Aquatic Fate and Toxicity of III/V Semiconductor Materials in the Presence of CMP NPs

(Task #: 425.052)

Seed Project: Initial Sorption & Toxicity Screening of III/V Ions *(Task #: 425.047)*

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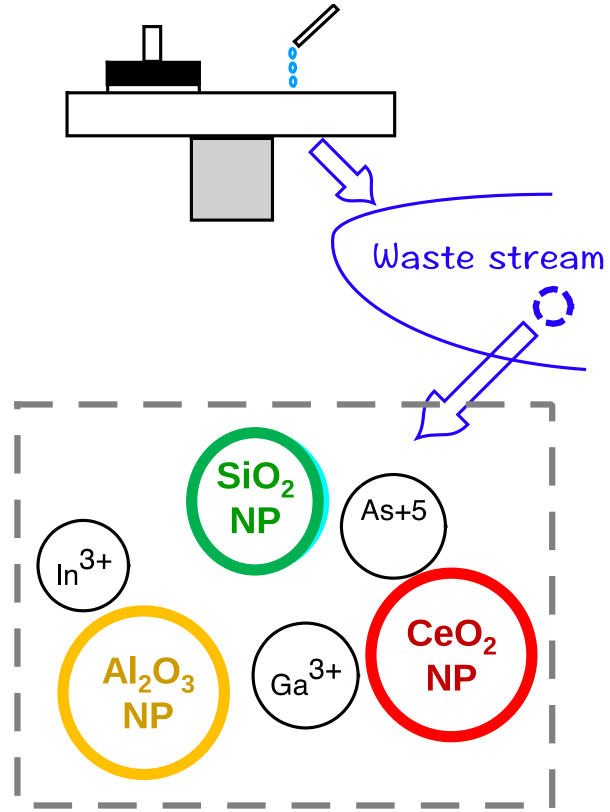
Research background

- Post-CMP waste effluent may contain III/V ions and engineered nanoparticles (NPs) from CMP slurries.

- Little is known about the ecotoxicity of Ga^{3+} and In^{3+}.

- Concerns of "synergistic" environmental risk by III/V ions and NPs from CMP slurries.

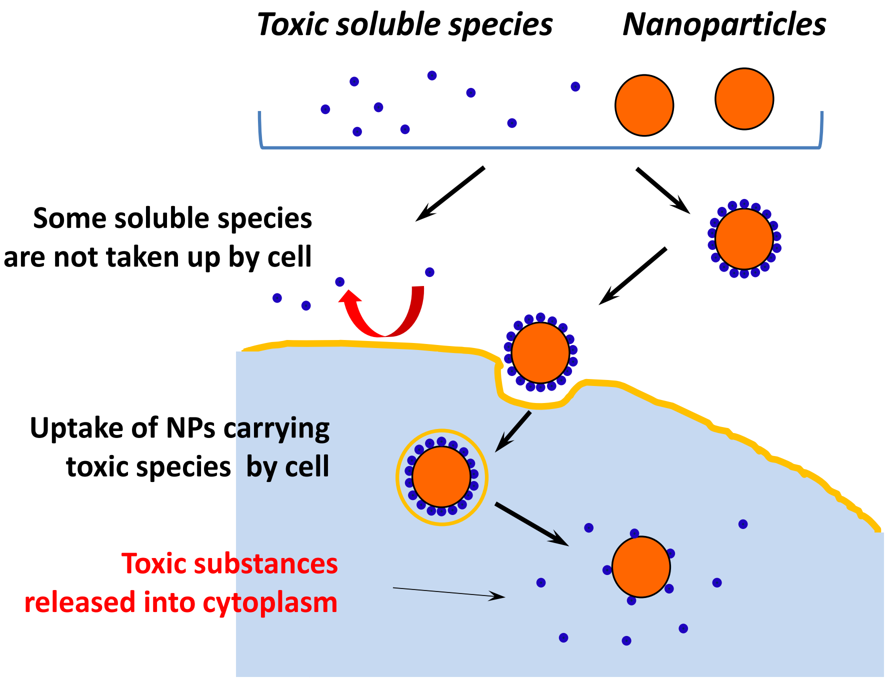


Chemical mechanical polishing (CMP) of III/V materials (e.g. GaInAs)

Hypotheses

- The high reactivity and surface area of NPs can lead to accumulation of toxic substances at NP surfaces.

- Engineered NPs can facilitate the entry of the adsorbed molecules into cells and this "*Trojan horse*" mechanism can enhance the adverse effects of toxic substances.



Schematic illustrating the role of NPs as carriers (Trojan horses) that facilitate the uptake of toxic contaminants by cells.

Objectives

Aim:

Investigate the adsorption of III/V materials (As, Ga and In) by CMP NPs and explore how these interactions impact the environmental fate, biological uptake, and aquatic toxicity of both the III/V materials and the NPs.

Objectives:

- Evaluate the capacity of CMP NPs to adsorb III/V species.
- Model aqueous surface complexation of III/V materials onto CMP NPs.
- Investigate the ecotoxicity of CMP NPs and III/V species in the absence/presence of NPs.
- Elucidate the role of CMP NPs in enhancing III/V ion uptake by cells.

Experimental Results

1. Aqueous surface complexation of III/V species onto CMP NPs.

2. Ecotoxicity of III/V ions.

3. Toxicity testing of CMP NPs and III/V species using the zebrafish embryonic model.

1. Quantify aqueous surface complexation of III/V species onto CMP NPs

Paul Westerhoff and Xiangyu Bi

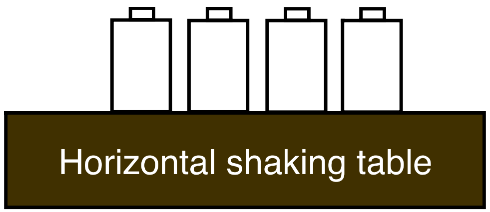
Arizona State University

Materials & Methods

Key characteristics for the **model CMP slurry** composition

Properties	Colloidal SiO_2 c-SiO_2	Fumed SiO_2 f-SiO_2	CeO_2	Al_2O_3
Primary metal concentration	27 g Si/L	50 g Si/L	9.6 g Ce/L	29 g Al/L
Diameter by TEM (nm)	36 ± 9	ND#	39 ± 19	38 ± 16
Zeta potential at slurry pH (mV)	-21	-50	43	55
pH	2.5 – 4.5	10	3-4	4.5-5.0
Other additives	802 mg acetate/L	< 1% KOH	--	135 mg nitrate/L

