Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Supplementary Information

Natural Inorganic Nanoparticles – Formation, Fate, and Toxicity in the Environment

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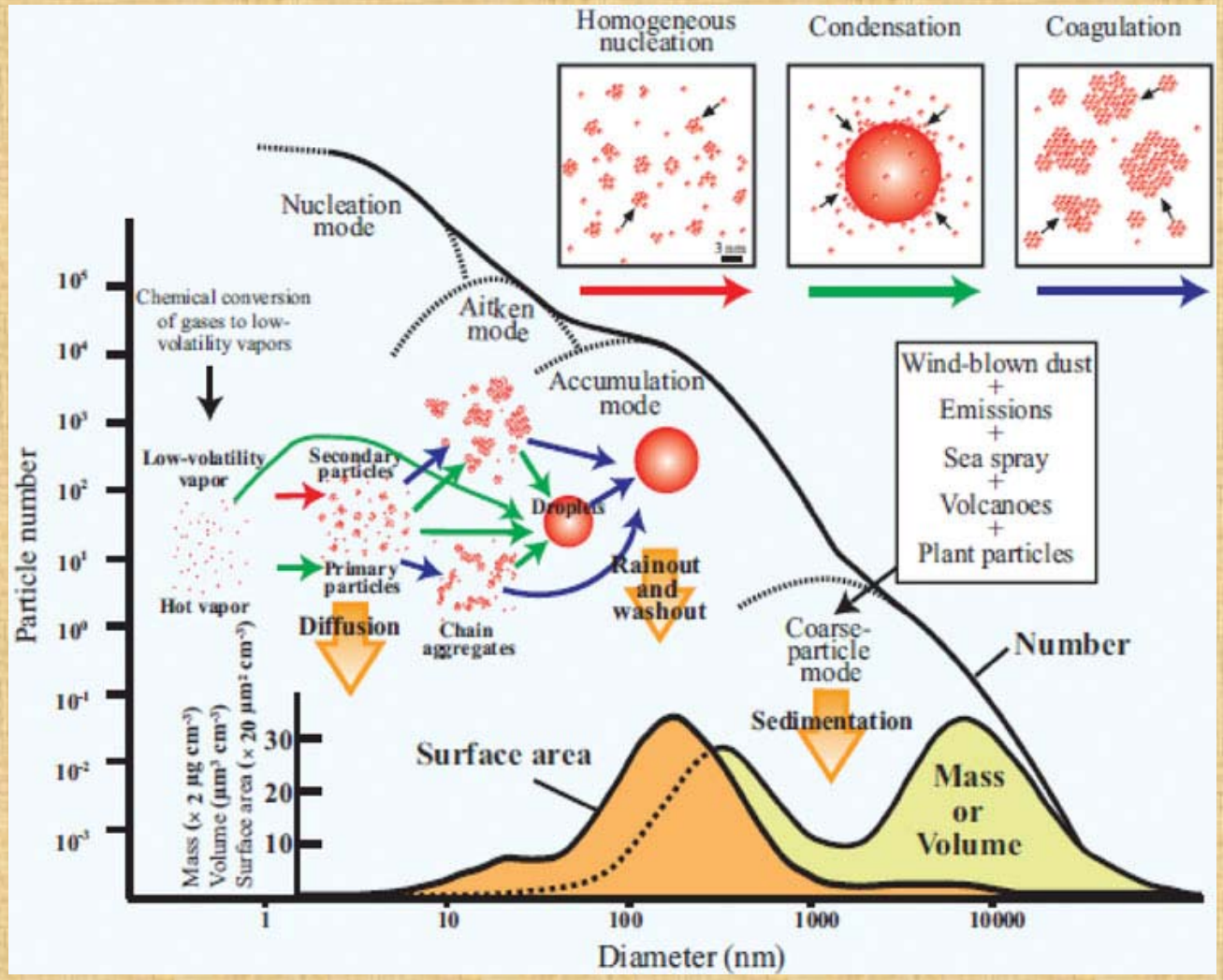
Aerosol Particles Size Distribution in Environmental Samples

