Nanomaterials down the drain: perception and reality

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Abstract

Public concern over the discharge of nanomaterials to wastewater treatment systems has caused at least one product to be taken off the market. This poster discusses wastewater discharges containing nanoscale materials and potential risks [1], considering:

- *Mass balance approach.* Preliminary research suggests the levels of wastewater discharges of some nanomaterials [2], the extent to which those materials are treated in publicly owned treatment works (POTW) [3], and the toxicity levels of such materials to certain test organisms. This poster uses a mass balance approach to synthesize the results of such research and estimate the potential discharges to POTW. It also discusses the toxicological implications of these discharges.
- *Regulatory restrictions on discharges.* The U.S. Environmental Protection Agency (EPA) is evaluating how best to adapt environmental regulations developed for "conventional" pollutants to nanomaterials [4]. This poster briefly discusses the regulatory and policy approaches being considered .

Introduction

With some 600 commercial products reportedly on the market now [5] and more under development, nanomaterials are entering municipal wastewater treatment plants. That realization has heightened concerns about the effects of these materials on treatment plants and the potential for release of free nanoscale materials into the environment. No comprehensive studies on the problem have yet been published.

Nanoscale materials could be included in wastewater discharges as a result of several scenarios:

- Manufacturing processes involving nanoscale materials could discharge these materials
- The use as intended of certain products that contain a nanoscale material component could result in discharges to a POTW or to water bodies
- The potential for nanoscale materials embedded in decomposing consumer products discarded in landfills to migrate into the environment is not clear

Uncertainties regarding these discharges, and those surrounding the risks nanoscale materials may pose to human health and the environment could inspire a backlash against specific nano-enabled products, particularly consumer products.

The concentration of a nanomaterial in wastewater depends primarily on:

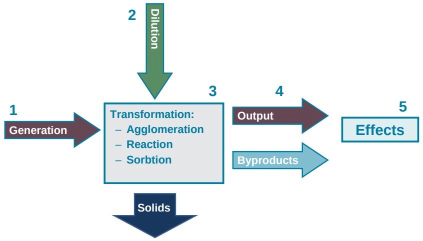
- The amount produced or used locally
- Whether the nanomaterials are fixed in a matrix or free
- The concentration of the free nanomaterial in the commercial product
- The fraction that is washed down the drain
- The degree of agglomeration or adsorption which occurs in aqueous solution that changes the form of the nanoparticle or removes it from solution
- The extent of dilution

The case study to the right illustrates the issue.

Case study

How much silver could reach a wastewater treatment plant?

Preliminary mass balance on silver generation during laundry cycle using the SilverCare™ function:



1. Generation

Samsung describes SilverCare™ washing machine option in different ways [6-9]:

- 400 billion silver ions generated during each wash cycle; OR
- "Electro currents nano-shave two silver plates the size of large chewing gum sticks", which reportedly last for 3,000 wash cycles; OR
- Use of washing machine reportedly releases 0.05 grams per year.

Are these nano silver particles or ionic silver?

Key and Maas [10] indicate that electrolysis of a silver electrode in deionized water produces colloidal silver containing both metallic silver particles (1-25 wt%) and silver ions (75-99 wt%). The silver particles observed in colloidal silver generally range in size from 5 to 200 nm. This information suggests – but certainly does not conclusively prove – that the SilverCare™ washing machine discharges a mixture of silver ions and silver nanoparticles.

2. Dilution

Wash cycle uses 12.68 gal water [11]

Typical residence generates 70 gallons wastewater per person per day [12]

Unknowns:

- Number of people in community?
- Number of SilverCare™ washing machines in community?
- Amount of laundry per person per day?
- Other sources of non-domestic wastewater in community?

3. Transformation

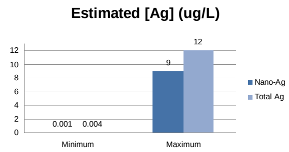
Unknowns:

- Samsung: silver "sticks to the fabric" [8]
- Sorption to other solids?
- Agglomeration?
- Chemical/ biological reactions?

4. Output

Results of preliminary mass balance:

- First approximation of concentration entering wastewater treatment plant.
- Range of assumptions generates range of estimates.
- Maximum estimate is an extreme upper bound estimate.
- Minimum does not reflect all sources of dilution, thus is a conservative estimate.



5. Effects

Acute ambient water quality criterion (not nano-specific) 3.2 ug/L [12].

Few experiments have tested the toxicity of nano Ag at relevant concentrations.

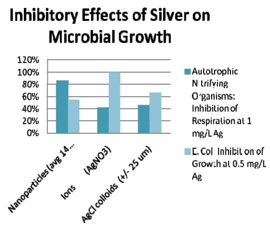
Existing data show potential for toxicity but are not conclusive.

