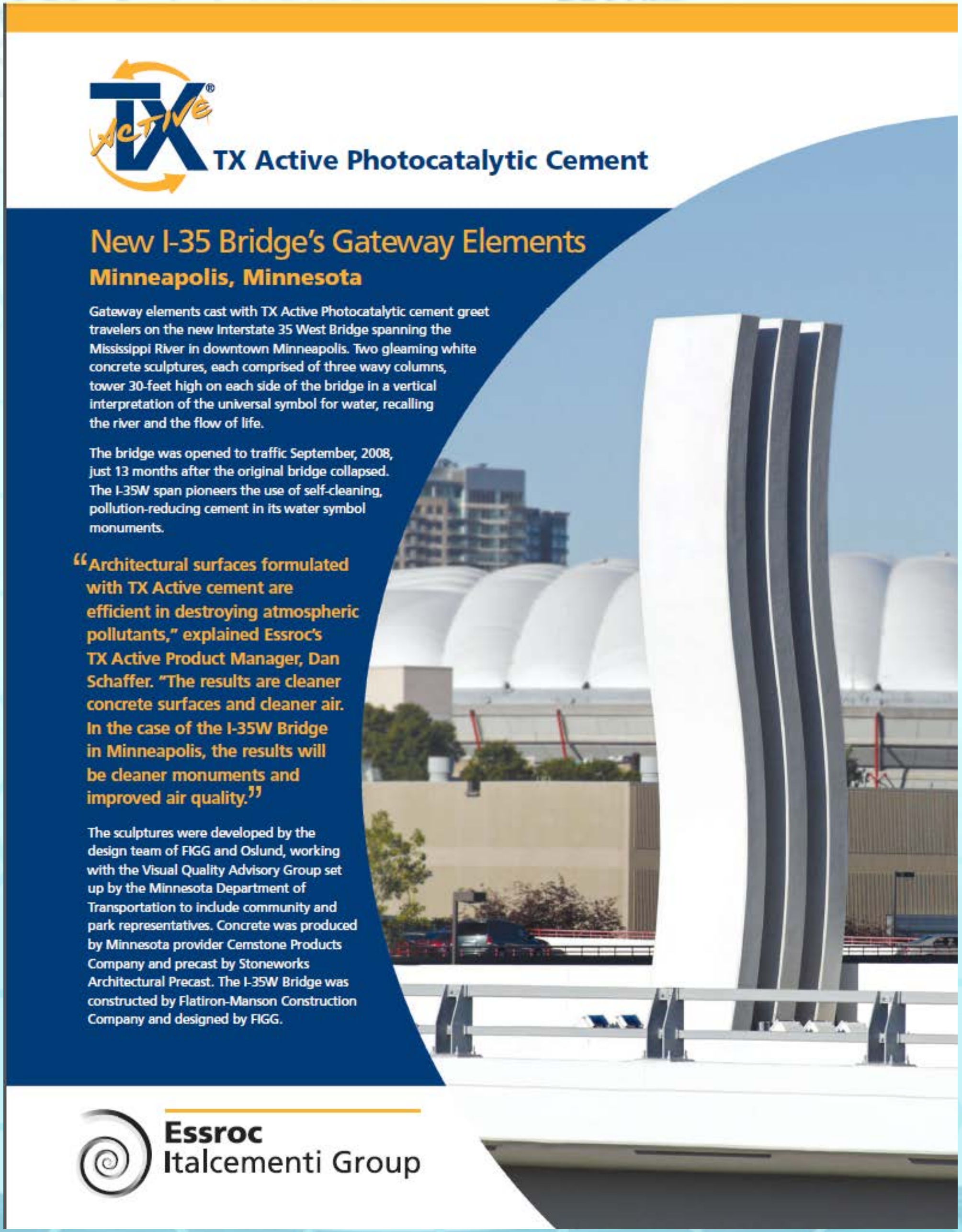
Shibin Li et. al, 2015

Dio Padre Misericordioso Church, Roma
("Jubilee Church")

200 m2 surface area / g
"TX Active"

Italcementi's Borgarello said their research shows that: "In Milan if you just use the material in 15 per cent of the surface of the city you can reduce by 50 percent the pollution."