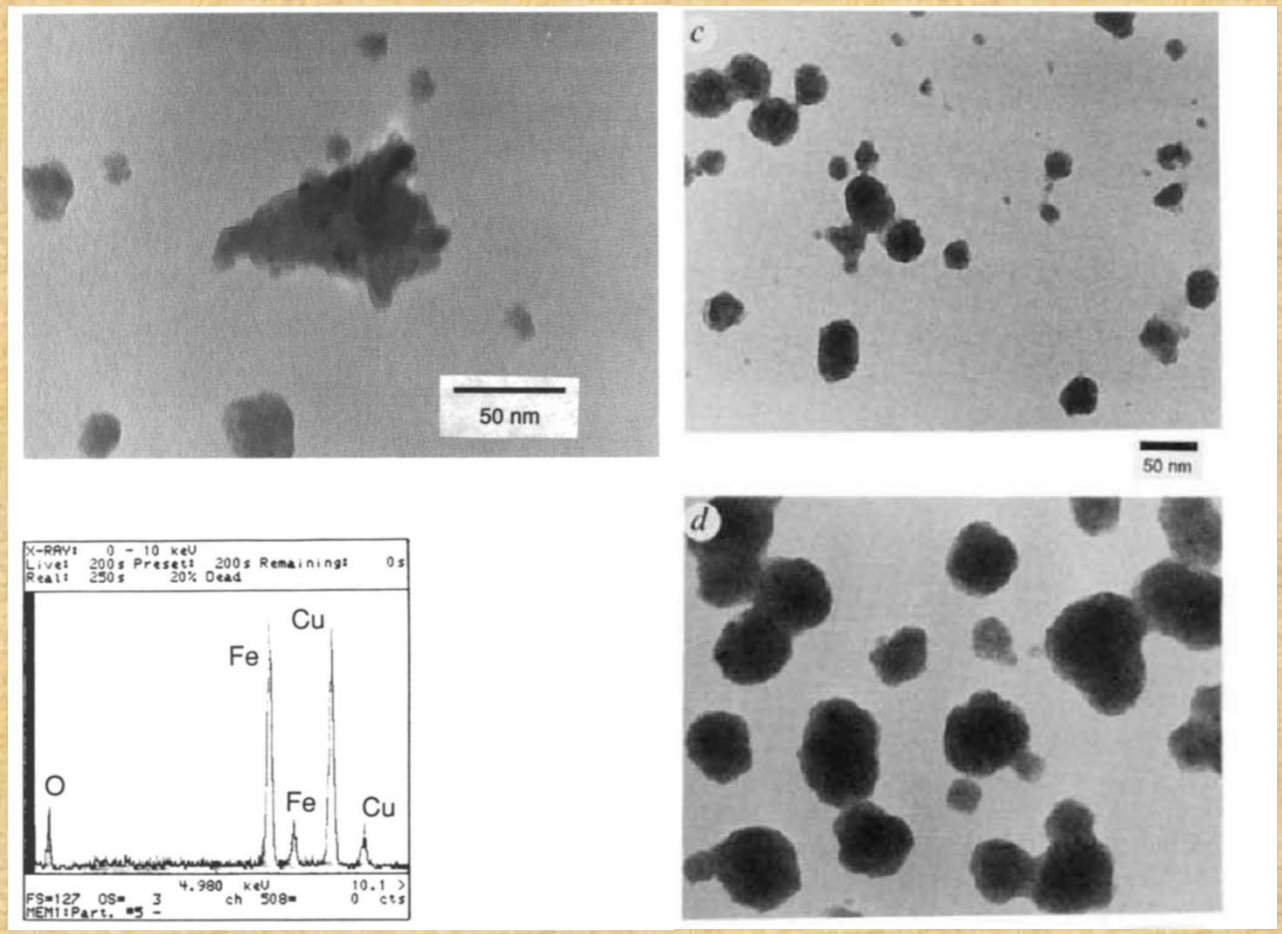


Bakshi et al. *Crit. Rev. Environ. Sci. Technol.* 2015**, 45,** 861-904.

Slide 2. Aerosol particle size distribution schematic diagrams for various parameters in an idealized environmental sample and their formation mechanisms

Nanoparticles in Sea Water

(a)

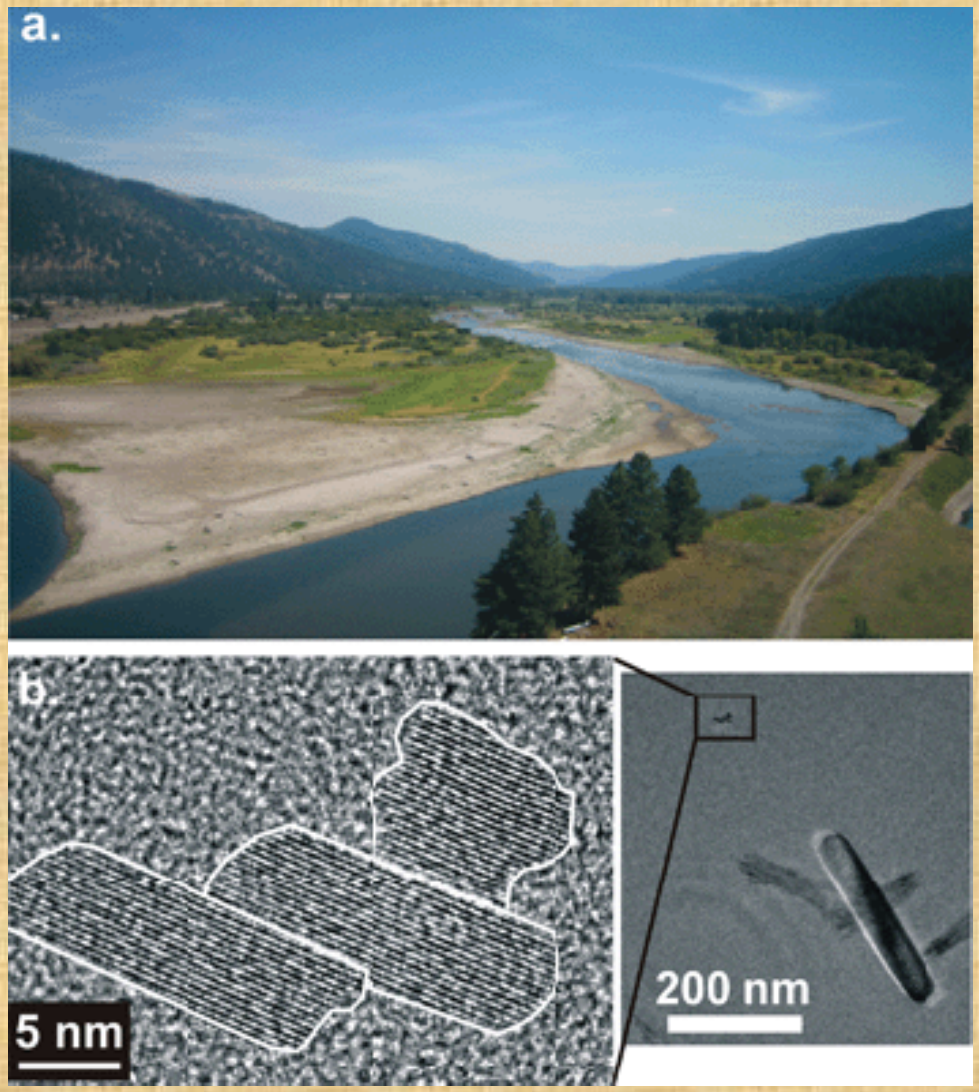


(b)

Wells and Goldberg, *Nature* 1971, **353**, 342-344.
Wells and Goldberg, *Mar. Chem.* 1992, **40**, 5-18.