Materials & Methods: Adsorption Isotherms

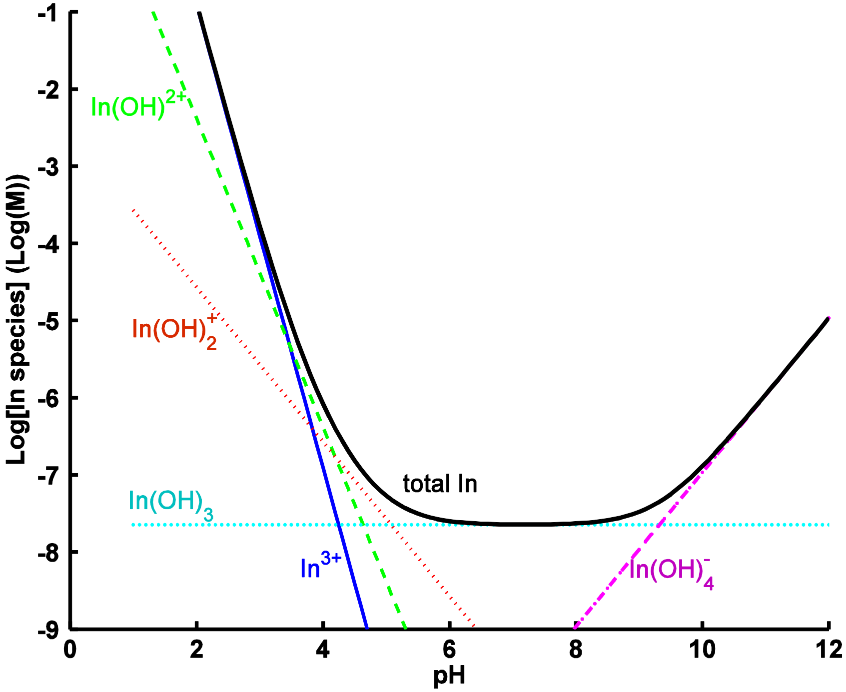


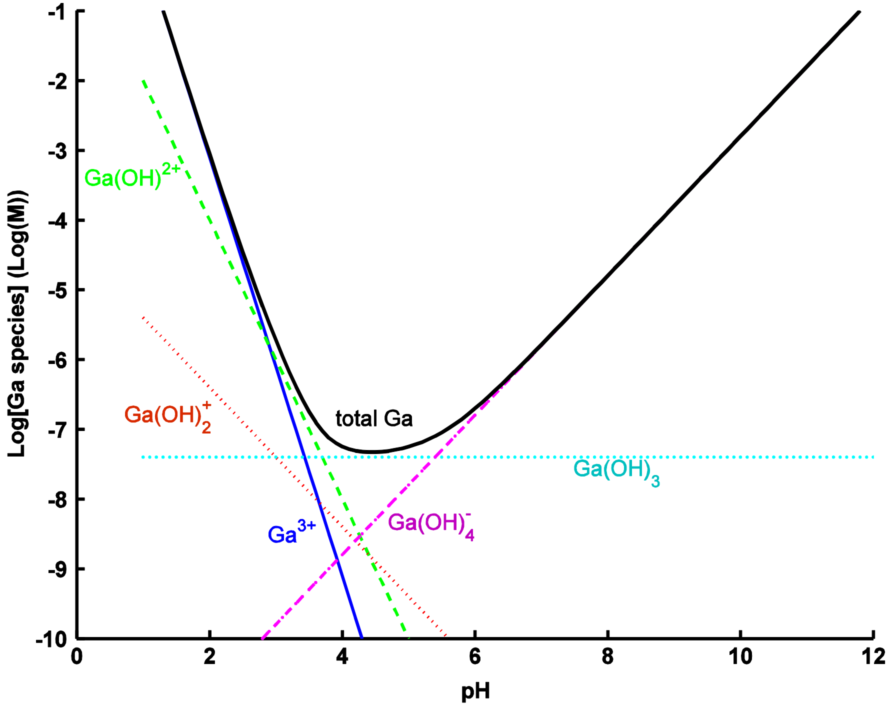
- In^{3+}, Ga^{3+}, or As(V) spiked into CMP NP dispersions.
- Background of 0.1 M NaCl.
- Shaking for 3 days.

- Separation of NPs using centrifugal ultrafiltration (30k Da).

Filtrate analyzed by ICP-MS

Aqueous solubility of Ga^{+3} and In^{3+}

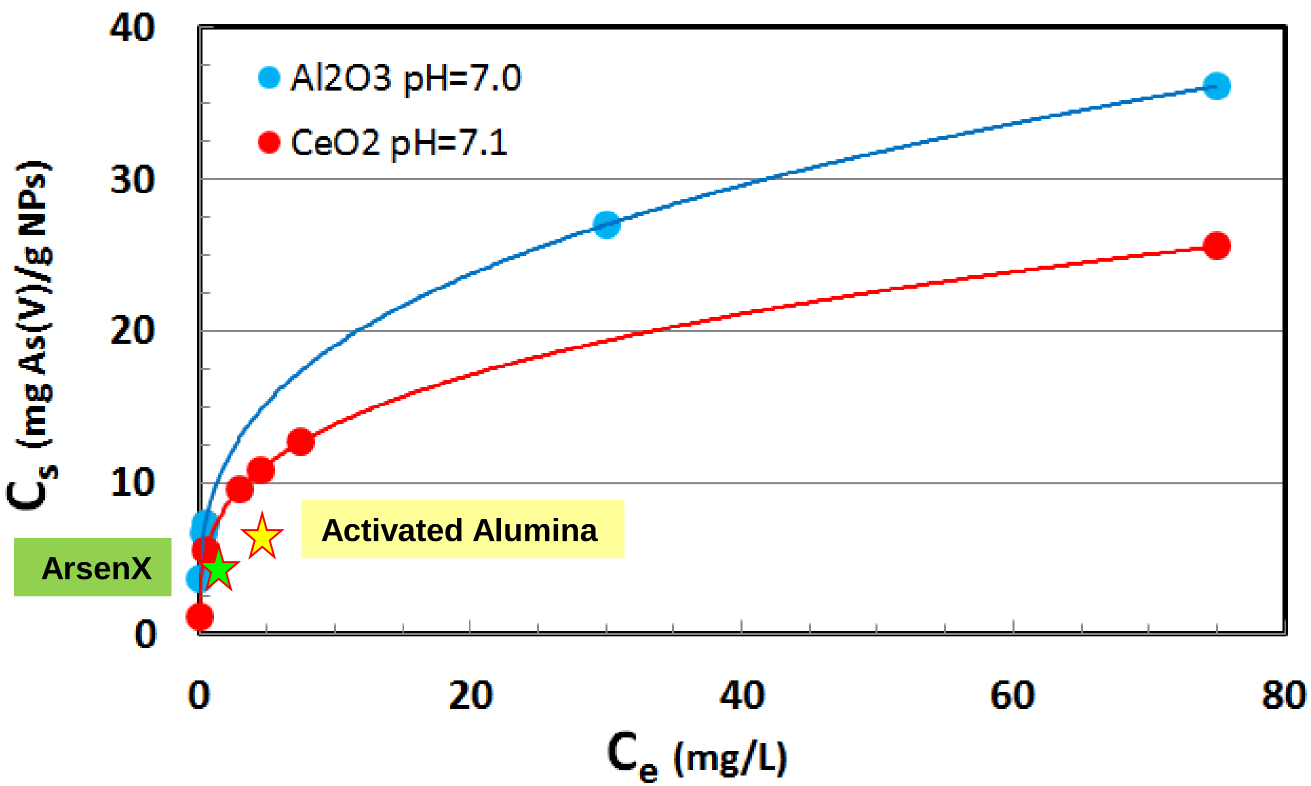




Equilibrium constants from Biryuk et al.,1969; Baes Jr. et al., 1986; Aksel'rud et al., 1959; Wood, 2006; Feitknecht et al, 1963)

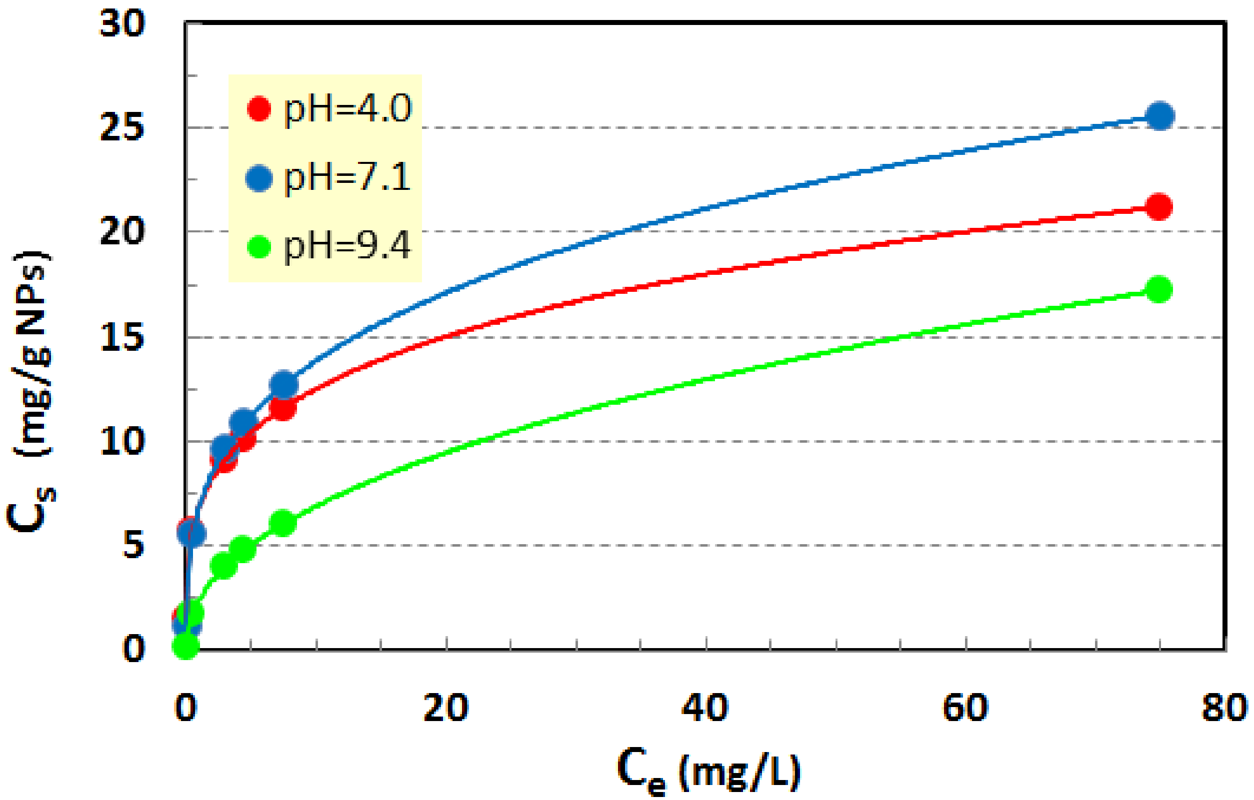
- Ga^{3+} and In^{3+} are sparingly soluble at neutral pH values.
- Citrate was added to enhance the solubility of Ga^{3+} and In^{3+} in some adsorption tests.

Adsorption of As(V) by CMP NPs



- As(V) is sorbed by CeO_2 and Al_2O_3 NPs.
- As(V) adsorption by SiO_2 NPs was negligible.