(Milan: Approximately 181 Km^2, 70 mi^2)



Memorial sculpture at the site of the Minneapolis I-35 Bridge Collapse

i.active Saylor's

Streetscape Project Transforms City Span from Gritty to Green

Chicago, Illinois

An environmentally-focused streetscape project is transforming one of Chicago's oldest urban roadways from gritty to green.

Officially termed the Cermak/Blue Island Sustainable Streetscape Demonstration Project, the Chicago Department of Transportation (CDOT) launched the project in May, 2011. The vision is now blooming amid garden-like bioswale planters with shade trees, walkways constructed of recycled content, solar bus shelters, and pollution reducing bike paths and parking lanes made of TX Active concrete pavers.

According to a report by ENR Midwest: "Photocatalytic pavers, formulated with TX Active cement from Essroc Italcementi Group, reflect urban heat while also reducing air pollution." They invitingly surface the bike and parking lanes along the Blue Island Avenue segment of the project.

The CDOT project team worked with Paveloc of Marengo, IL, now owned by Unilock, to develop a permeable paver system to filter rainwater, further enhancing the pavements sustainability.

Bike lanes and parking areas are surfaced with permeable photocatalytic pavers.

Essroc Italcementi Group

i.active Saylor's

Highway Research Project Paving Way to Cleaner Environment

St. Louis, Missouri

A small stretch of Highway 141 in St. Louis, Missouri may be paving the way to a healthier future.

A research project currently underway will analyze the ability of concrete surfaces formulated with TX Active photocatalytic cement to reduce environmental pollutants from vehicle exhaust.

Air and water quality impacts on the 1,500 feet of road and pervious shoulder will be monitored for one year by researchers from Iowa State University and the University of Missouri at Kansas City.

To conserve resources, an innovative dual stage slip form paving process was used, allowing only the top two inches of concrete to employ the TX Active "smog eating" cement. This is one of the first projects in the US to use dual stage slip form paving.

The research project is an initiative of the Missouri Department of Transportation in collaboration with the Federal Highway Administration, the National Concrete Pavement Technology Center at Iowa State's Institute for Transportation, Lehigh Hanson, Inc. and the Essroc Italcementi Group. Construction services were provided by Fred Weber, Inc. from St. Louis, Missouri.

Dual stage slip form paving process allows TX Active formulated concrete to be used only in the top two inches of the pavement.

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Essroc
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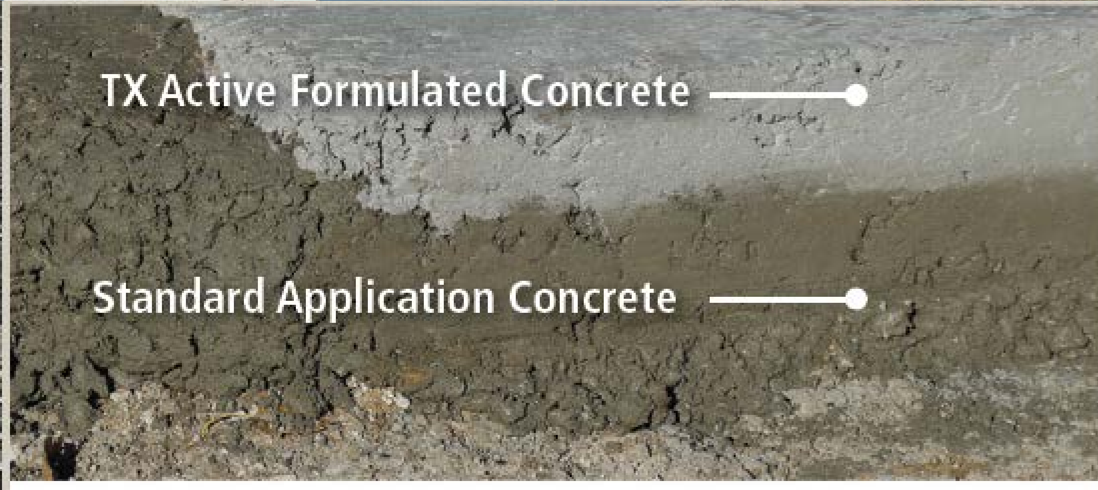


Dual stage slip form paving process allows TX Active formulated concrete to be used only in the top two inches of the pavement.