Slide 3. (a) A Transmission Electron microscopy (TEM) images of a marine aggregates and its associated energy-dispersive spectrum (EDS) spectrum showing it is composed largely of iron. The large copper peak, and probably much of the oxygen peak, are from the specimen grid **(b)**.TEM images from samples Collected at Santa Monica basin station.

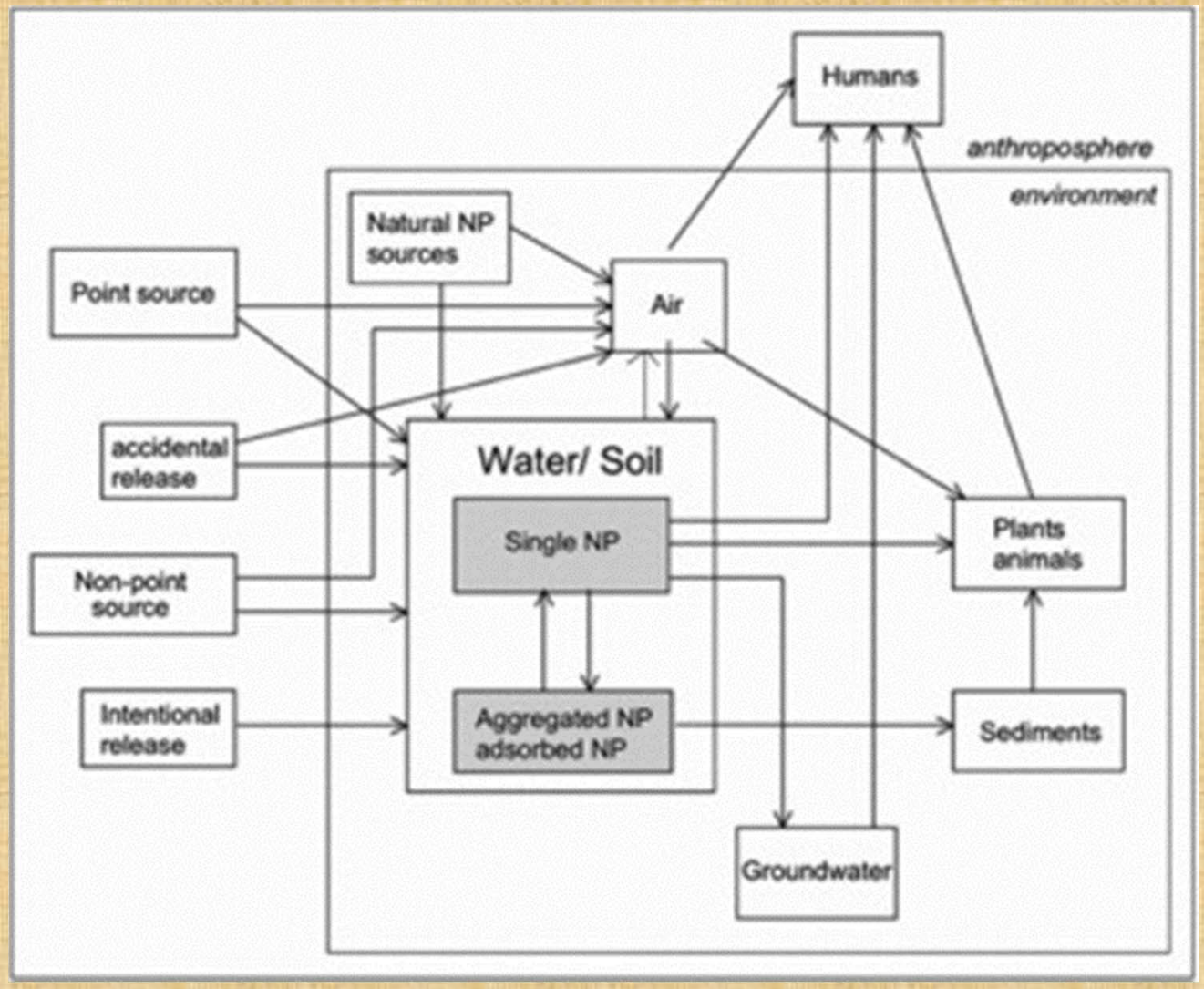
Nanoparticles in Clark Fork River in Western Montana, USA



Wigginton et al. *J. Environ. Monit.* 2007, **9**, 1306-1316.

Slide 4. Aquatic environmental nanoparticles in The Clark Fork River in western Montana, USA. HR-TEM image of 5-15 nm sized particles taken directly from the surface water of river. Crystallinity is apparent based on the presence of well-defined lattice fringes.