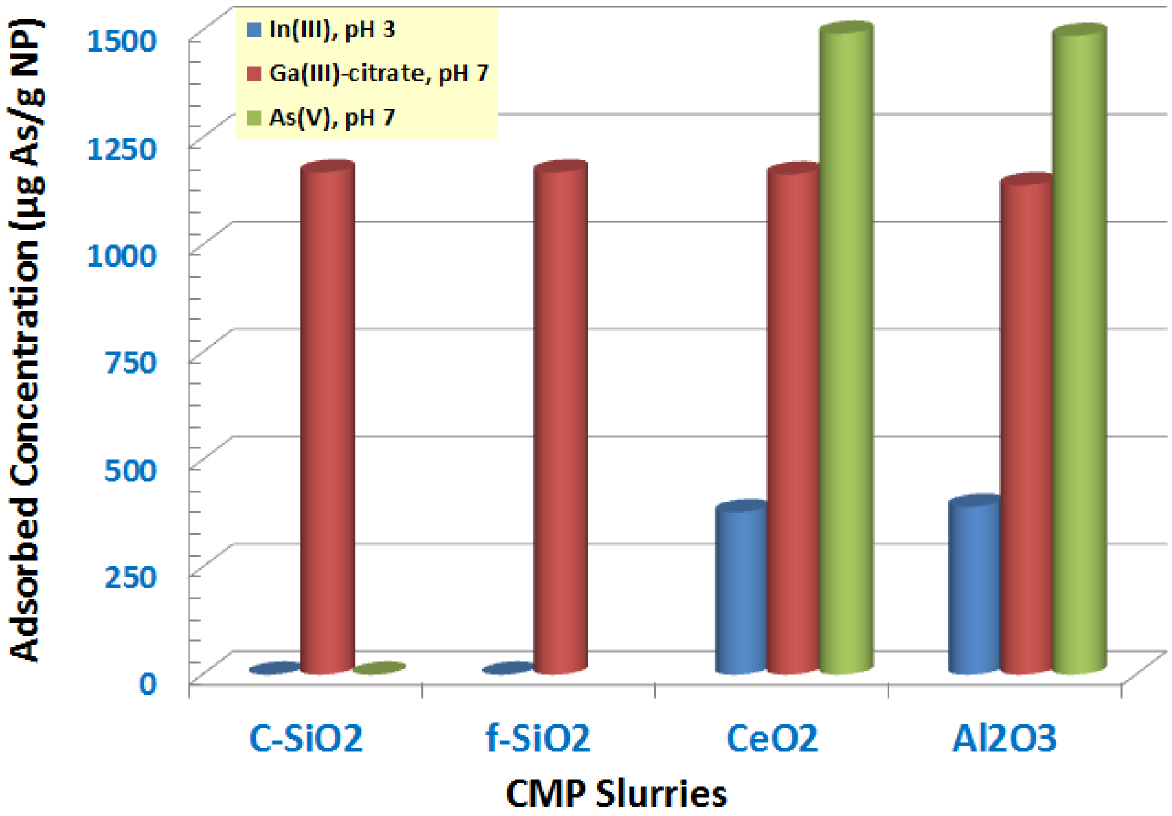
Effect of pH on As(V) sorption by CeO_2 NPs



- The affinity of CeO_2 and Al_2O_3 NPs for As(V) is pH dependent.

Adsorption capacity of CMP NPs:

(Initial adsorbate concentration = 0.01 mM)



- CeO_2 and Al_2O_3 exhibit higher adsorption capacity toward In^{3+} and AsO_4^{3-} than SiO_2.

Summary

- Al_2O_3 and CeO_2 NPs shown to adsorb all the III-V ions tested.
- SiO_2 NPs only adsorbed Ga^{+3}–citrate.
- Adsorption of As(V) by CMP NPs dependent on pH.

NEXT STEPS:

- Complete isotherms over range of concentration & pH levels.
- Parameterize surface adsorption models.

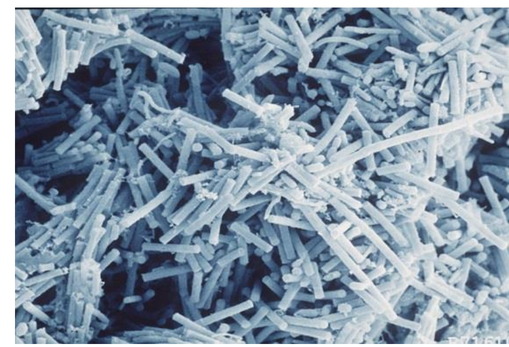
2. Ecotoxicity screening of III/V species

Reyes Sierra, Adrian Gonzalez, Emily Orenstein, Jim A Field

Department of Chemical & Environmental Engineering
University of Arizona

2. Ecotoxicity of III/V ions: Objectives

Assess the toxicity of As(III), As(V), In^{3+} and Ga^{3+} towards key microbial populations in biological wastewater treatment and organisms used in effluent toxicity monitoring:

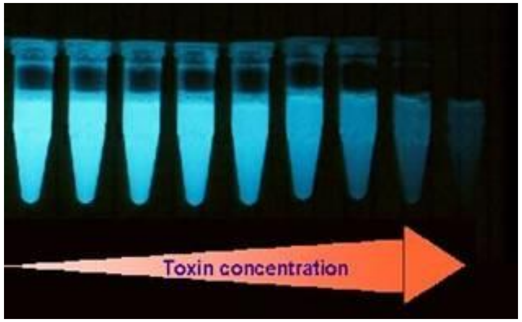


- Heterotrophic aerobic bacteria in activated sludge
- Methanogenic microorganisms in anaerobic sludge
- *Aliivibrio fischeri* (Microtox)
- Water fleas (*Daphnia*)

Methodology

- **Methanogenic inhibition bioassay (anaerobic microorganisms)**
  - $CH_3COOH \longrightarrow CH_4 + CO_2$
- **O_2 respiration inhibition bioassay (aerobic microorganisms)**
  - $CH_3COOH + 2\,O_2 \longrightarrow 2H_2O + 2CO_2$
- **Microtox:**

  Inhibition of bioluminescence (*Aliivibrio fischeri*)

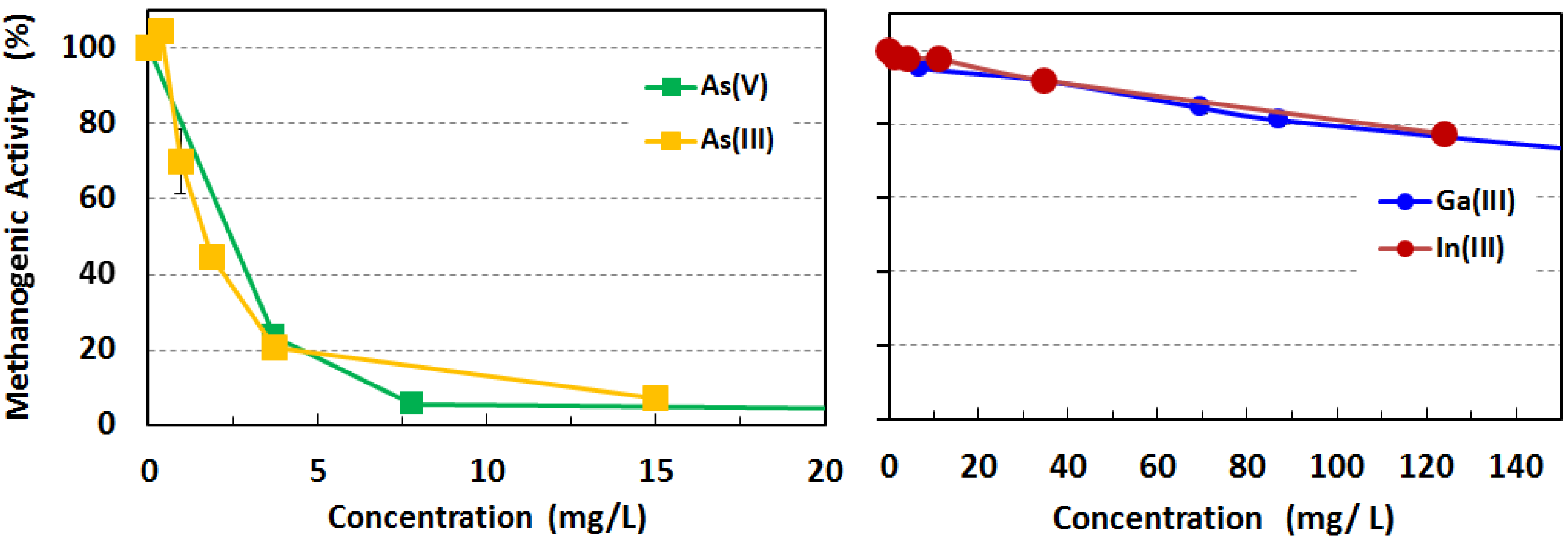


(http://myweb.scu.edu.tw/~94134001/2.files/image009.jpg)