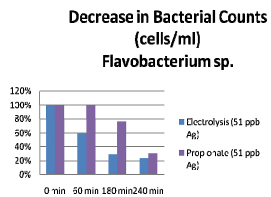
Table 1: Toxicity Tests on Silver Nanoparticles

Ag Solutions	Test	Results	Ref.
500, 1000 µg/L Ag nanoparticles (avg. 14 ± 6 nm)	Extant respirometry – autotrophic nitrifying organisms	1000 µg/L nano Ag inhibited respiration by 86 ± 3%; Ag ions ($AgNO_3$) and AgCl colloids at same concentration inhibited respiration by 42 ± 7% and 46 ± 4%, respectively.	[13]
	Microtiter Fluorescence Assay – *E. coli*.	500 µg/L nano Ag inhibited growth by 55 ± 8%; Ag ions ($AgNO_3$) and AgCl colloids at same concentration inhibited respiration by 100% and 66 ± 6%, respectively.	
1 – 5,000 µg/L colloidal Ag (5-20 nm)	Zebrafish embryos	No effect on development or survival in first two weeks; at highest concentrations, "found a clear effect on gene expression in most cases"	[14]
10 to 50 µg/L Ag nanoparticles (15 nm)	PC-12 neuroendocrine cells from *Rattus norvegicus*	Decreased mitochondrial function	[15]
25, 80, 130 nm Ag nanoparticles	Rat liver cells	Cells internalized nanoparticles; agglomeration limited cell penetration	[16]
Up to 10,000 µg/L Ag nanoparticles (15 nm)	Cell line established from spermatogonia isolated from mice	Reduced mitochondrial function and cell viability between 5,000 and 10,000 µg/L; estimated EC50 (i.e., concentration which would provoke a response half way between the baseline and maximum response) 8,750 µg/L	[17]

Is nano silver more toxic to bacteria than other forms of silver?

- Choi et al [13] tested the effects of nano silver, silver ions, and silver colloids on two bacterial colonies: autotrophic nitrifying bacteria from a bioreactor seeded from a sewage treatment plant, and heterotrophic bacteria, *Escherichia coli*. Their results showed that nano Ag was more toxic than silver ions to the nitrifying bacteria, but less toxic than silver ions to *E. coli*.
- Early research by NASA showed that silver generated from electrolysis of elemental silver was more toxic than silver propionate [18]. While the study did not distinguish between nano silver and ionic silver per se, the electrolysis process apparently paralleled that in the SilverCare™ washing machine. The results showed a decrease in bacterial population at concentrations as low as 51 µg/L.





Regulatory controls

The Clean Water Act (CWA) governs discharges of "pollutants" into "waters of the United States." In its *Nanotechnology White Paper*, the U.S. Environmental Protection Agency (EPA) states that "[d]epending on the toxicity of nanomaterials to aquatic life, aquatic dependent wildlife, and human health, as well as the potential for exposure, nanomaterials may be regulated under the CWA." [4]

The National Pollutant Discharge Elimination System (NPDES) established under CWA Section 402 includes: the issuance, by either EPA or a state with an EPA-approved permitting program, of point source discharge permits containing numeric, pollutant-specific effluent limitations (technology-based or water quality-based); routine and frequent monitoring of treated wastewater to determine compliance; and reporting to the permitting authority of the effluent monitoring results.

Wastewater containing nanoscale materials is subject to effluent limitations, whether technology-based or water quality-based, set forth in an NPDES permit. To date, EPA has not publicly released how it intends to develop effluent limitations specifically for engineered nanoscale material-containing wastewaters. However, EPA's Office of Pesticide Programs' (OPP) December 2006 determination that Samsung Electronics' silver ion generating washing machine requires pesticide registration under FIFRA was prompted by concerns expressed to OPP by the National Association of Clean Water Agencies (NACWA) and an organization representing California POTWs about the effects on wastewater treatment plants from silver ions.

Conclusions

As the commercialization of nanoscale materials grows, and the consumer use of products containing nanoparticles increases, so will the discharge of nanomaterials to wastewater treatment plants. Limited data are available to estimate such discharges. While the CWA protects against toxic discharges, the uncertainty surrounding the possible effects of nanoscale materials may result in consumer backlash against some products. EPA is considering how best to address these issues, but little information is available publicly.

Interested parties should monitor the technical literature and regulatory and legal developments in this regard. Novel technologies require novel solutions and the interests of nanotechnology are best served by ensuring that nanoscale materials are managed prudently, thoughtfully, and carefully. Perhaps the best and most immediate defense against a potential consumer backlash is a good dose of precaution, the use of Life Cycle Analysis to evaluate end-of-life impacts, and an enduring commitment to product stewardship and environmental protection. And, as with any emerging environmental issue, clear, timely, and accurate communication with the public and other stakeholders goes a long way in distinguishing between perception and reality.

Please see hand out for list of references.

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