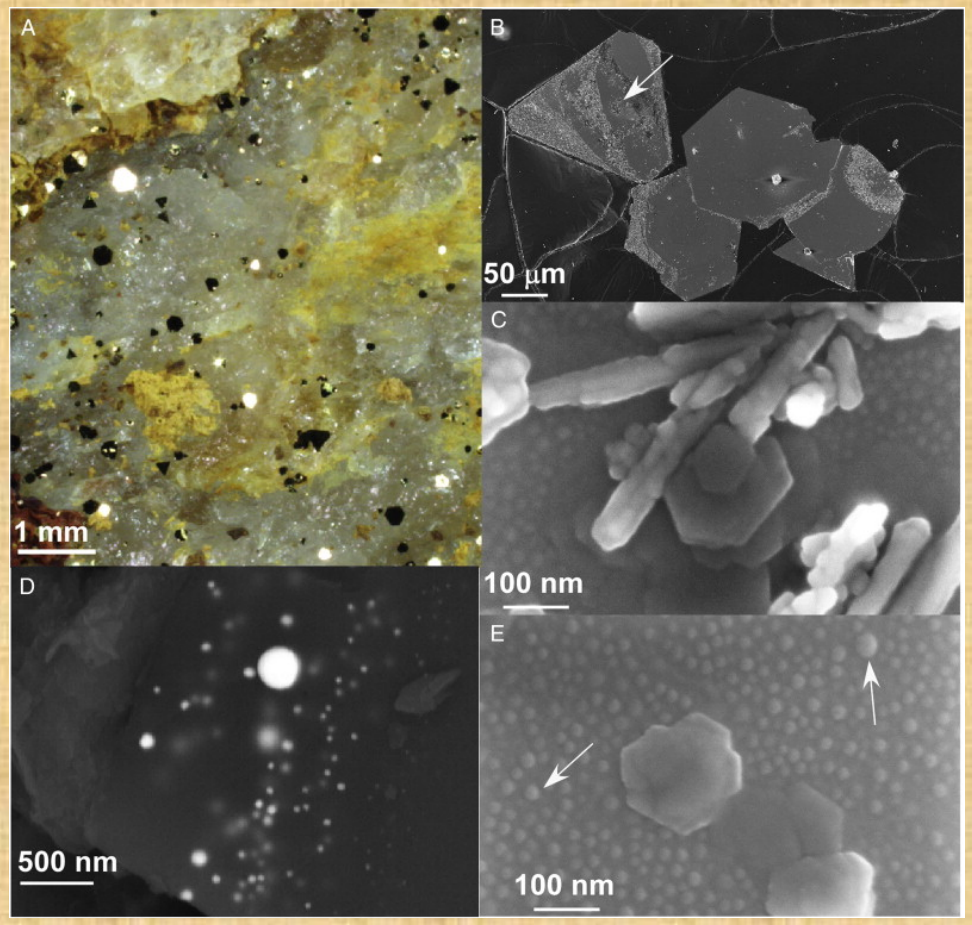
Pathways of Nanoparticles into the Environment



Bakshi et al. *Crit. Rev. Environ. Sci. Technol.* 2015, **45**, 861-904.

Slide 5. Pathways of nanoparticles into the environment.

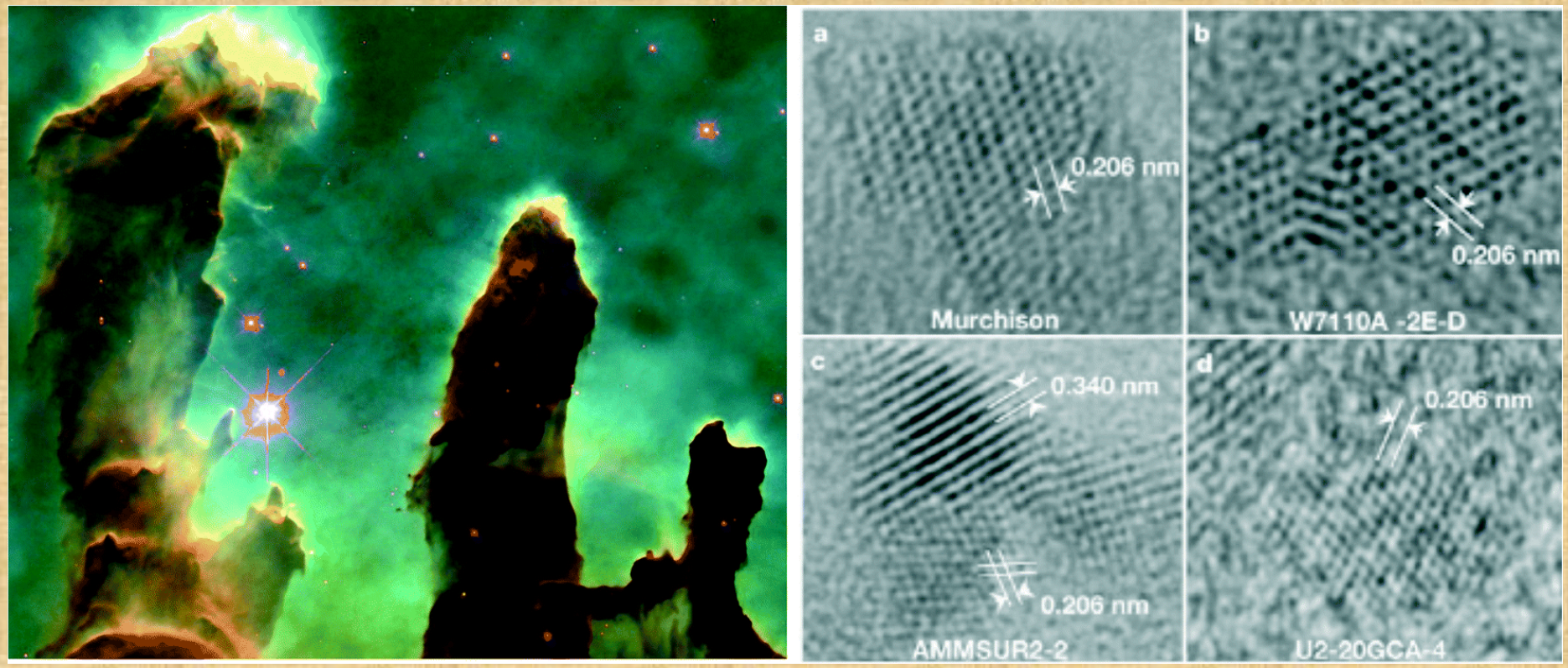
Natural Gold Nanoparticles



Hough et al. *Ore Geol. Rev.* 2011, **42**, 53-61.

