Bioavailability and Toxicity of Silver: Nanoparticles versus Released Ions

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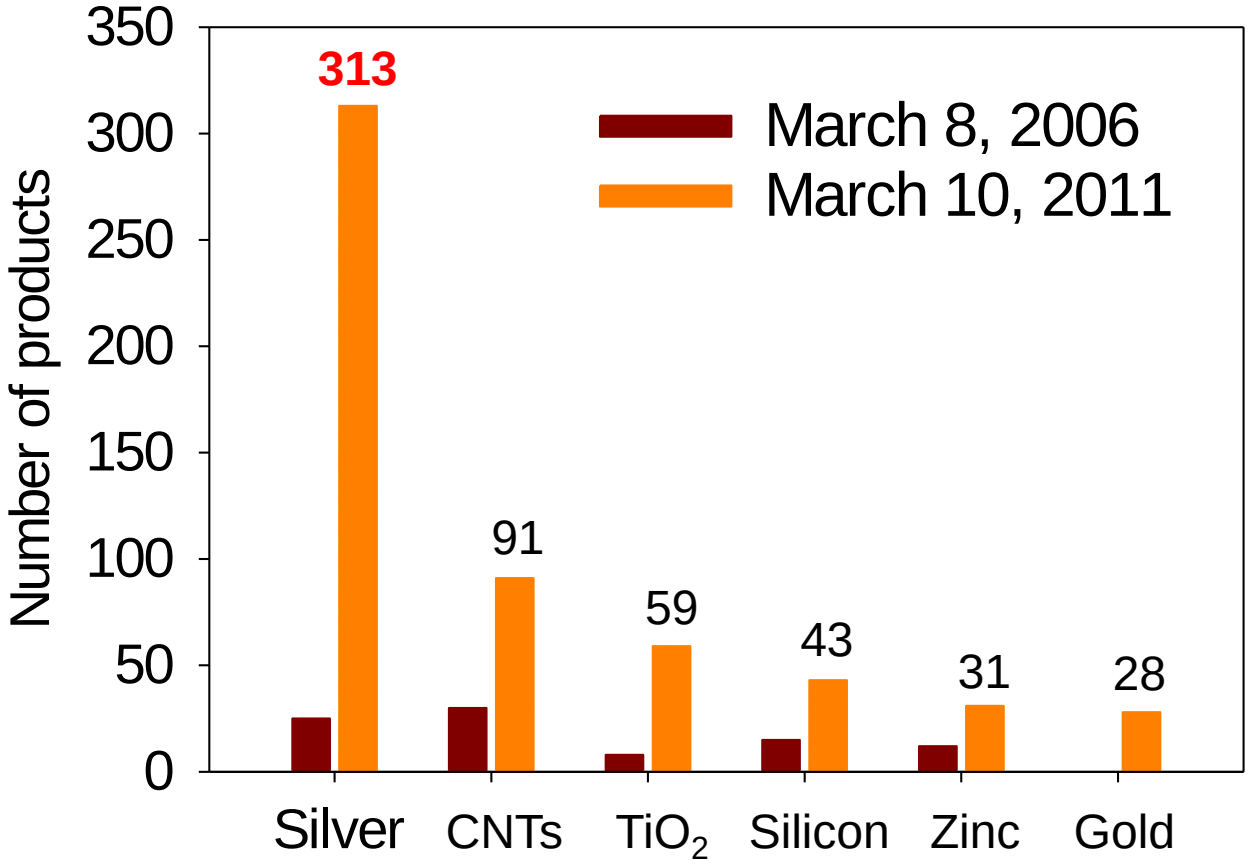
Panel 8