Paving blocks


Railway stations

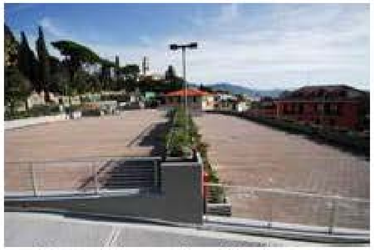

Reduced speed zones


Decorated concrete


Streets and walkways

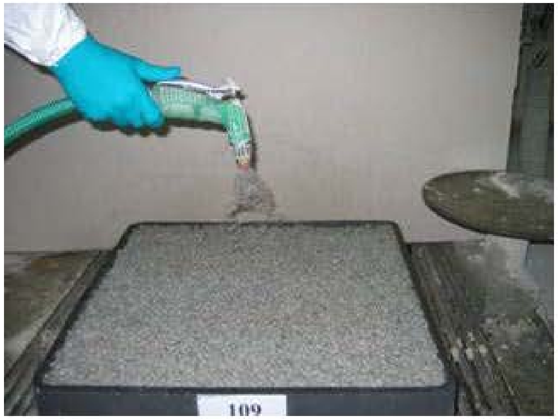

Shopping centers


Sport centers


Parking buildings

from: Italcementi Group promotional presentation

Pervious concrete

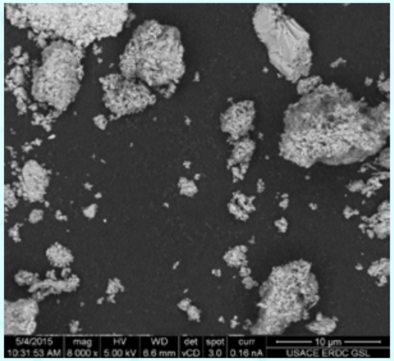


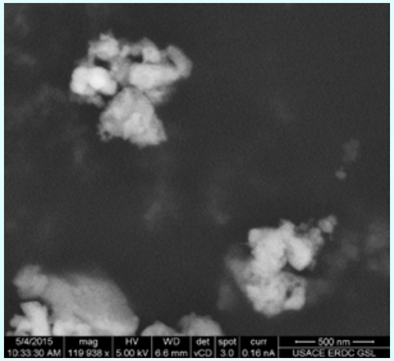
from the laboratory…

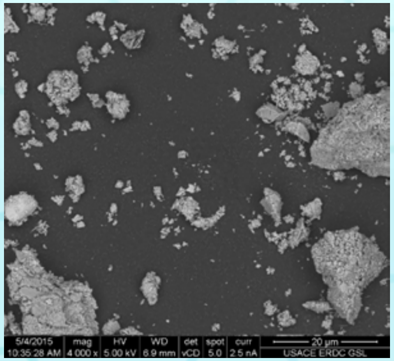
…to the field

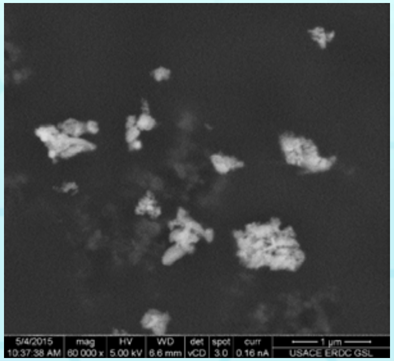
from: Italcementi Group promotional presentation