Slide 6. Golden Virgin Pit in Western Australia. Closer examination of the surface of a weathered quartz fracture shows the supergene nanoparticulate gold population hosted on larger gold particles. A) light microscope image of black and shiny Au triangular and hexagonal crystals; B) FEG-SEM image of Au nanoplates; C) a close up of the darker band arrowed in B with nanoparticulate hexagonal Au (grey hexagons) and halloysite (rods); D) gold nanospheres; E) 20 nm nanospheres arrowed in the background next to coarser Au NPS .

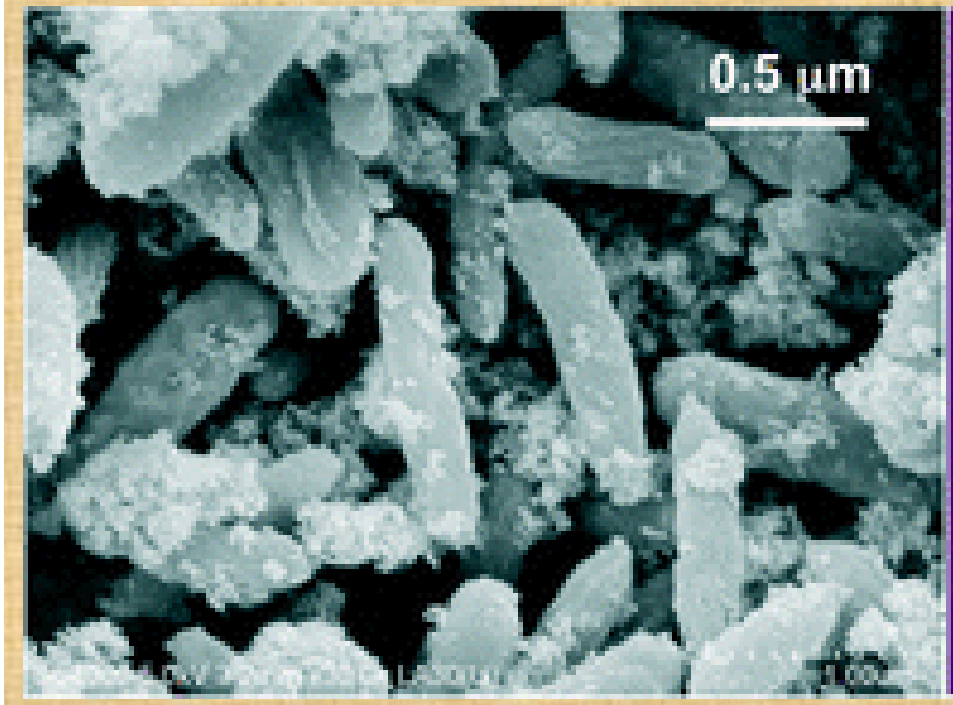
Nanostructures in Extraterrestrial Objects

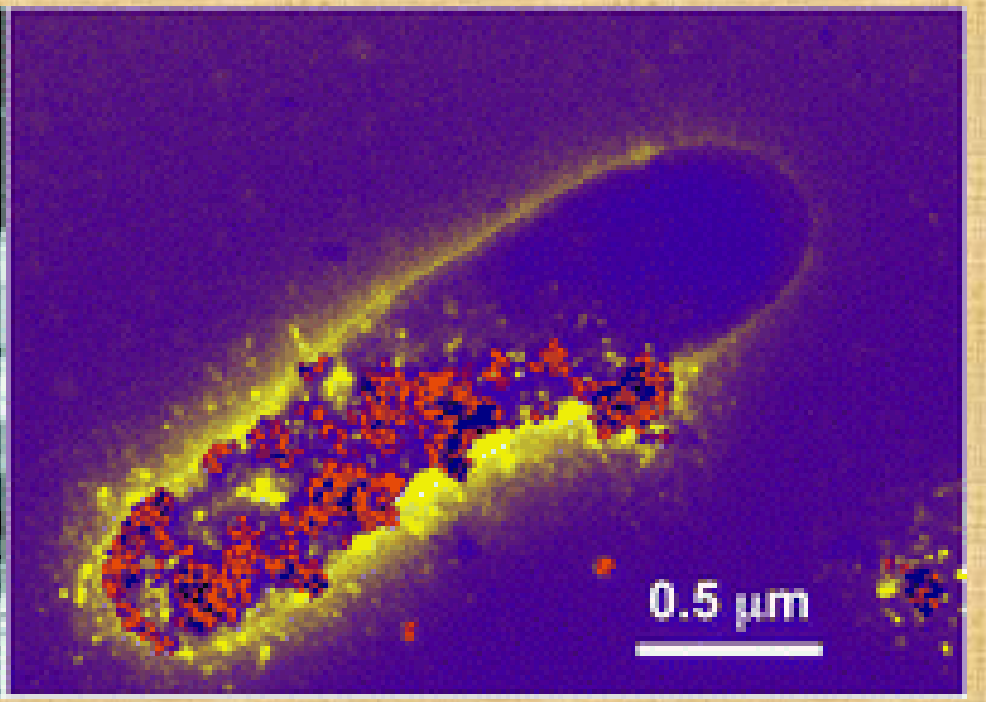


Dai et al. *Nature*, 2002, **418**, 157-159.

Slide 7. **Left)** A portion of the Eagle Nebula - NASA/Hubble Space Telescope image, which are pillars of gas and dust many light-years in length. This dust contains a vast assortment of oxide, silicate, carbide, nitride, carbonaceous, and organic nanomaterials as determined by astronomical observations (particularly infrared spectroscopy), as well as the direct analysis of "stardust" collected during space missions and isolated from meteorites **Right)** Nanodiamonds (averaging 3 nm, as small as 1 nm with <150 carbon atoms) isolated from the Murchison meteorite.