Most Widely Used Nanomaterials In Commercial Products

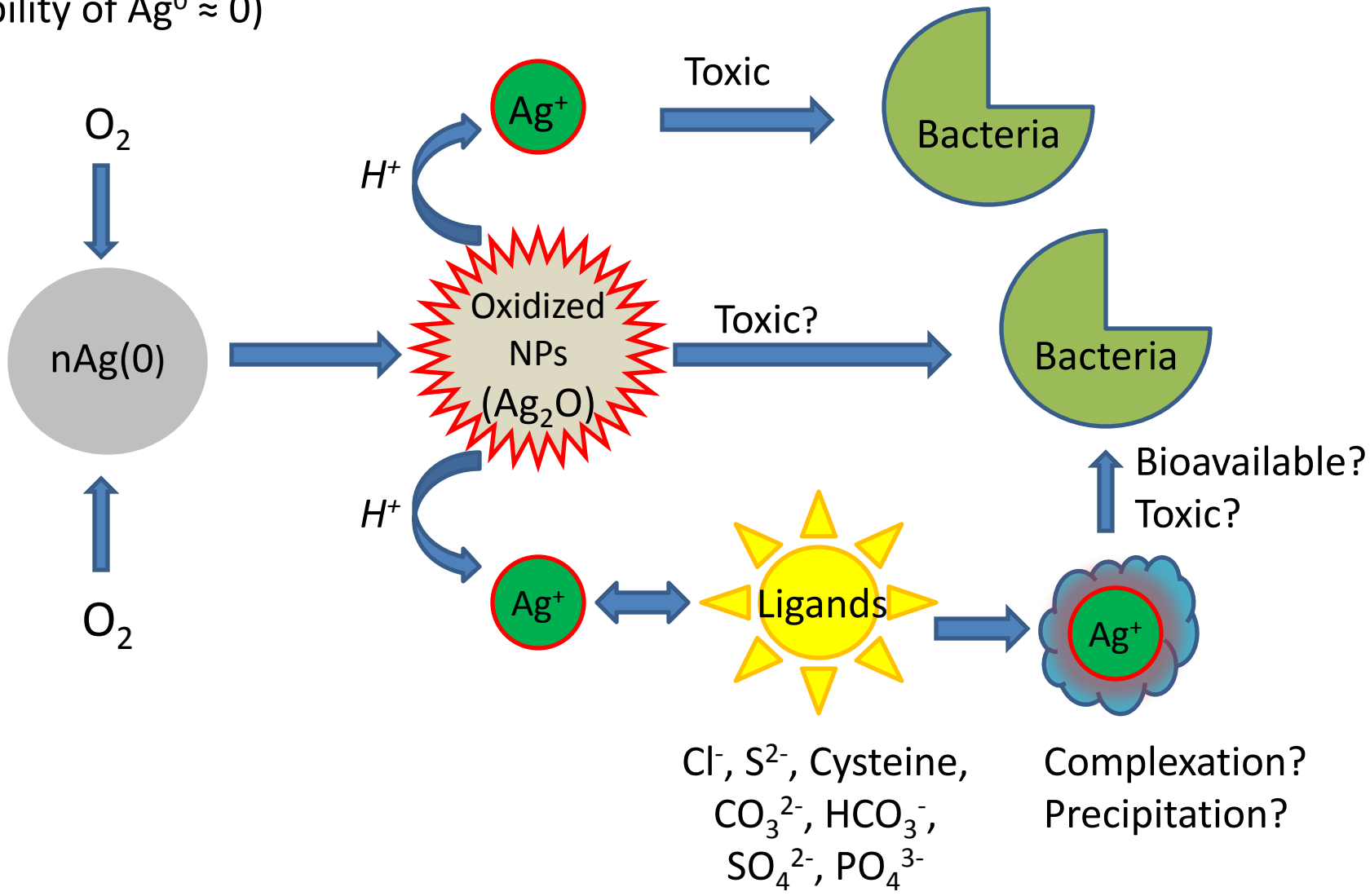


***Source**: Woodrow Wilson-The project on emerging nanotechnologies*

Bioavailability and Toxicity of nAg

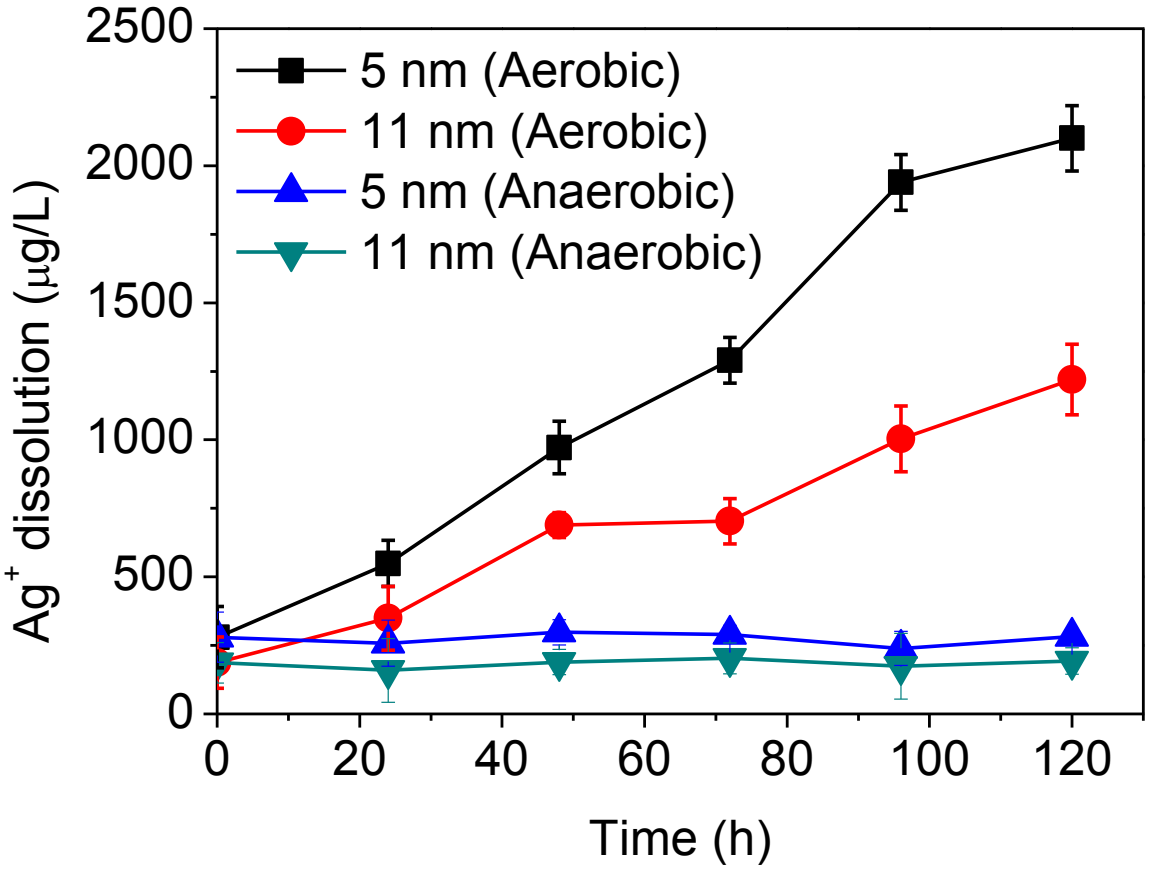
Ag^+ is released only if nAg(0) is oxidized: $4Ag^0 + O_2 + 4H^+ \leftrightarrow 4Ag^+ + 2H_2O$

(Solubility of $Ag^0 \approx 0$)



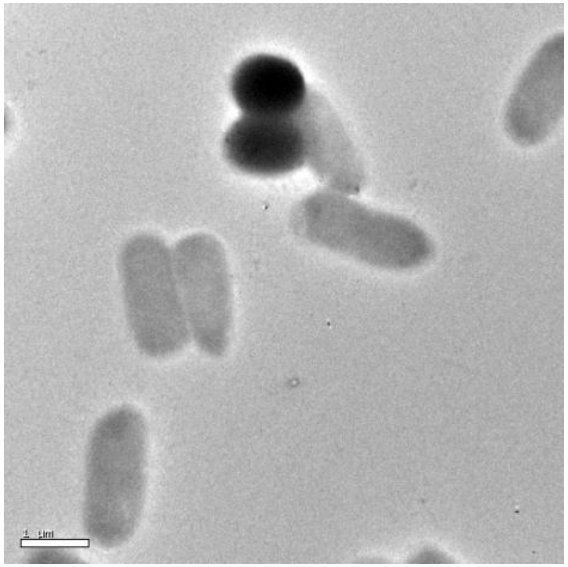
No Ag^+ release under Anaerobic Conditions

(Faster release for air-exposed smaller particles)