- **Acute toxicity, *Daphnia magna*:**

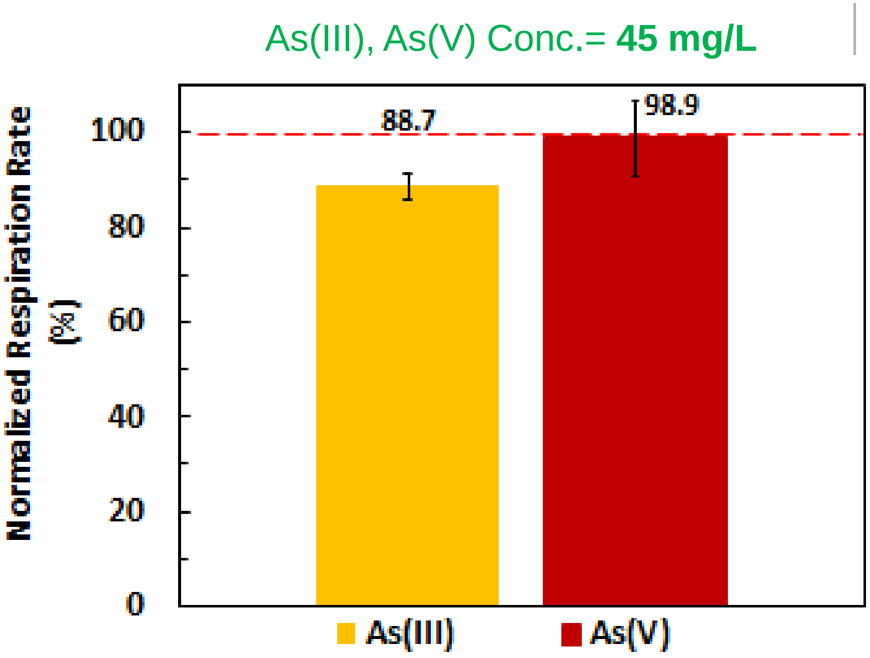
  EPA test method, 48 h

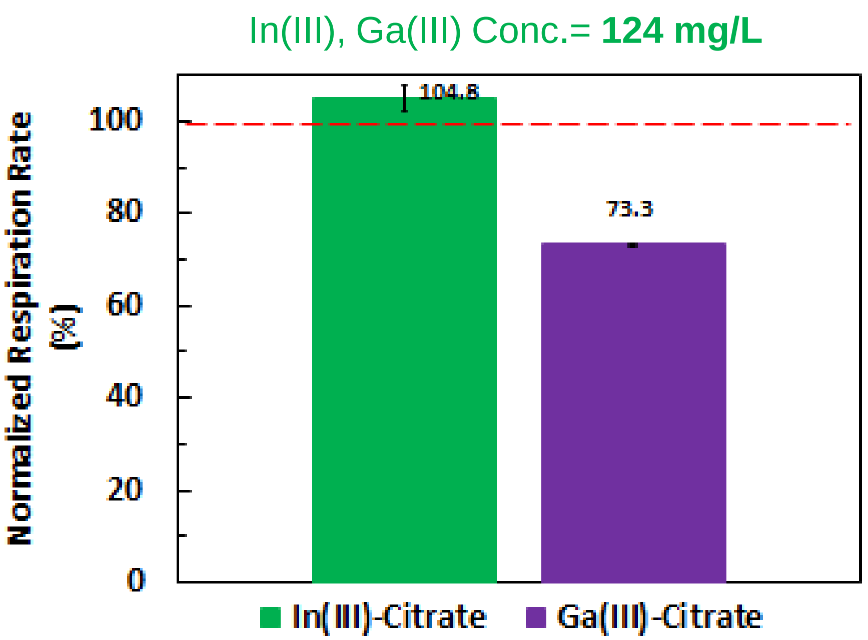
Methanogenic Inhibition by III/V Ions



- As(III) and As(V) are severe inhibitors of methanogenesis (IC50= 1.7 and 1.5 mg/L).
- Ga^{3+}- and In^{3+} citrate only caused moderate inhibition at the highest concentrations tested (IC20 = 96-107 mg/L).

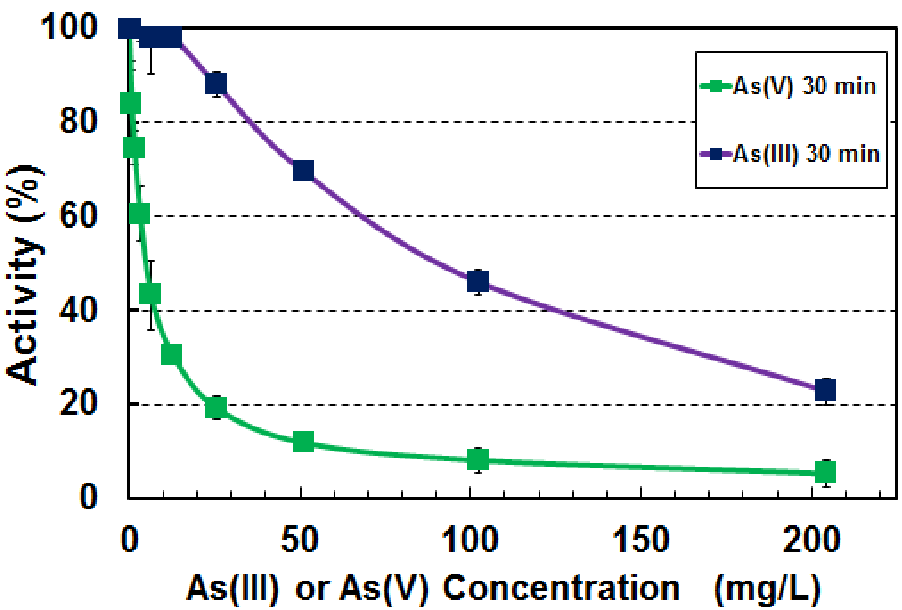
Inhibition of O_2 respiration by activated sludge

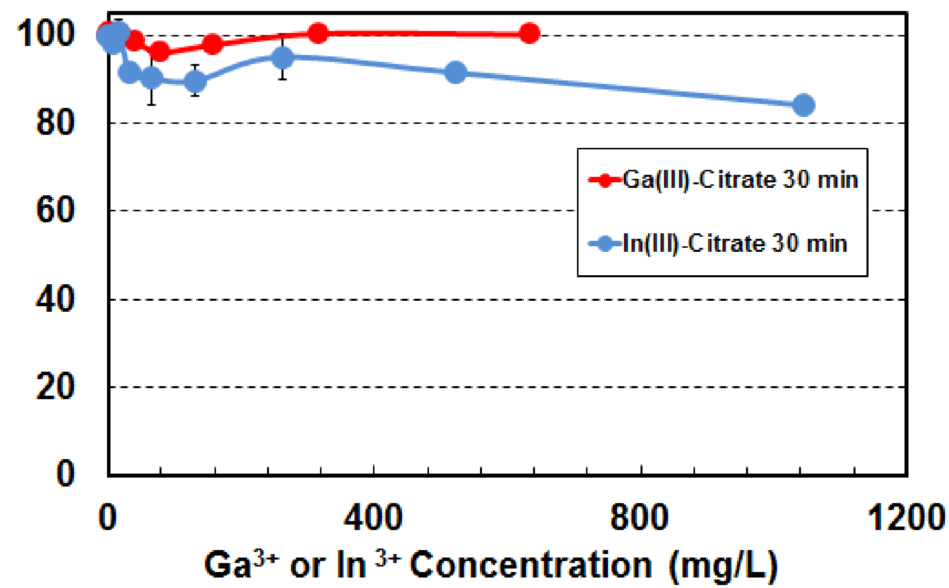




- The III/V species caused no or only mild inhibition to aerobic heterotrophic bacteria at relatively high concentrations in short-term bioassays.
- Experiments involving extended exposure to As recommended to assess its long-term impact on bioreactor treatment performance.

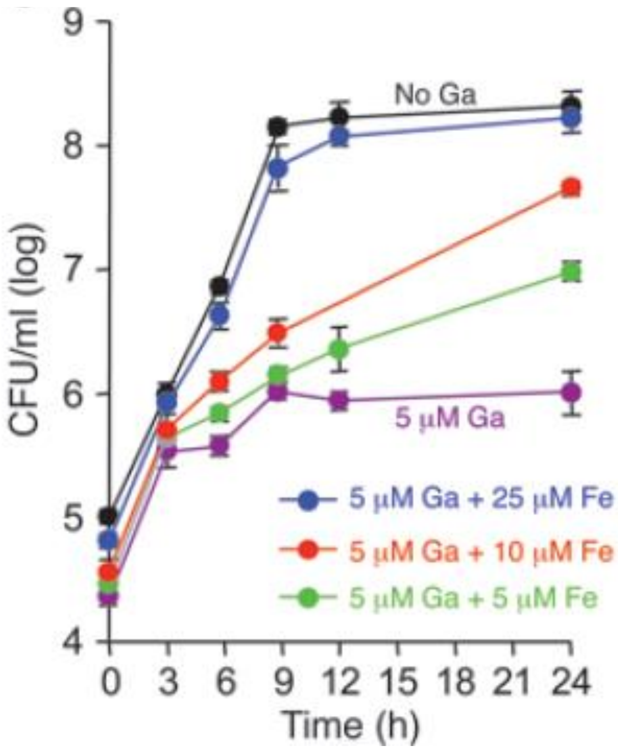
Inhibition of *A. fischeri* (Microtox assay)