Nanoparticles in Microbial Community

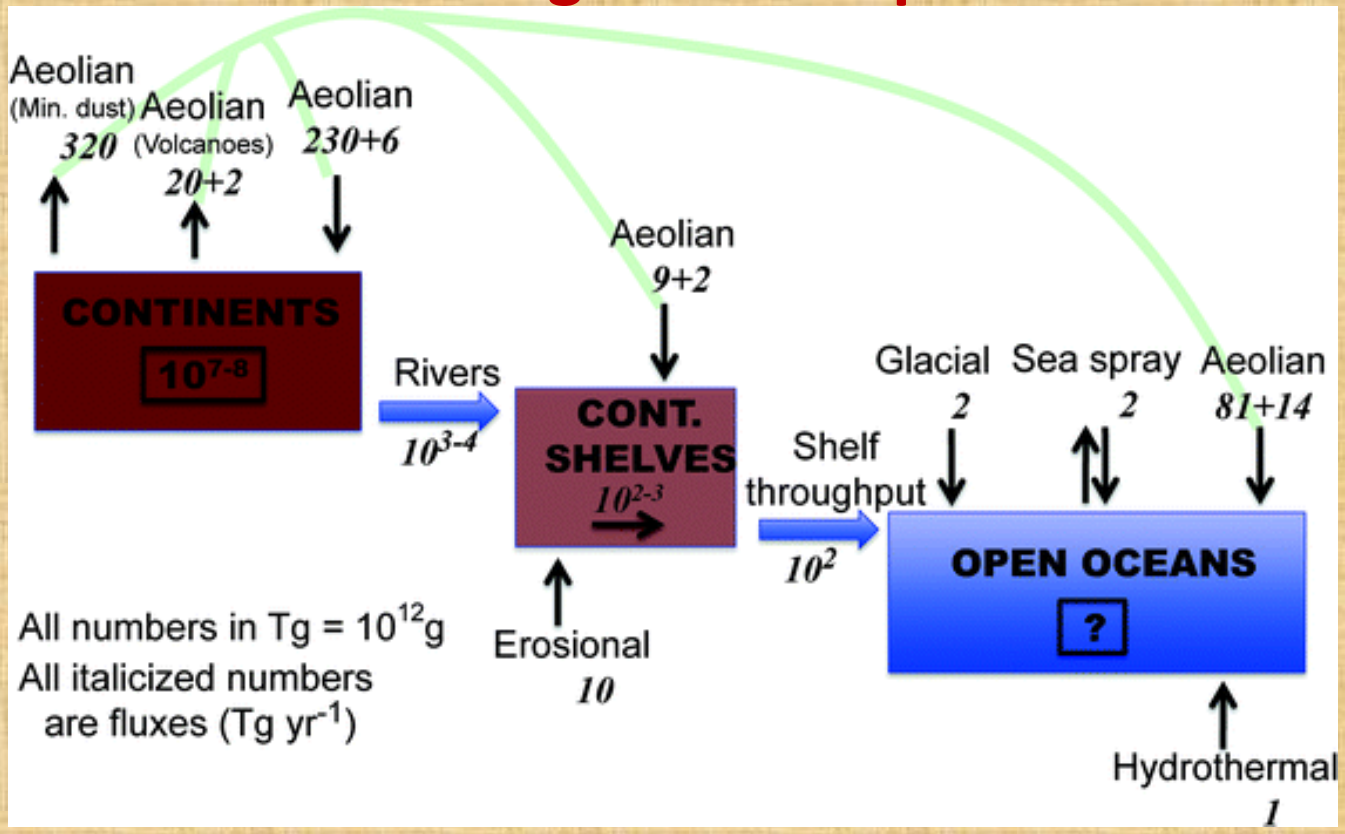




Bose et al. *Geochim.Comsochim. Acta,* 2009, **73**, 962-976.
Kroto et al. *Proc. Natl. Acad. Sci. U.S.A,* 2012, **109**, 10042-10046.

Slide 8. (Left) *Geobacter sulfurreducens* and *Thiobacillus denitrificans* accompanied by **magnetite nanoparticles** that act as interspecies electron transfer agents. These allow for microbial community cooperative functions; in this case promoting acetate oxidation coupled to nitrate reduction under anaerobic conditions. **(Right)** The cell of Shewanella oneidensis MR-1, a facultative anaerobe capable of dissimilatory iron reduction, the respiration is through 30 nm hematite particles. The rate of respiration depends on the nanoparticles‘ aggregation state, size, shape and exposed crystal faces.

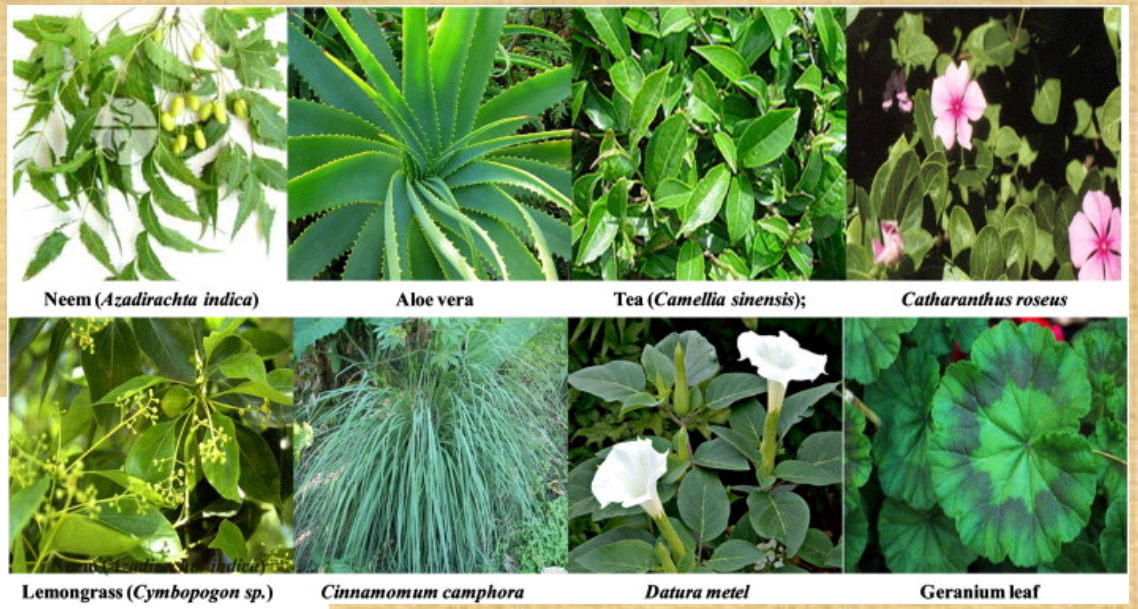
Global Distribution and Movement of Natural Inorganic Nanoparticles