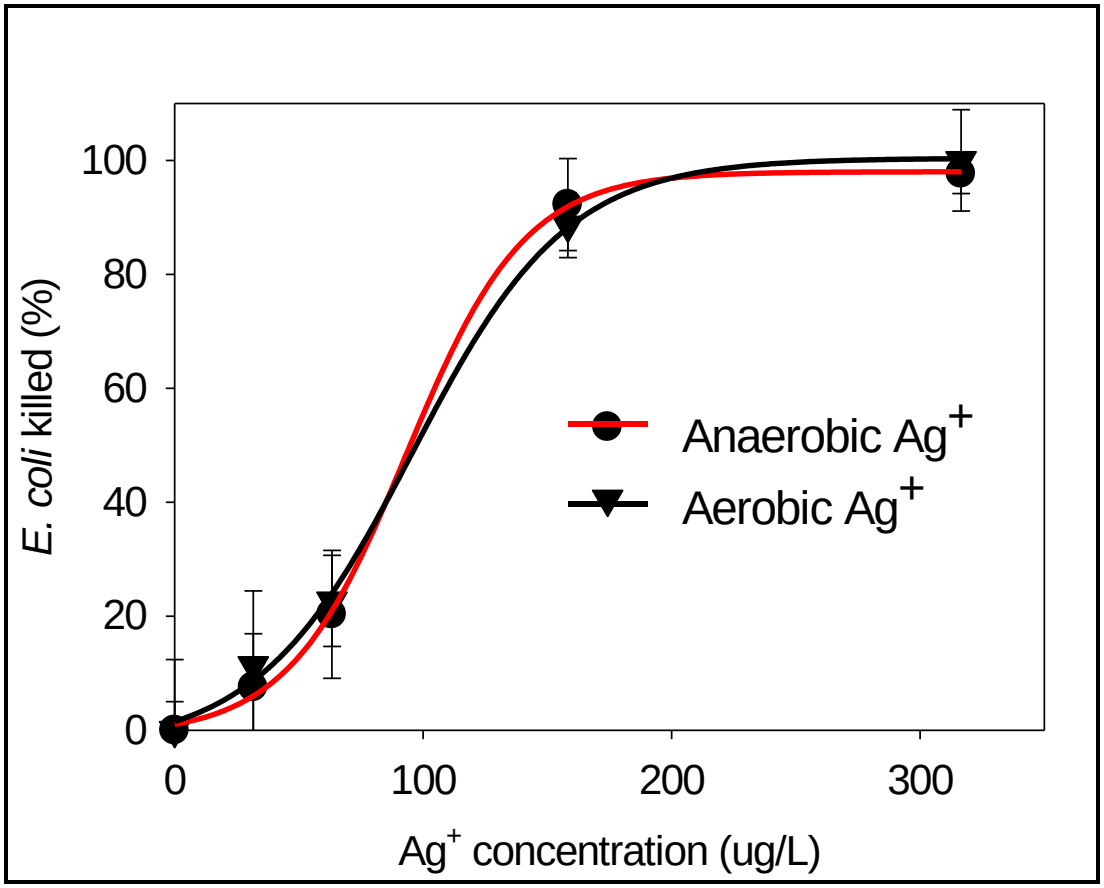


Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271−4275.