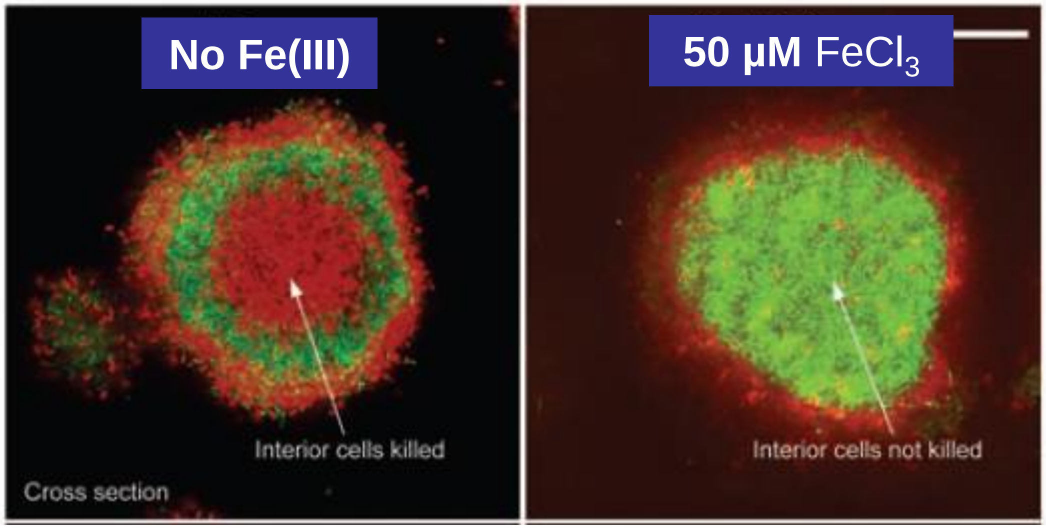




- As(III) and As(V) inhibited bioluminescence by *A. fischeri* at low to moderate concentrations (30-min IC50= 91 and 5 mg/L, resp.) .
- Ga^{3+}- and In^{3+}-citrate didn't exert any significant inhibition at very high concentrations.

Inhibition by Ga^{3+} & In^{3+}: Impact of available Fe





Ga^{3+} (100 uM) kills established biofilms of *Pseudomonas aeuroginosa. The cells are protected in Fe^{3+} (50 uM) is present (Kaneko et al. 2007).*

- Ga^{3+} toxicity is enhanced when Fe^{3+} levels are low. (E.g. Olakanmi et al. 2010; Kaneko et al. 2007; Rzhepishevska et al. 2011).
- Ga^{3+} is an **iron-mimic** and can interfere with Fe^{3+} metabolism.

Summary

- In^{3+}- and Ga^{3+}-citrate displayed very low inhibition at relatively high concentrations in all the tests.
- As(III) and As(V) were generally highly inhibitory to the microorganisms tested, except aerobic bacteria, and to *Daphnia*.

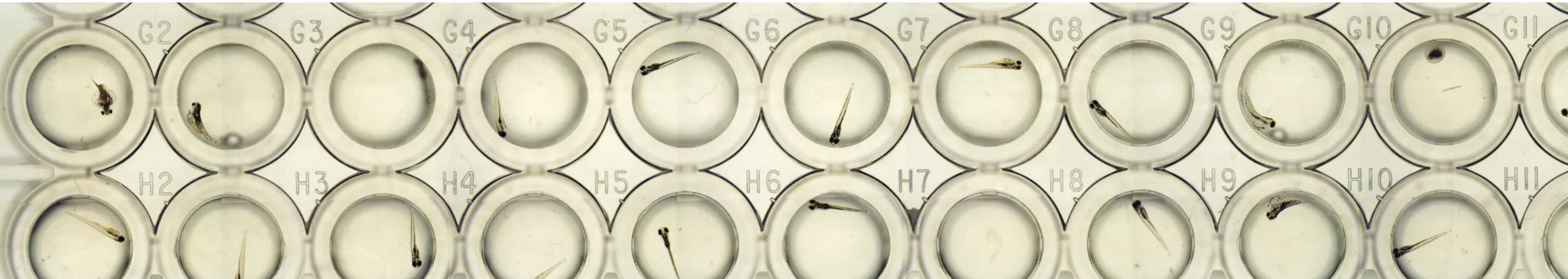
NEXT STEPS:

- Investigate the impact of **iron** on Ga^{+3} and In^{+3} toxicity.
- Evaluate the potential microbial toxicity of CMP slurries towards aerobic and anaerobic microorganisms common in wastewater treatment systems.
- Test for synergistic or antagonistic "Trojan Horse" effects.

3- Toxicity testing of CMP NPs and III/V ions using the zebrafish embryonic model

Reyes Sierra[1], Paul Westerhoff[2], Christopher Olivares[1], Xiangyu Bi[2], Jim A. Field[1], Michael Simonich[3], Robert Tanguay[3]

[1] Univ. Of Arizona, [2] Arizona State University, [3] Oregon State University



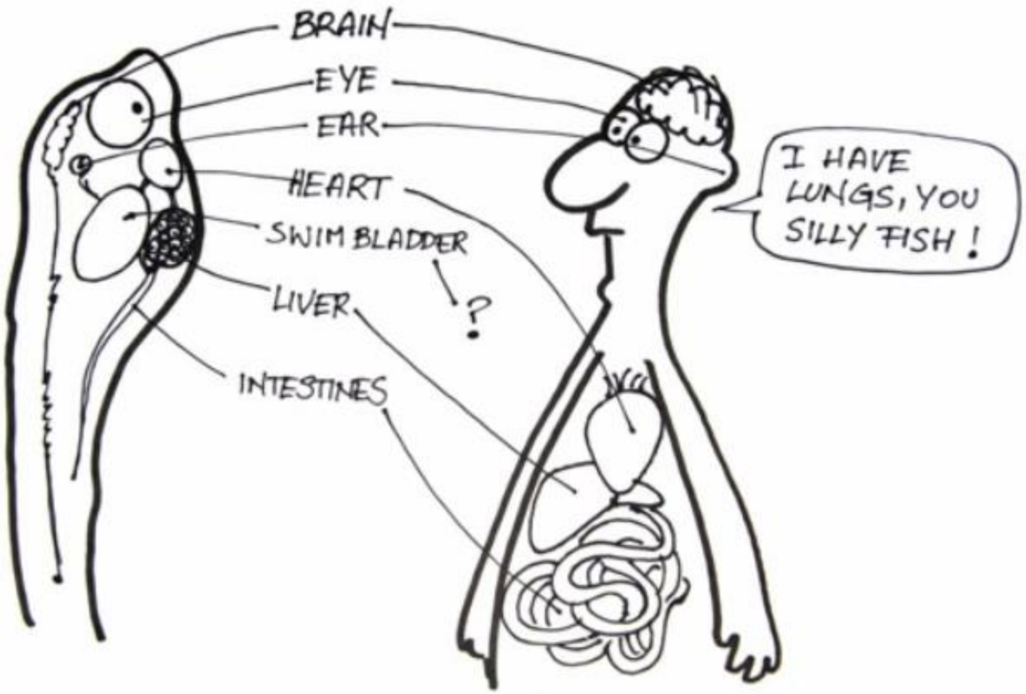
Zebrafish embryo toxicity testing

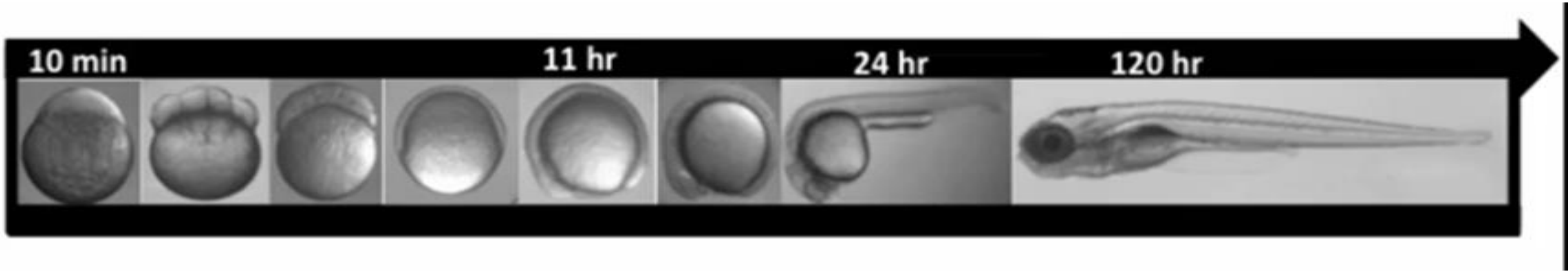
- In collaboration with Prof. Robert Tanguay / Oregon State University.

- Leveraged with funding from:
  - **EPA** (LCnano) Project - https://engineering.asu.edu/lcnano/
  - **NIH** - K.C. Donnelly award to C. Olivares.