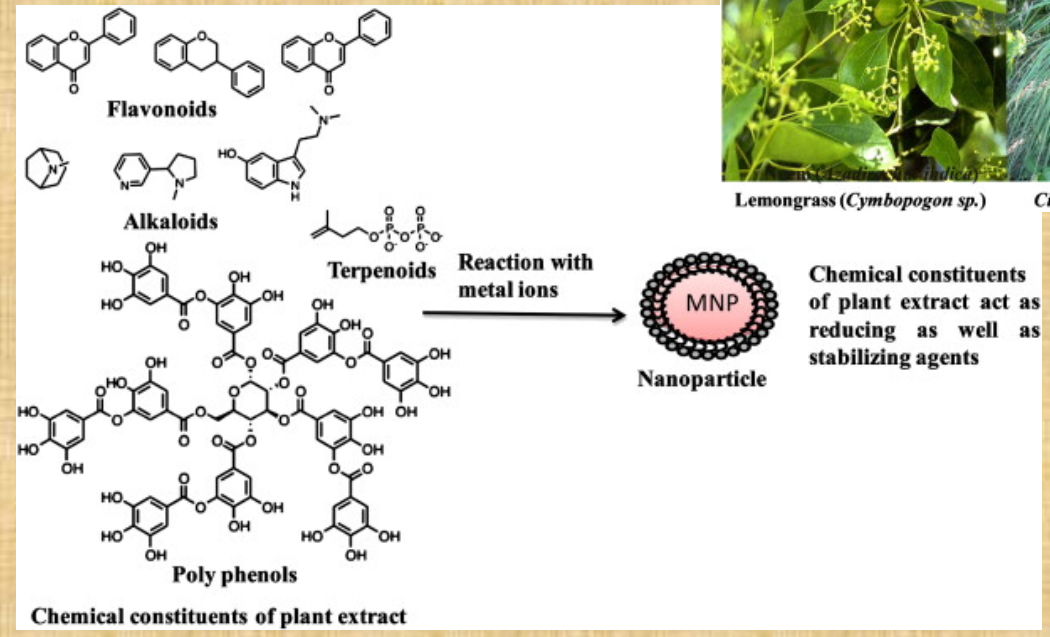


Hochella et al. *Environ. Sci.: Nano,* 2015, **2**, 114-119.

Slide 9. The global budget for naturally occurring inorganic nanoparticles. All numbers are in units of terragrams (Tg = 10^{12} g). All italicized numbers are fluxes (Tg per year), and the numbers in rectangular boxes are reservoir sizes, if known. Some of the nanomaterial fluxes are listed as two components, explained as follows: for the volcanic input to the atmosphere, 20 Tg is due to SO_2 aerosol formation, and 2 Tg is due to mineral ash. For the three aeolian inputs to the continents, continental shelves, and the open oceans, the first number is due to the 320 Tg continental mineral dust output, and the second number is due to the 22 Tg volcanic output.