Similar Ag^+ Toxicity under Aerobic & Anaerobic Conditions



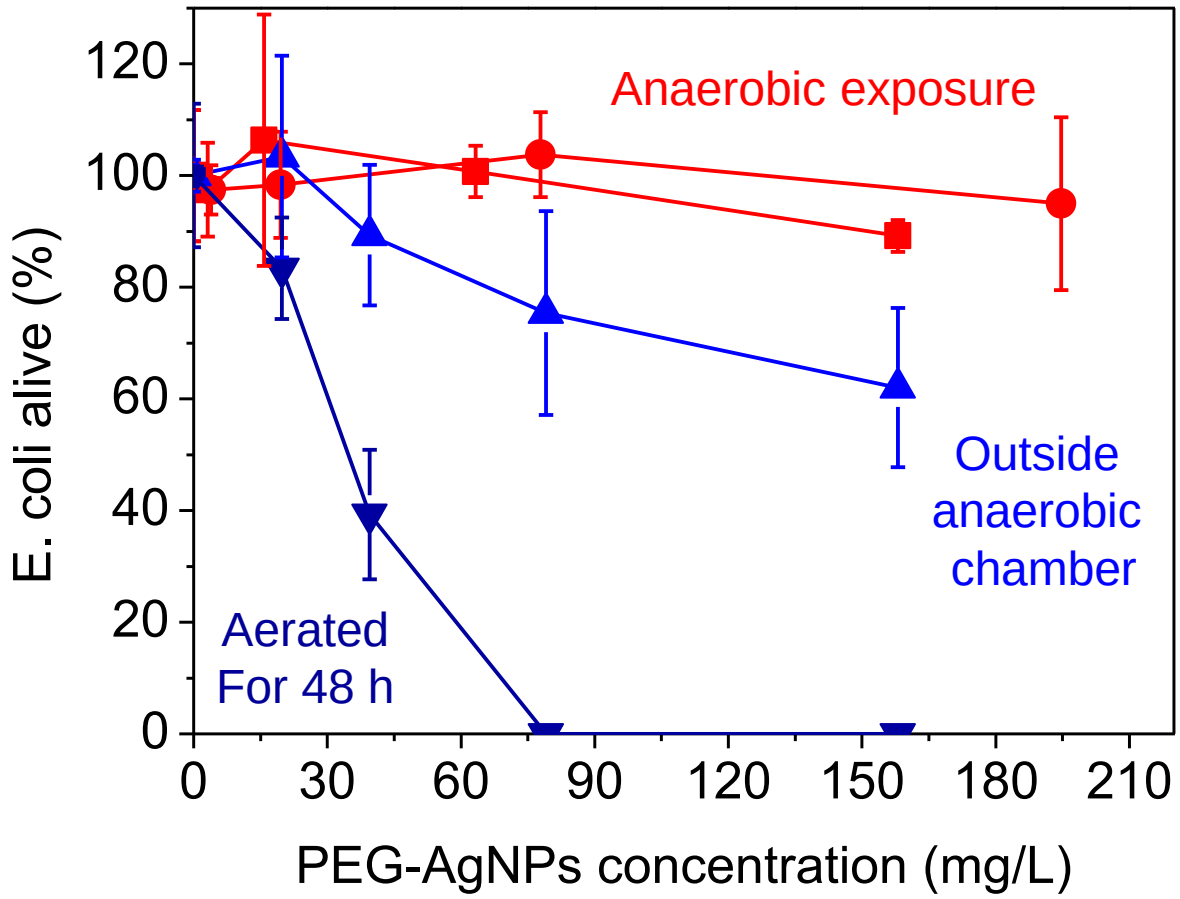
***E. coli* is facultative**



Statistically undistinguishable difference

Xiu Z., J. Ma and PJJ. Alvarez, *Environ. Sci. Technol.*, **2011**

No Toxicity Without Ag^+ Release



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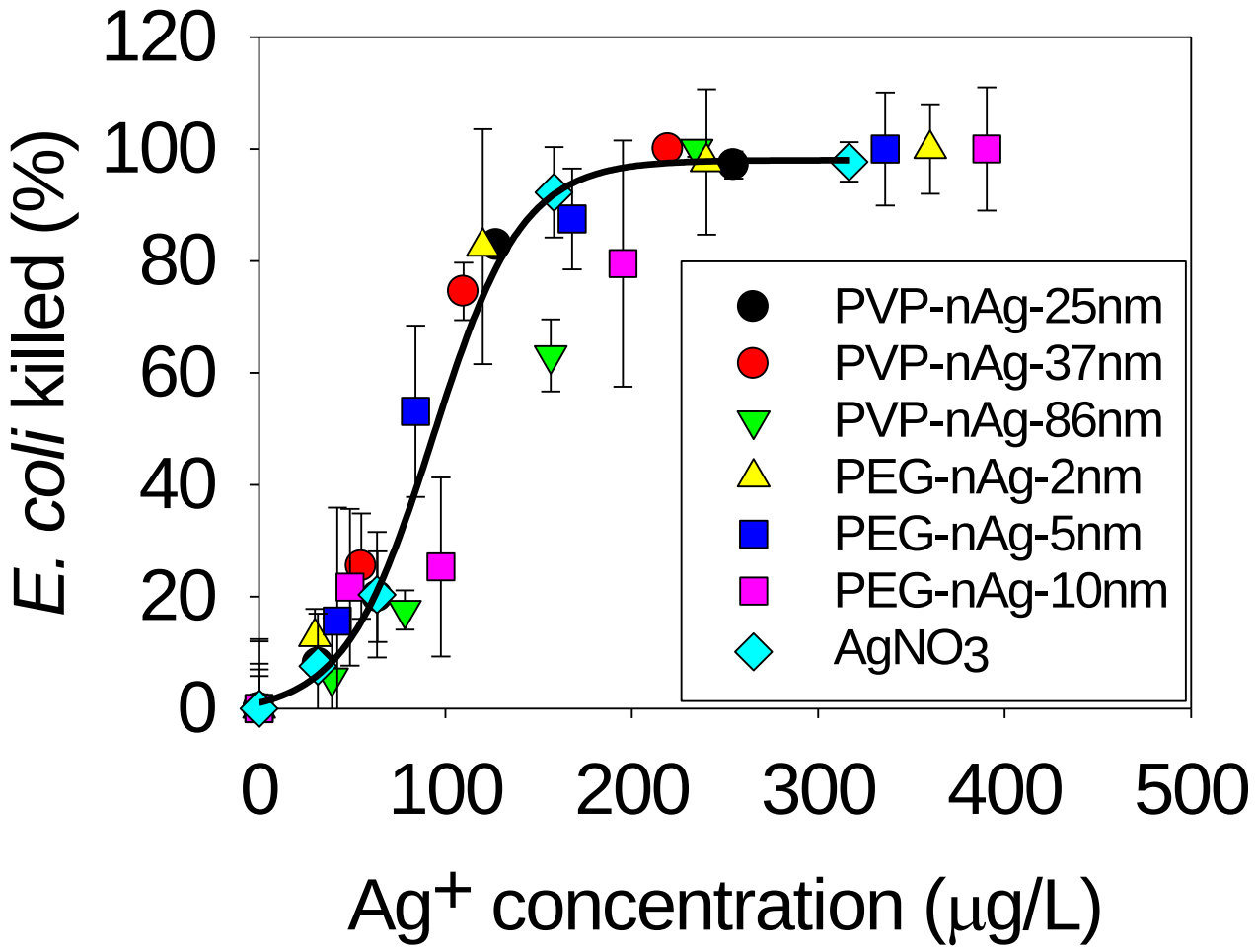
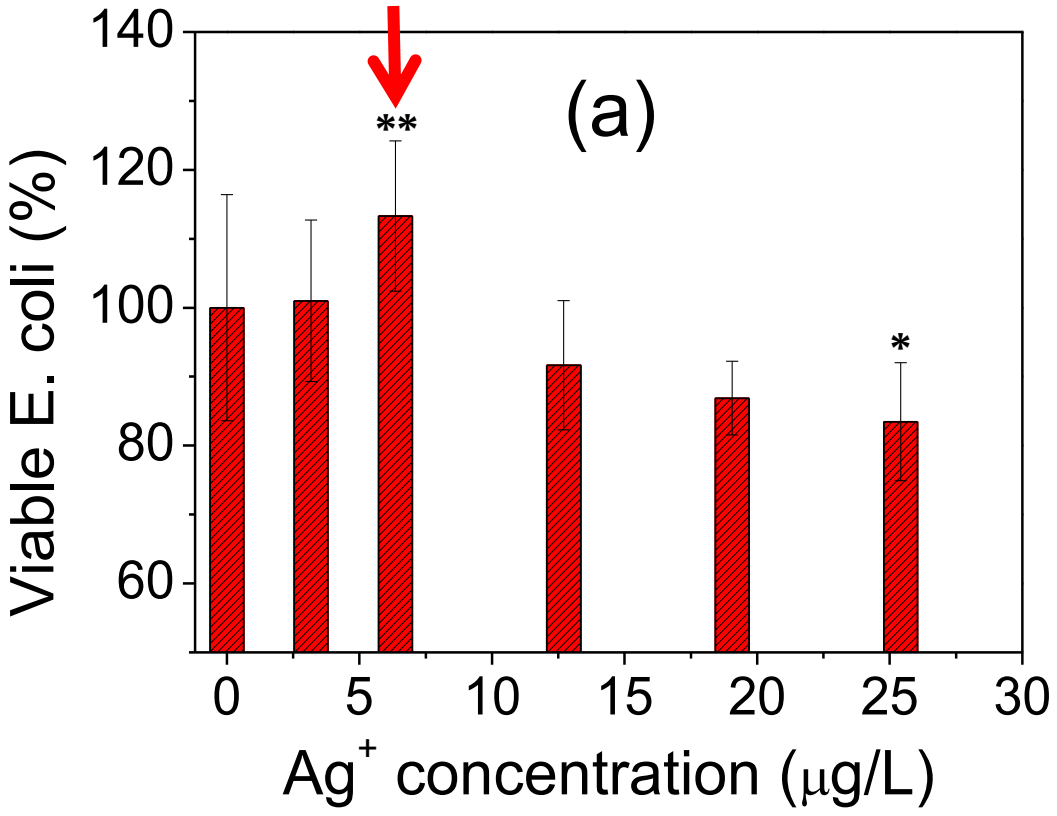