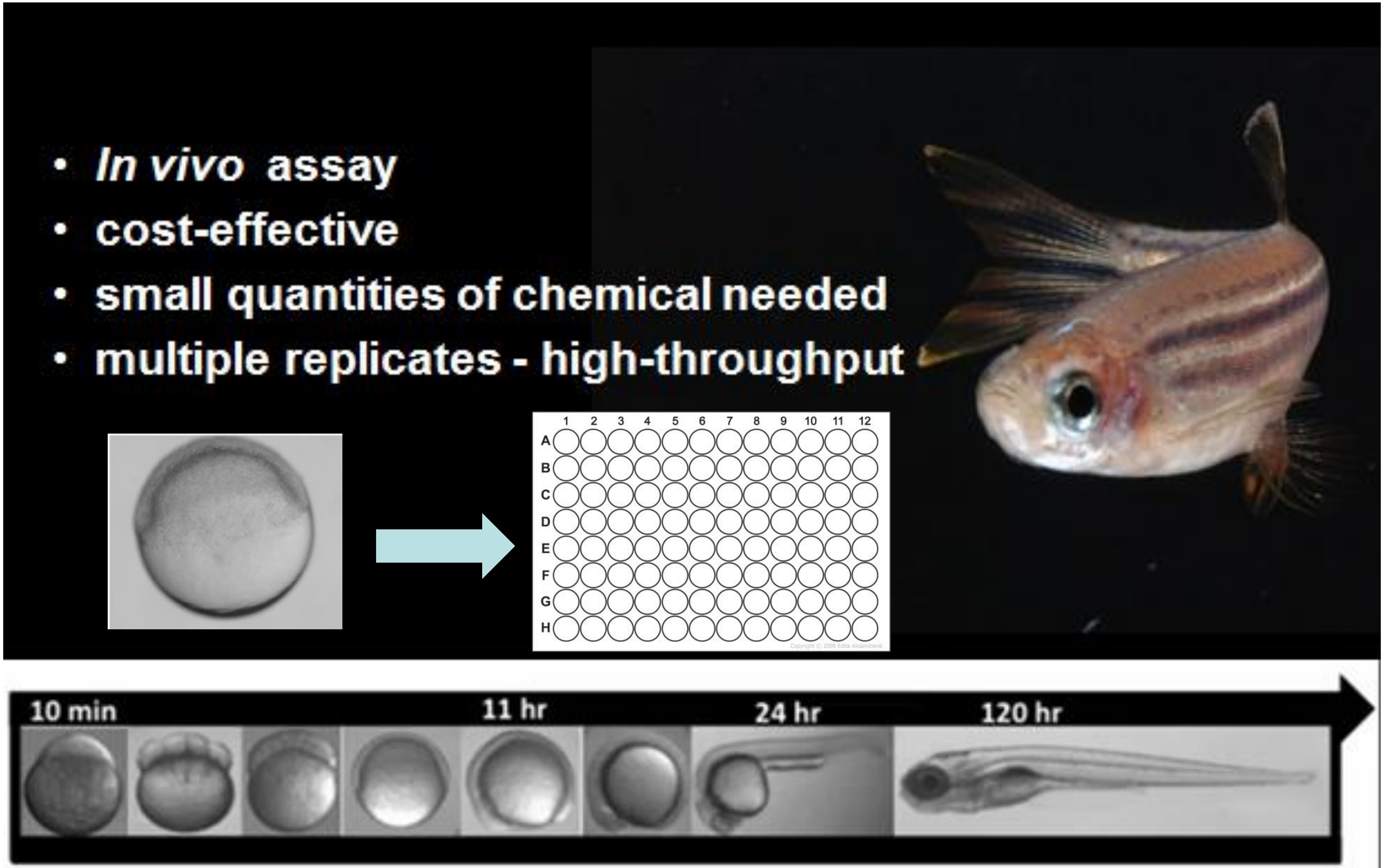
Zebrafish embryo model

- **Acute and chronic effects**
- **Short generation and development time**
- **70% homologous genes to humans**
- **Genome sequenced in 2013**
- **EPA Toxcast (1076 chemicals tested)**
  - **Truong et al. 2014. *Tox Sci.* 137(1), 212–233**





Zebrafish embryo model



What is assessed?

Lethality:

mortality at 24 and 120 hpf

Behavior:

Responses to light/ dark

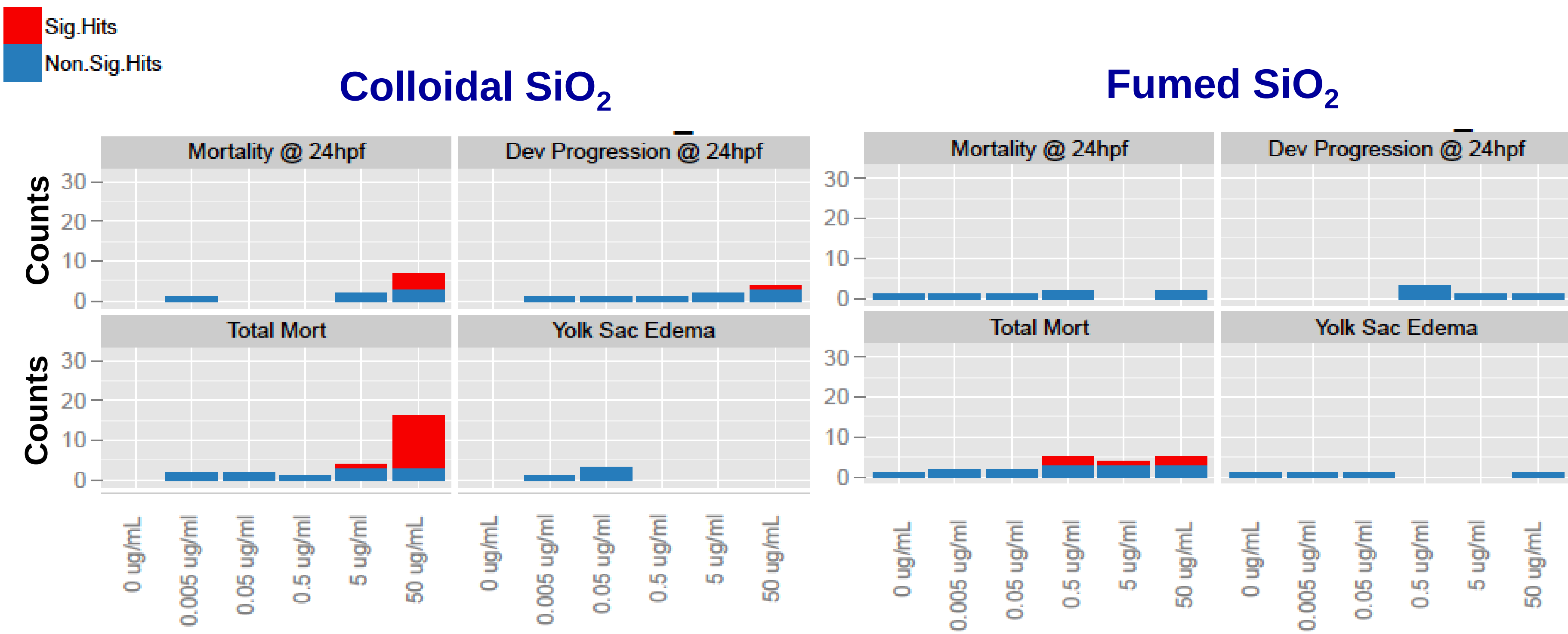
Development

24 hpf:
- development delay
- spontaneous movement
- notochord

120 hpf:
-yolk sac edema
-body axis
-eye defect
-snout
-jaw
-otic vesicle
-pericardial edema
-brain
-somite
-pectoral fin
-caudal fin
-pigment
-circulation
-truncated body
-caudal fin
-notochord
-touch response