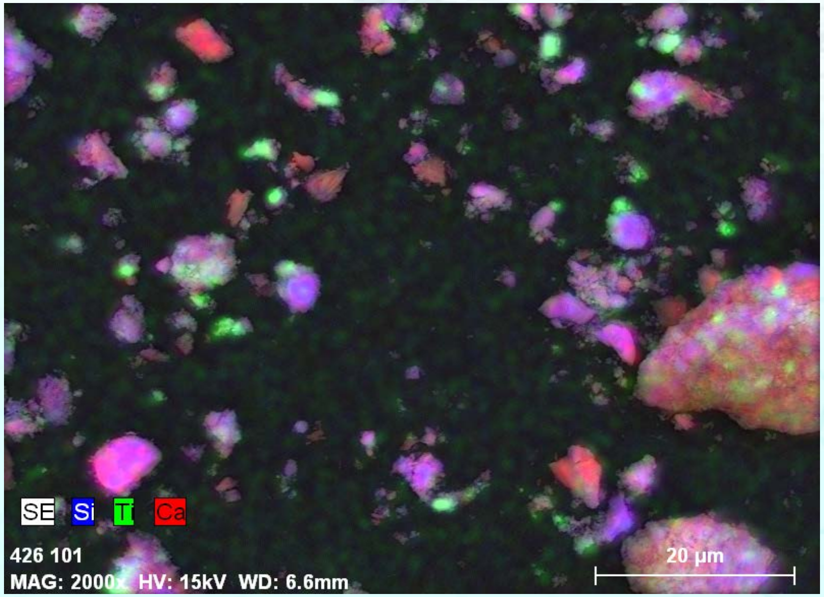
Cementitious TiO2

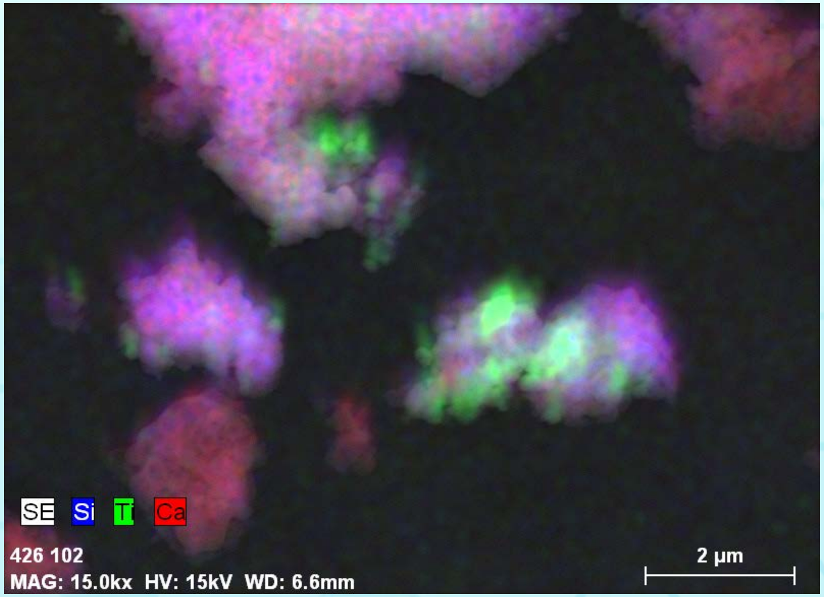




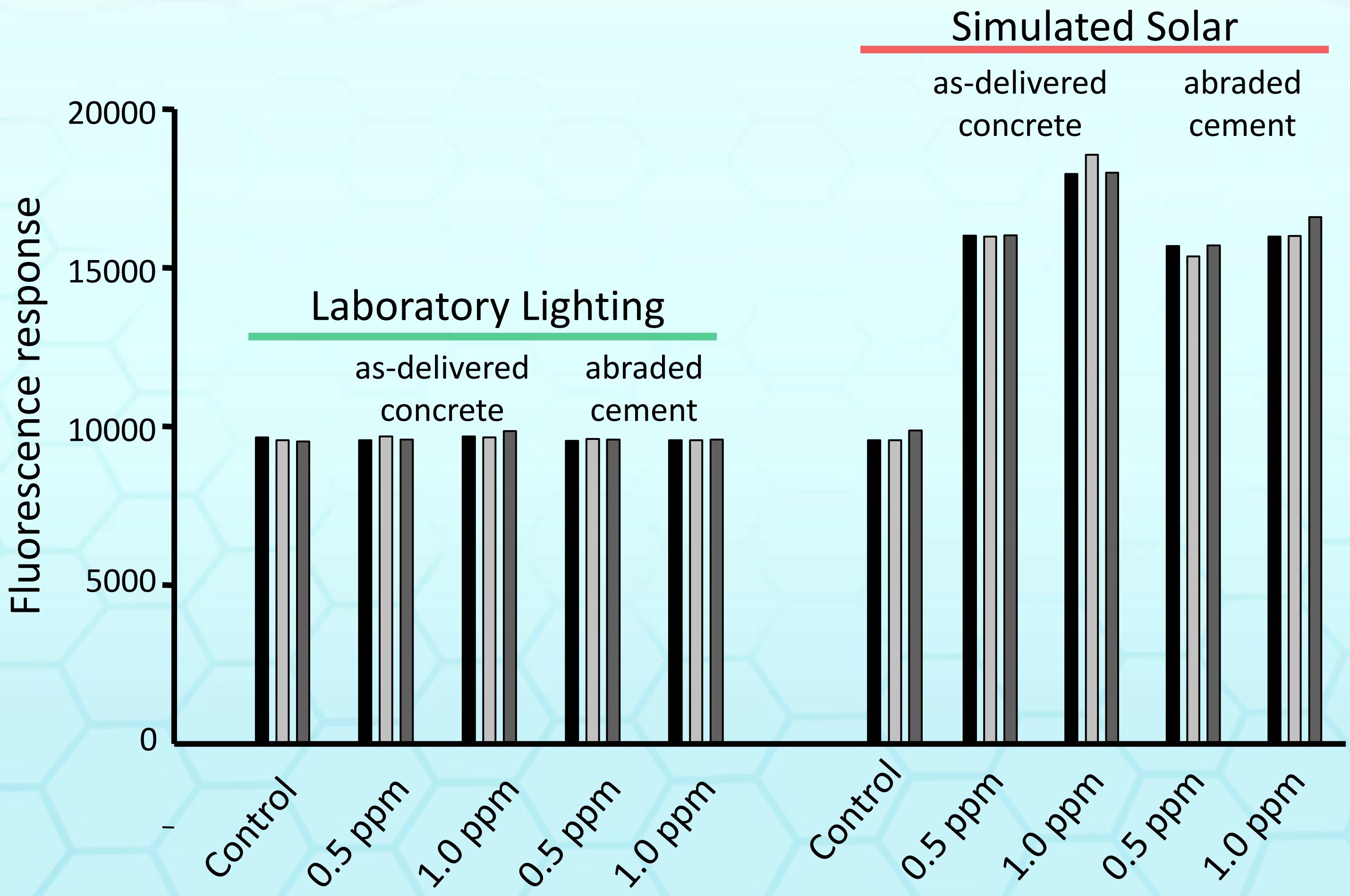








Dye Degradation of As-Delivered Concrete Abraded Cement



Shibin Li, et al. unpublished data

Cementitious TiO2

- Potential exposure will be dependant on volume applied and surface area, wear, abrasion, weathering, construction, demolition, etc.
- Released form = complex matrix
- Exposure? % mass TiO2, surface TiO2, photon dosimetry, analysis...
- Will/should exposure be limited to sediments?
  - Pseudo persistence
  - New set of exposure/dosimetery issues...

These factors will apply to many other product-based nanomaterials

Summary

- Exposure in controlled studies, and in regulatory testing, is irrevocably linked to exposure estimation and risk for potentially-released nanomaterials

- Deficiencies in exposure quantification add uncertainty to risk assessment, and to development of models, particularly for modifying factors

- Formal guidance that will address exposure quantification is under development

OECD Project: Guidance Document on Aquatic (and Sediment) Toxicology Testing of Nanomaterials