nAg Toxicity Can Be Explained by Dose-Response of Released [Ag^+]



Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271−4275.

“What does not kill you makes you stronger”

Friedrich Nietzsche



Stimulatory effect after 6 h exposure to low Ag^+ concentration **(Hormesis?)**

Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271−4275.

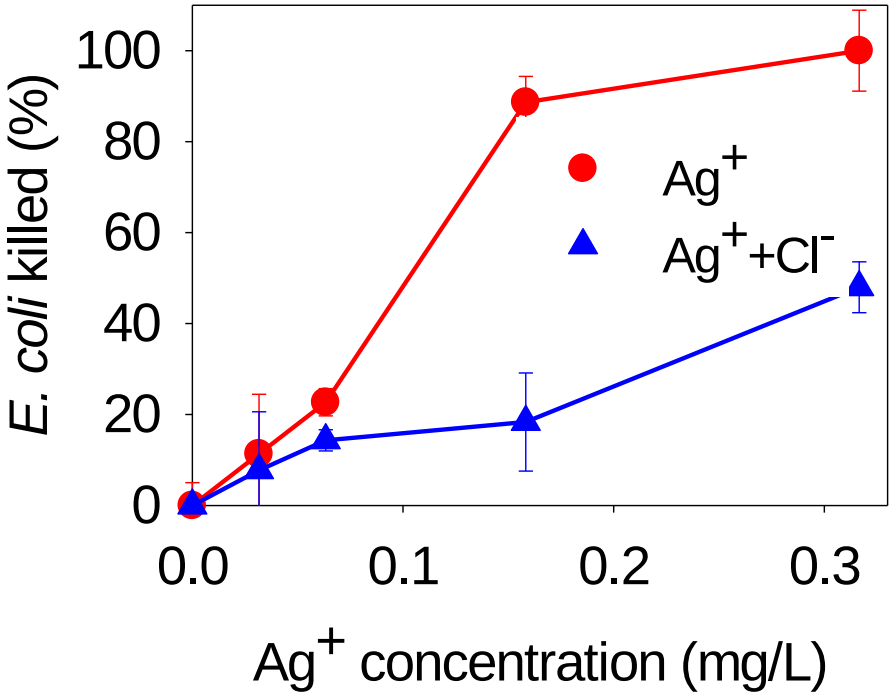
But AgNPs are Sometimes Reported To Be More Toxic Than Ag^+….