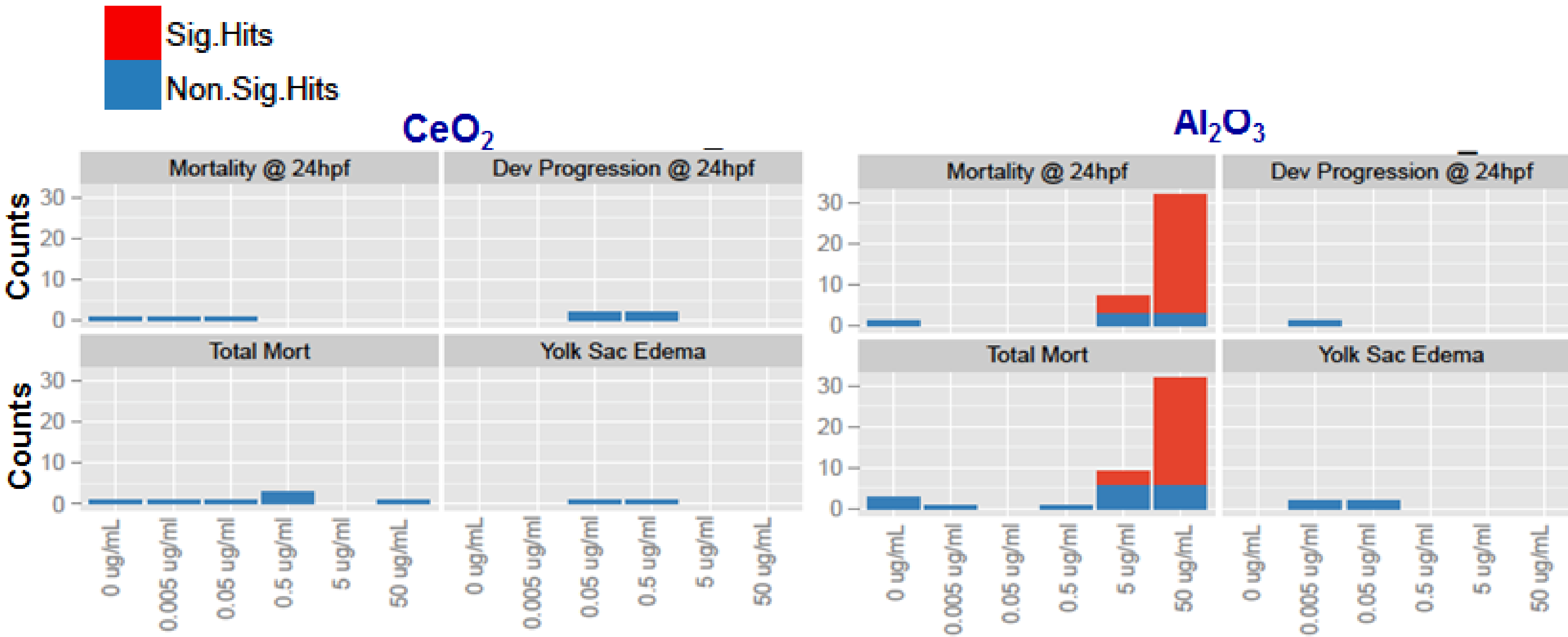
Hours post-fertilization = hpf

Toxicity of CMP NPs to zebrafish embryos: Lethal and developmental effects



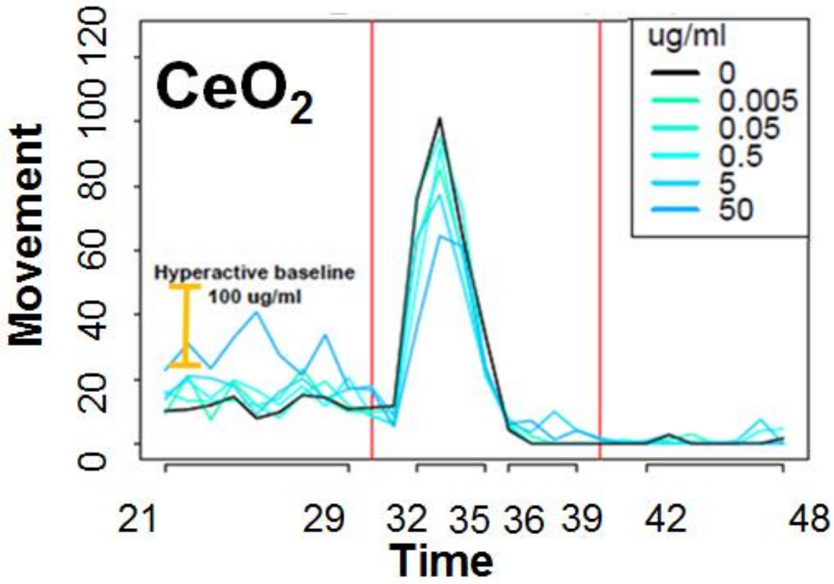
- Fumed SiO_2 exerted no mortality or other effects below 50 mg/L.
- Colloidal SiO_2 began showing potential effects near 50 mg/L.

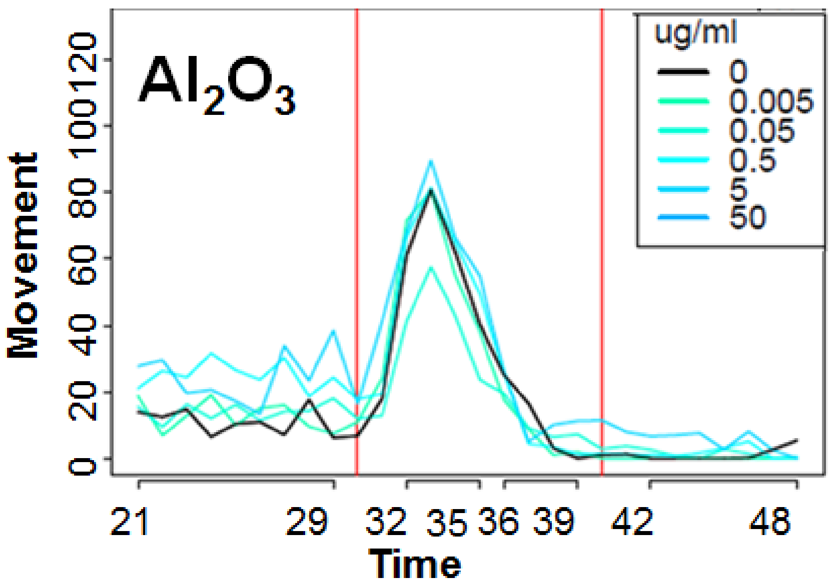
Toxicity of CMP NPs to zebrafish embryos: Lethal and developmental effects



- CeO_2 exerted no mortality or other effects below 50 mg/L.
- Toxicity was induced by Al_2O_3, and attributed to dissolution of Al^{3+}.

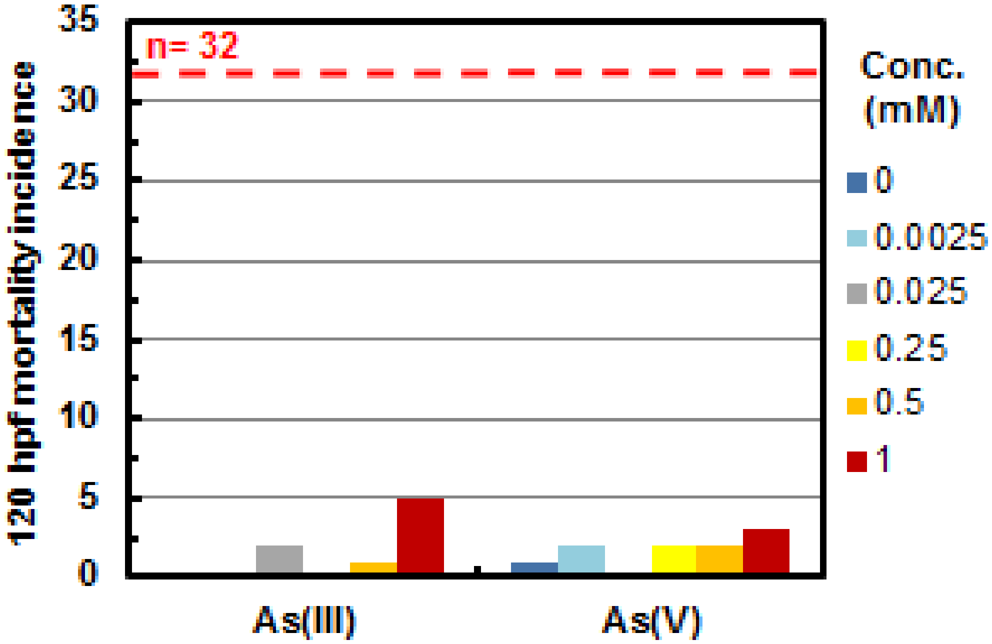
Impact of CMP NPs on the behavior of zebrafish embryos





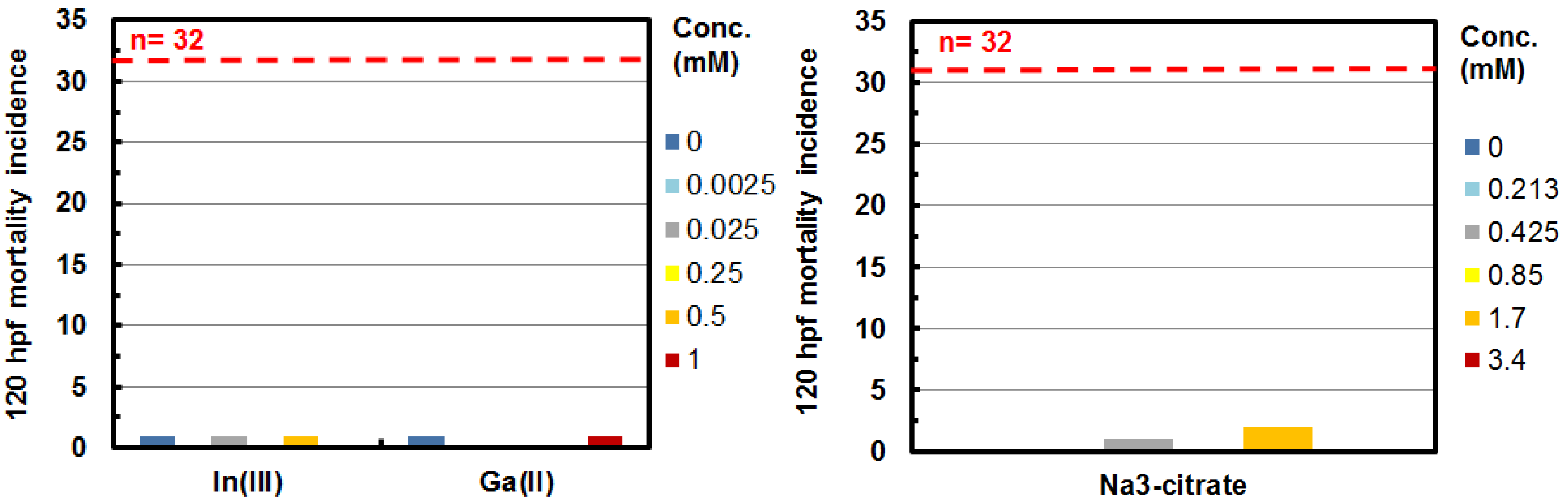
- CeO_2 : Modest hyperactivity in the baseline phase (100 mg/ L) .
- SiO_2 and Al_2O_3 slurries did not impact zebrafish embryo behavior.