Formation of Nanoparticles from Plant Extracts

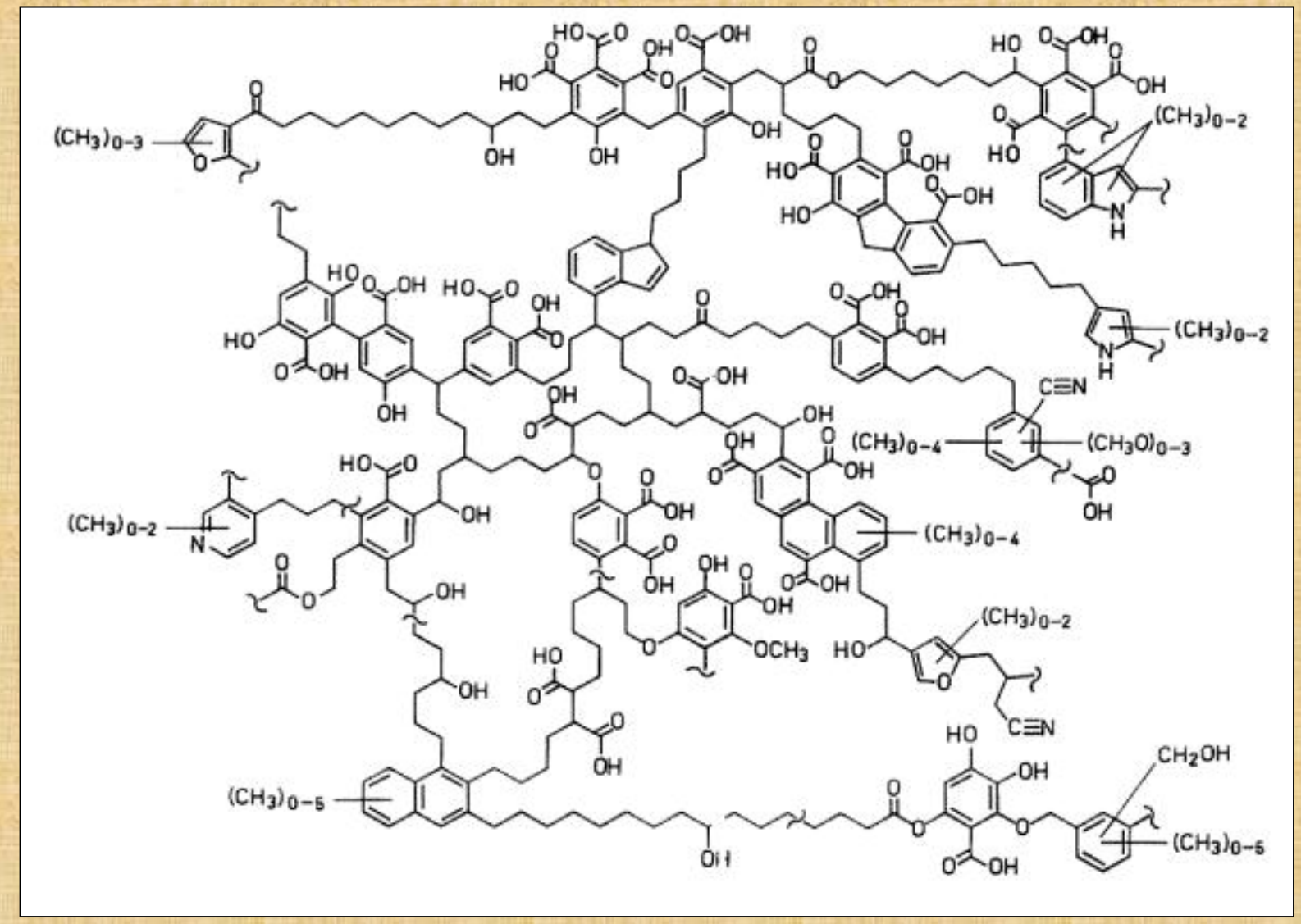




Mittal et al. *Biotechnol. Adv.* 2013, **31**, 346–356.

Slide 10. Possible chemical constituents of plant extract responsible for the bioreduction of metal ions to nanoparticles.

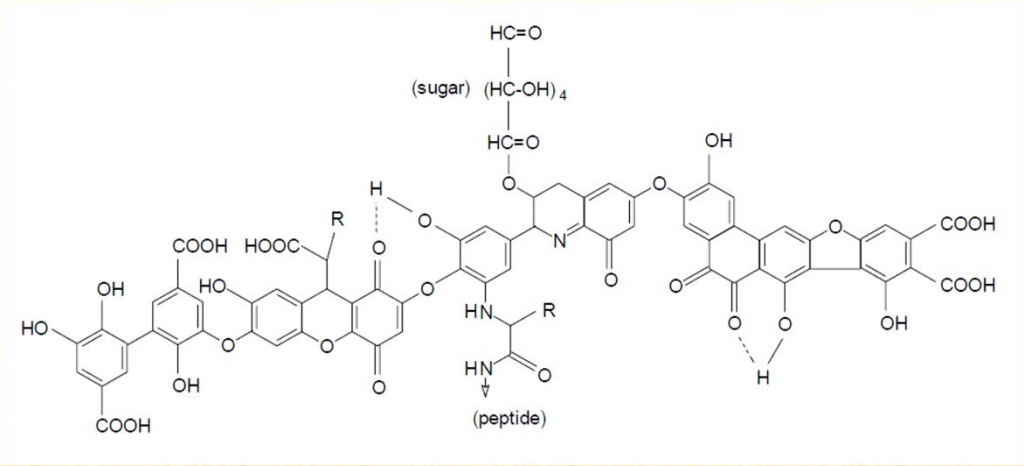
Chemical Model Structure for Soil Organic Matter

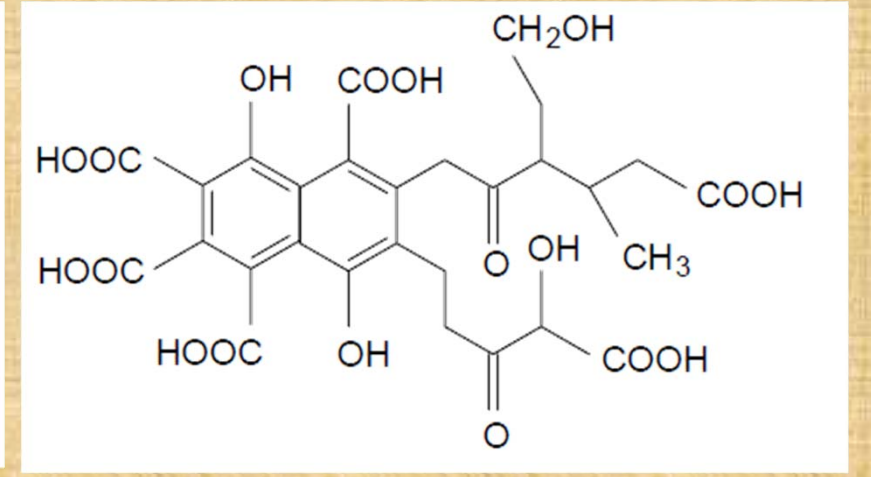


Schulten and Schnitzer, *Soil Science*, 1997, **162**, 115-130.

Slide 11. Proposed structure of soil humic acid.

Humic Substances





Humic Acids

- **Acid insoluble**

Fulvic acids

- **Soluble at all pH's**

Humin

- **Insoluble residue**

Buffle et al. *Anal. Chem.* 1977, **49**, 216-222.

Stevenson F.J.1982. Humus chemistry genesis, composition, reactions. Wiley Interscience, New York

Slide 12. Classification of humic substances