Minimum Inhibitory Concentration (mg/L)

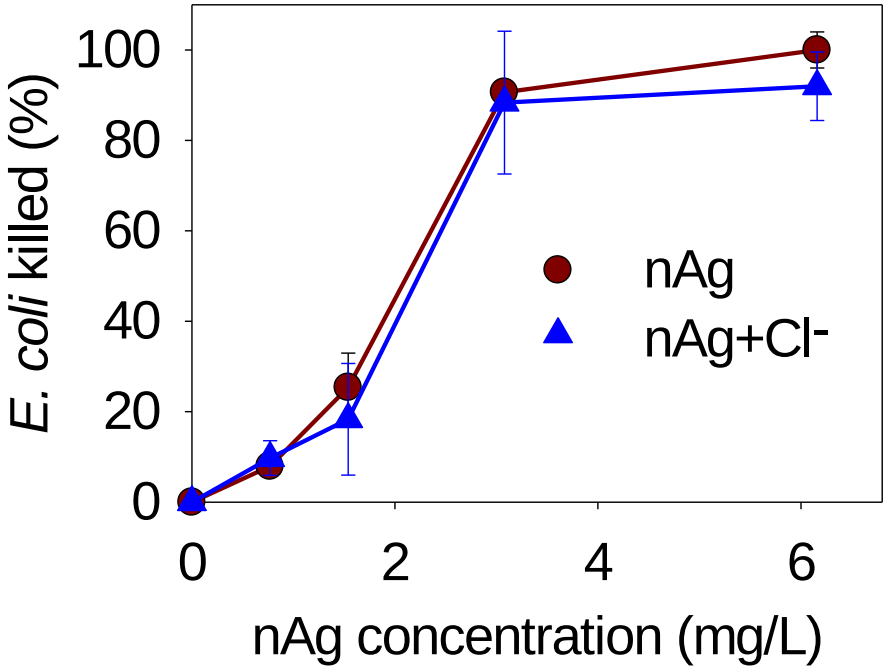
	E. coli	*B. subtilis*	*S. oneidensis*
$AgNO_3$	7.5	5.0	8.0
Biogenic AgNPs	2.0	0.5	3.0
Colloidal silver	6.0	2.0	6.5

Source: Suresh et al. *Environ. Sci. Technol.* 2010, 44, 5210–5215

When is nAg a Stronger Bactericide?



Max [Ag^+]: 3µM; [Cl^-]: 3µM



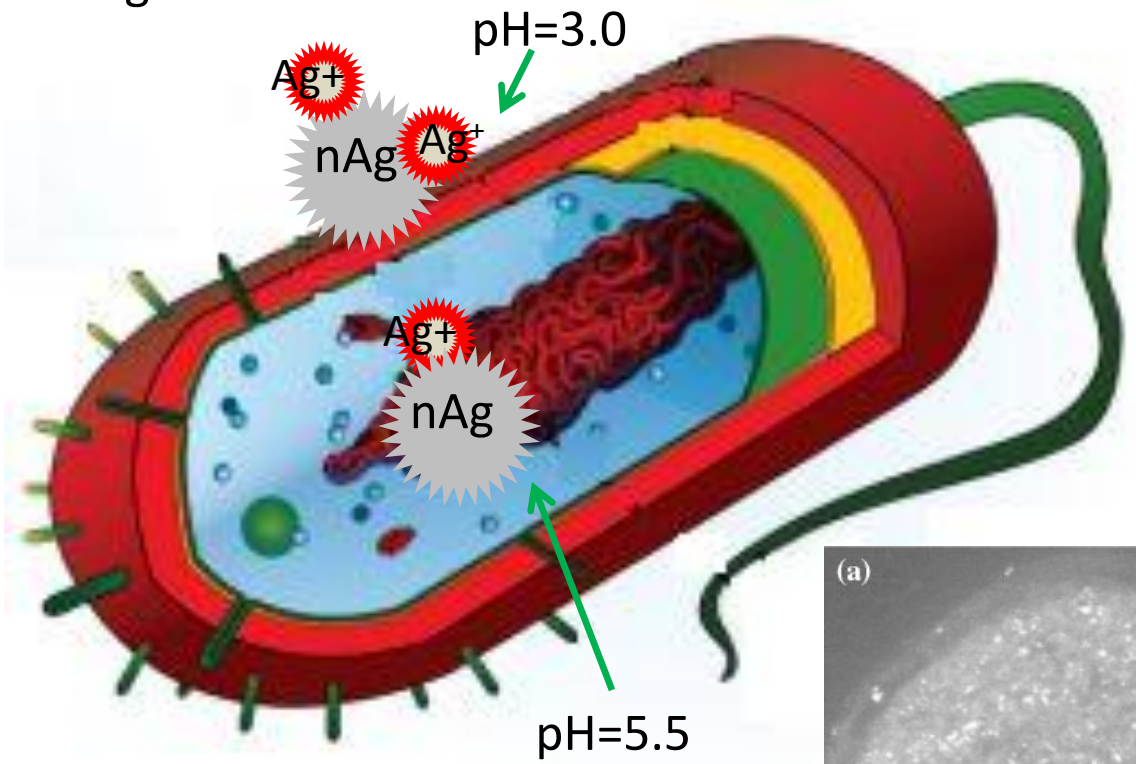
Max [nAg]: 57µM; [Cl^-]: 57µM

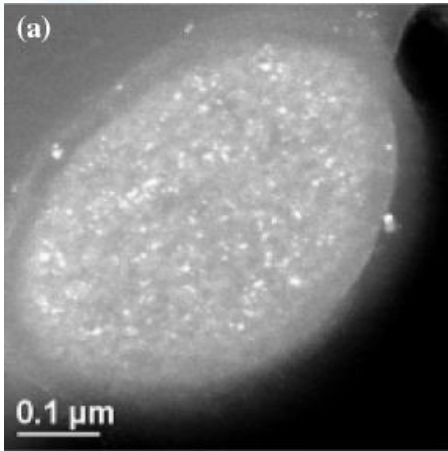
- Cl^- (& other ligands, NOM) reduce Ag^+ bioavailability and preferentially decrease its toxicity, even without precipitation
- nAg may then be more bioavailable & effectively deliver Ag^+