Toxicity of As(III) and As(V) to zebrafish embryos: Lethal and developmental effects



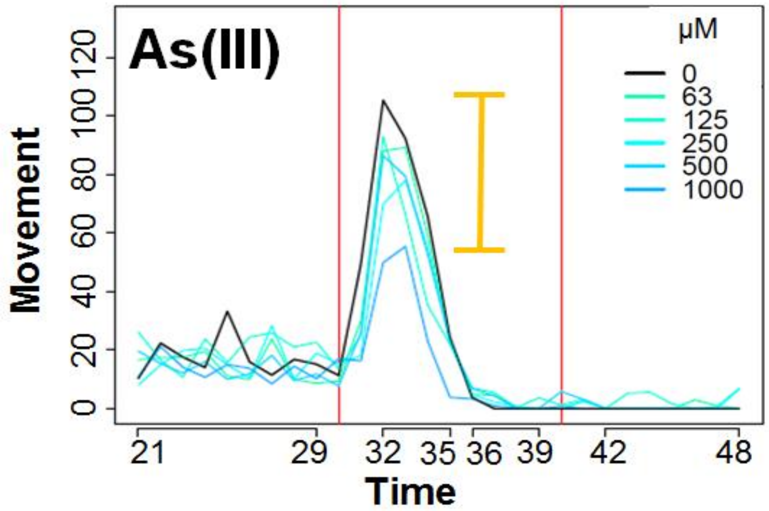
- Arsenate and arsenite only exerted very modest mortality at the highest concentration tested (1 mM or 75 mg/L).
- Developmental effects not detected at the highest concentration tested.

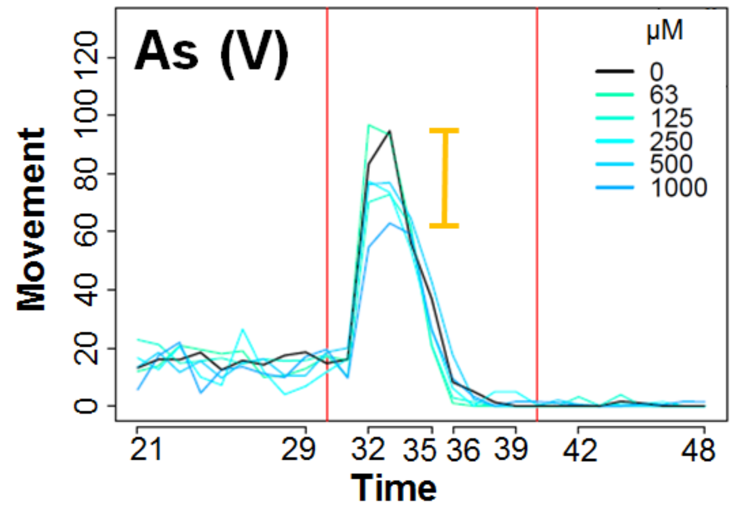
Toxicity of In(III)- and Ga(III) citrate to zebrafish embryos: Lethal and developmental effects

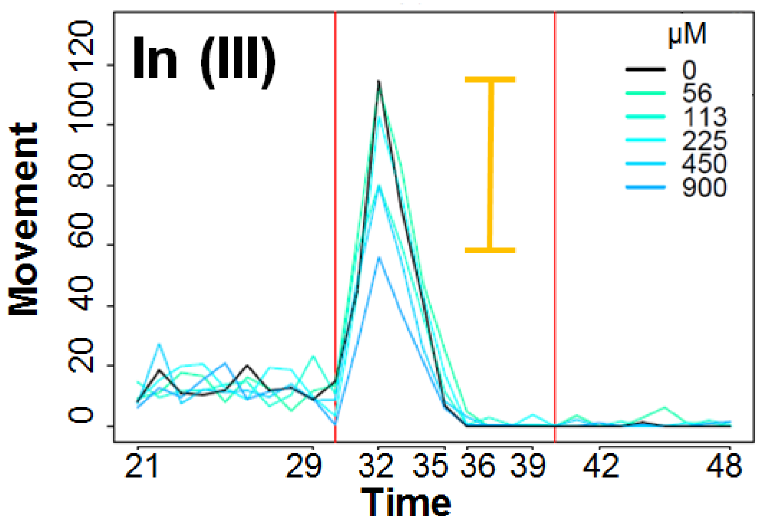


- In^{3+}- and Ga^{3+}-citrate did not exert lethal effects at the highest concentration tested (1 mM ≈ 115 mg In/L, 70 mg Ga/L).
- Sodium citrate (up to 3.4 mM) did not cause lethal or developmental effects.
- Developmental effects not detected at the highest concentration tested.

Impact of As(III) and As(V) on the behavior of zebrafish embryos







- As(V), As(III), In (III) : 0.9-1 mM caused hypoactivity upon first-time light exposure.
- Ga(III)- and Na-citrate did not affect embryo behavior.

Industrial Interactions and Technology Transfer

- **David Speed** (IBM Corp.)
  - Industrial liaison.
  - Co-principal investigator of a research proposal submitted to the National Science Foundation (NSF) which is currently under review.

- **Reed M. Content** (Global Foundries) - Industrial liaison.

- **Brian Raley** (Global Foundries) - Industrial liaison.

Publications, Presentations, and Recognitions/Awards

- **K.C. Donnelly Externship Award (NIH) to C. Olivares to perform zebrafish toxicity studies at Oregon State University (Dr. Tanguay lab).**

Cost Share (Other than ERC funding)

- $95k from Univ. Arizona WEES program for the purchase of ICP-OES instrument.
- $57.7k graduate scholarship to E. Orenstein (College of Engineering, UA).
- $16k , funding of Adrian Gonzalez Alvarez’s work at the UA.
- $8k, K.C. Donnelly Externship Award Supplement (NIH) to C. Olivares (UA).
- $25k/year, supplement salary of graduate student Xiangyu Bi (ASU).
- $10k from EPA LcNano project to support collaboration with Prof. Rob Tanguay.

References

- Aksel'rud, N.V., Spivakovskii, V.B., 1959. Basic chlorides and hydroxides of indium. Russian J. Inorg. Chem. 4, 449–453.
- Baes Jr. & Mesmer, 1986. The Hydrolysis of Cations. Krieger Publishing Co., Malabar, Florida. 489 pp
- Biesinger KE, Christensen GM. 1972. Effects of various metals on survival, growths, reproduction, and metabolism of *Daphnia magna*. *J Fish Res Board Can* 29:1691.
- Biryuk, E.A., Nazarenko, V.A., Ravitskaya, R.V., 1969. Spectrophotometric determination of the hydrolysis constants of indium ions. Russian J. Inorg. Chem. 14, 503– 506.
- Feitknecht, W., Schindler, P.,1963. Solubility constants of metal oxides, metal hydroxides and metal hydroxide salts in aqueous solution. Pure Appl. Chem. 6,129–199.
- Fikirdesici, S., A. Altindag and E. Ozdemir. 2012. Investigation of acute toxicity of cadmium-arsenic mixtures to Daphnia magna with toxic units approach. Turkish J. Zoology 36: 543-550.
- Johnson WW, Finley MT. 1980. *Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates*. U.S. Fish andWildlife Service, Washington, DC.
- Kaneko et al. 2007. The transition metal gallium disrupts Pseudomonas aeruginosa iron metabolism and has antimicrobial and antibiofilm activity. Journal of Clinical Investigation 117: 877-888.
- Olakanmi et al. 2010. Gallium disrupts iron uptake by intracellular and extracellular *Francisella* strains and exhibits therapeutic efficacy in a murine pulmonary infection model. Antimicrob. Agents Chemother. 54:244–253.
- Rzhepishevska et al. The antibacterial activity of Ga3+ Is influenced by ligand complexation as well as the bacterial carbon source. *Antimicrobial Agents Chemotherapy* 2011, *55*, (12), 5568-5580.

References

- Sanders HO, Cope OB. 1966. Toxicities of several pesticides to two species of cladocerans. *Trans Am Fish Soc* 95:165.
- Shaw, J.R., S.P. Glaholt, N.S. Greenberg, R. Sierra-Alvarez, C.L. Folt. 2007. Acute toxicity of arsenic to *Daphnia pulex*: Influence of organic functional groups and oxidation state. Environ.Toxicol. Chem. 26: 1532-1537.
- Stumm, W. 1992. Chemistry of the solid-water interface: processes at the mineral-water and particle-water interface in natural systems.
- Theegala et al. 2007. Toxicity and biouptake of lead and arsenic by Daphnia pulex. J. Environ. Sci. Health A 42: 27-31.
- Wang et al. Synergistic toxic effect of nano-Al2O3 and As(V) on *Ceriodaphnia dubia*. *Environ. Polluti*.2011, *159*, (10), 3003-3008.
- Wood, S.A., Samson, I.M. 2006. The aqueous geochemistry of gallium, germanium, indium and scandium. Ore Geol. Rev. 28: 57-102.