nAg Enhances Delivery of Ag^+ to Membrane and Cytoplasm

Natural ligands

Natural ligands





Morones et al.,2005

Risk = Hazard × Exposure

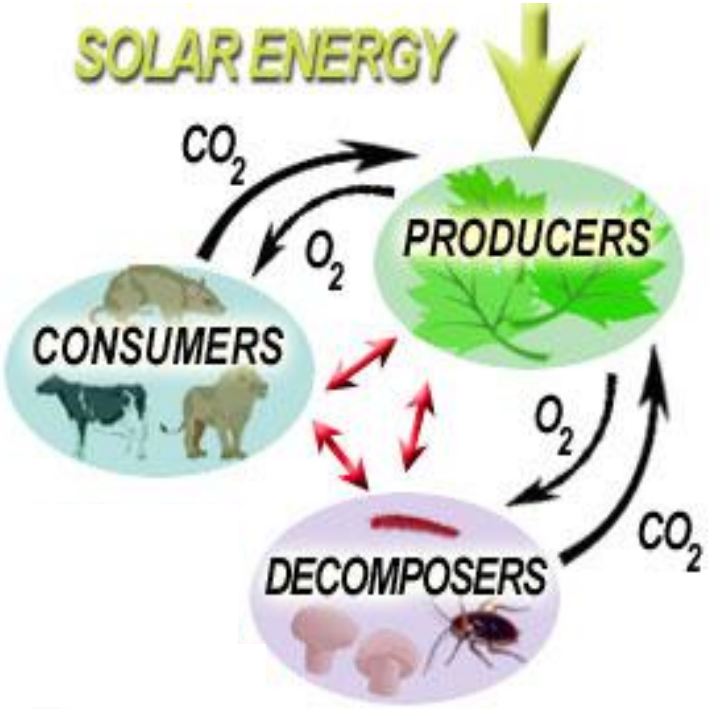
Hazard, but no exposure

Exposure but no hazard

Hazard as well as exposure

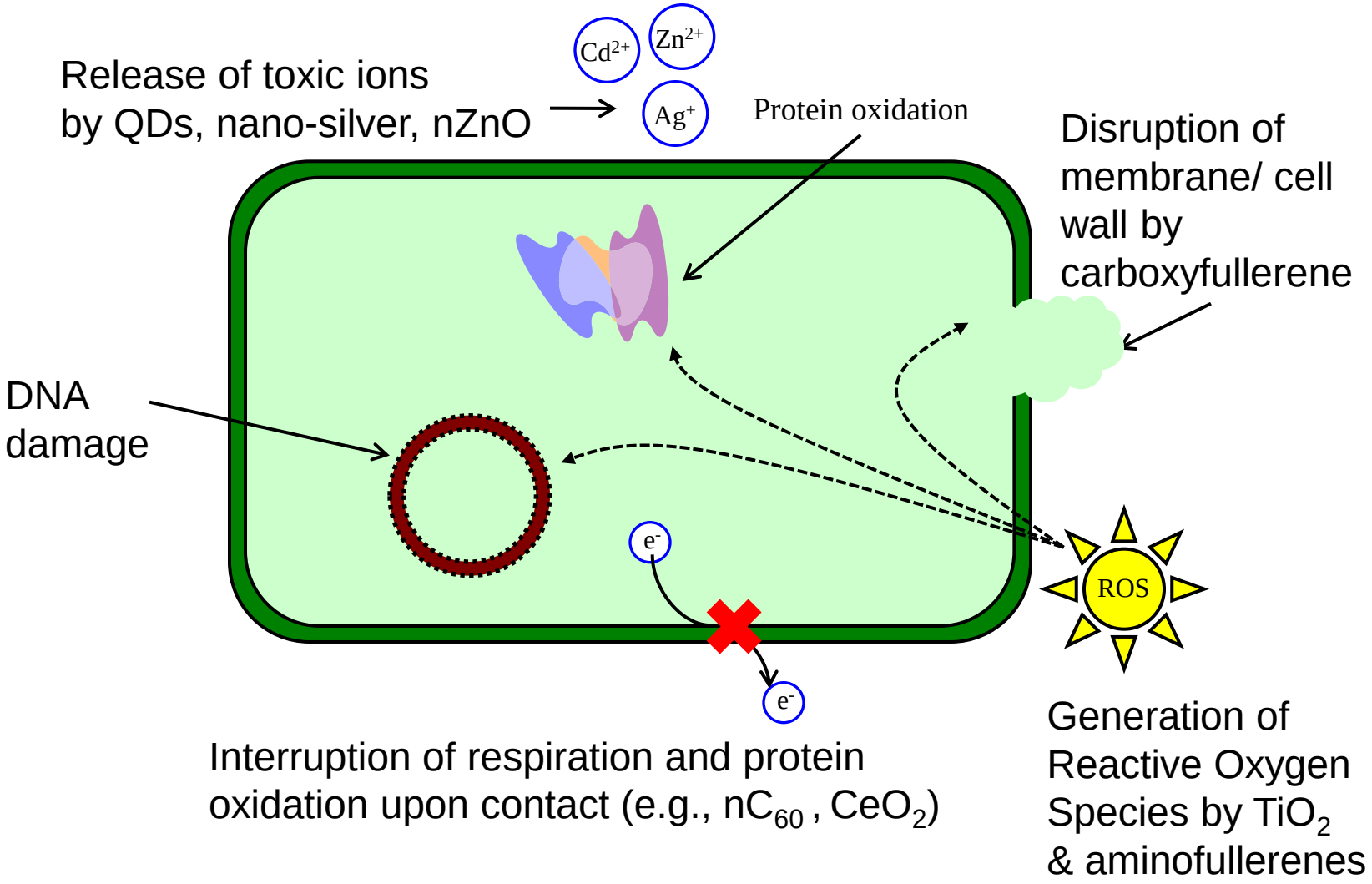
BACK UP SLIDES

Microbial-nanoparticle Interactions to Inform Risk Assessment

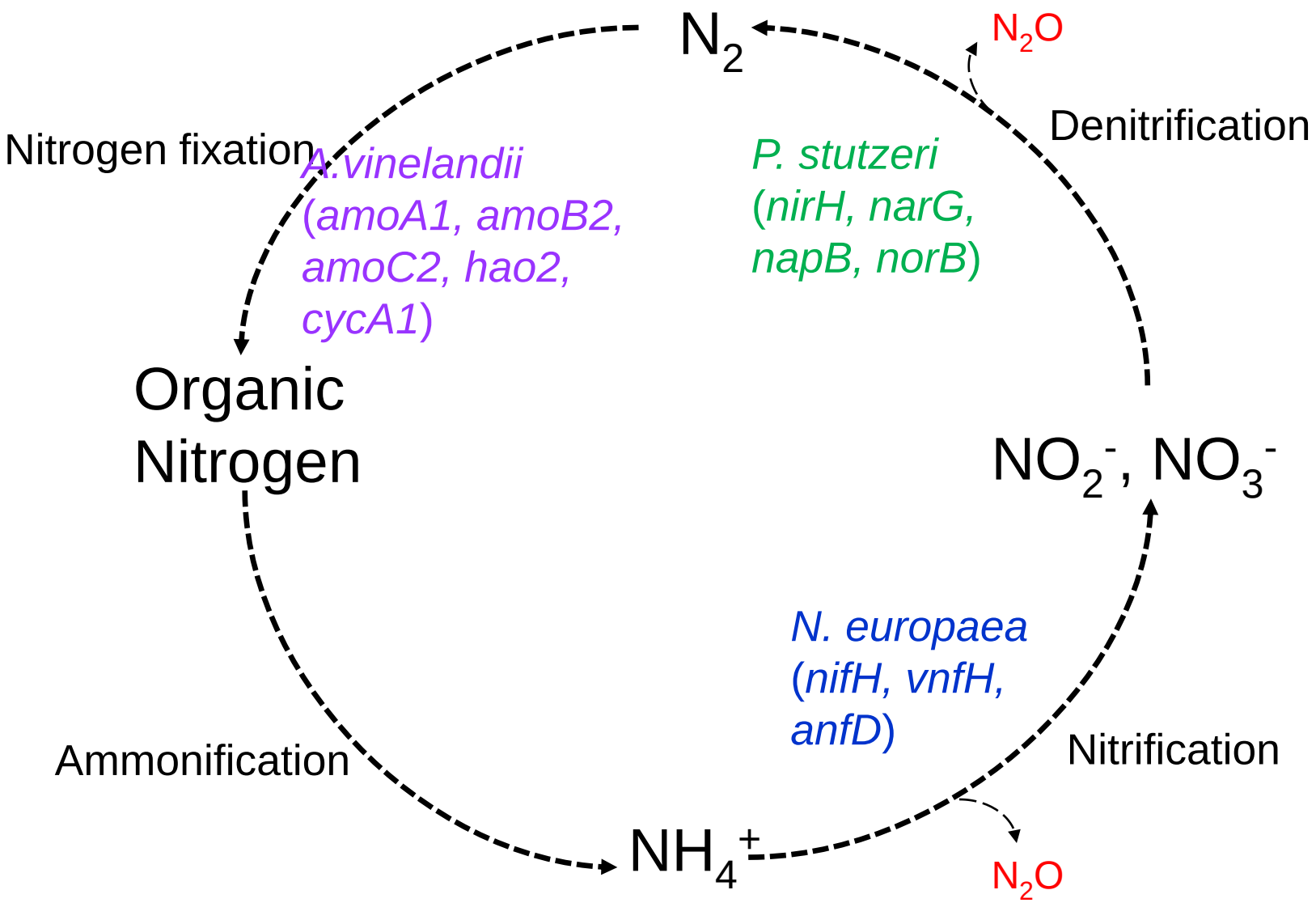


- Bacteria are at the foundation of all ecosystems, and carry out many ecosystem services
- Disposal/discharge can disrupt primary productivity, nutrient cycles, biodegradation, agriculture, etc.
- Antibacterial activity may be fast-screening indicator of toxicity to higher level organisms (*microbial sentinels*?)

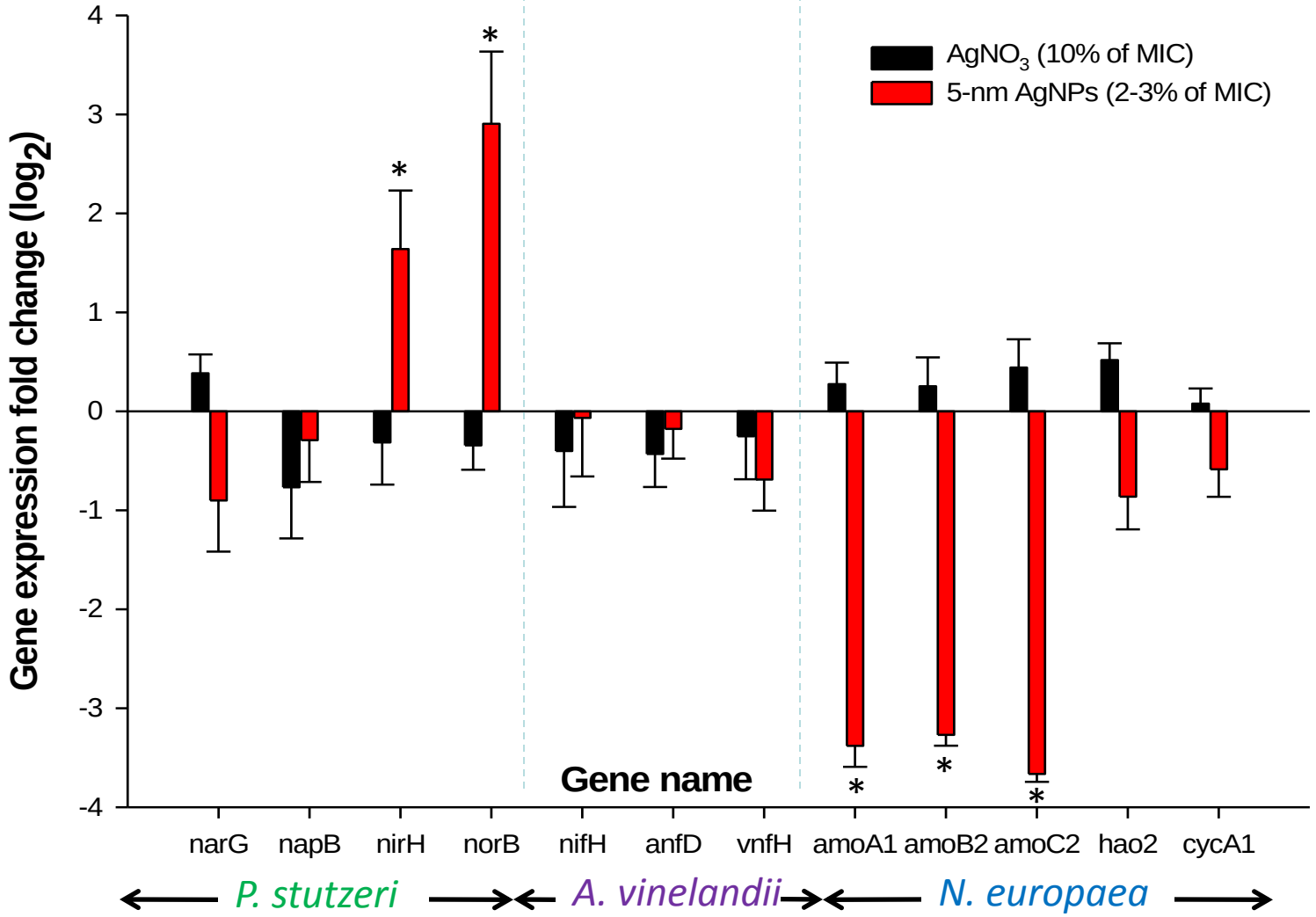
Bacterial Toxicity Mechanisms



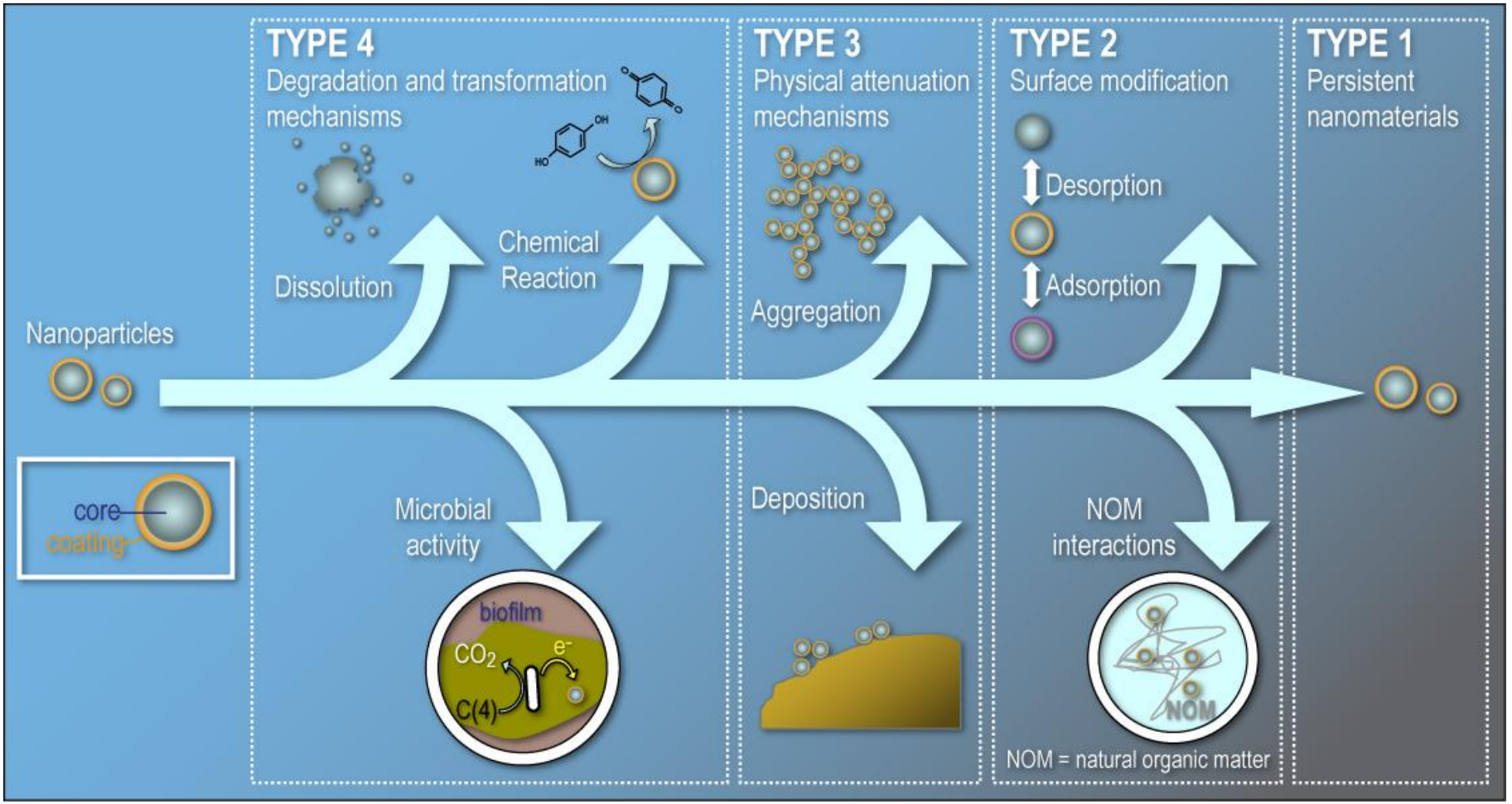
Potential Impacts to the N cycle:



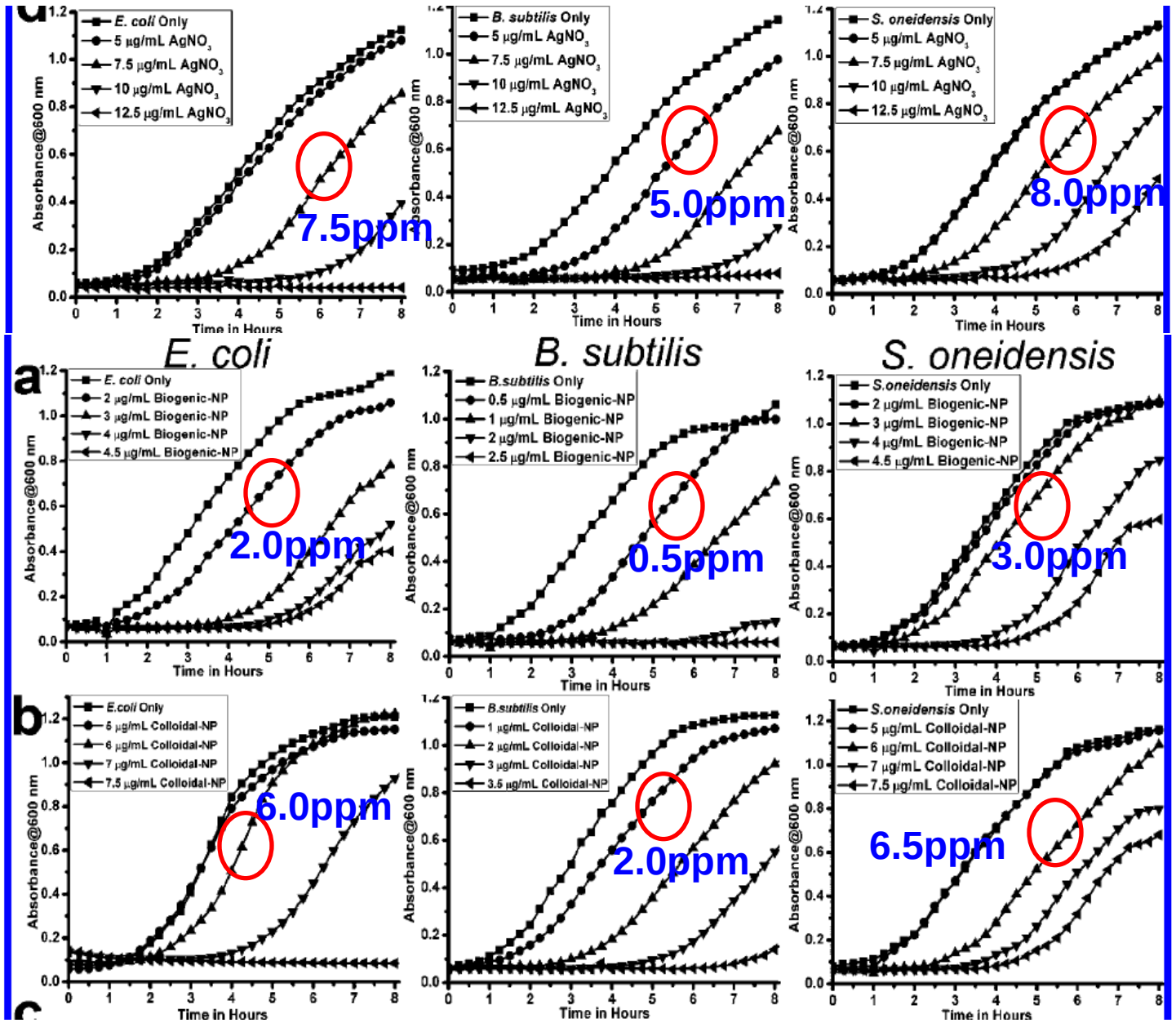
Sub-lethal concentration of AgNPs induced denitrification genes but repressed nitrification genes



Nanoparticle Modifications in the Environment



Alvarez P.J.J., V. Colvin, J. Lead and V. Stone (2009). Research Priorities to Advance Eco-Responsible Nanotechnology. ACS Nano 3(7): 1616-1619.



Suresh *et al., Environ. Sci. Technol. 2010, 44, 5210–5215*