Nanomaterials down the drain: perception and reality

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ABSTRACT

Public concern over the discharge of some nanomaterials to wastewater treatment systems has caused at least one product to be taken off the market. This paper explores the potential for nanomaterials to be included in the discharge of effluent to publicly owned treatment works, as well as water bodies generally, and the likely consequences of such releases. It uses a mass balance approach to quantify discharges for two case studies, to the extent possible. It also discusses regulatory restrictions that limit the discharges of nanomaterials. [1]

Keywords: wastewater, discharge, publicly owned treatment works, Life Cycle Analysis, Clean Water Act, nanosilver

1. INTRODUCTION

Nanoscale materials could be included in wastewater discharges as a result of several scenarios. First, manufacturing processes involving nanoscale materials could result in the inclusion of these materials in a facility's effluent. Second, the use as intended of certain products that contain a nanoscale material component could become part of the influent being treated at a publicly owned treatment work, or a contaminant in a lake or water body. Sunscreen lotions containing nanoscale materials come to mind. Finally, products incorporating nanomaterials eventually reach the end of their usable life and are discarded. The potential for nanoscale materials embedded in decomposing consumer products discarded in landfills at the end of their useful life to migrate into the environment is not clear. This uncertainty, coupled with other unknowns regarding the potential for nanoscale materials to cause risks to human health and the environment, could inspire a backlash against specific nano-enabled products, particularly consumer products.

This paper discusses wastewater discharges containing nanoscale materials and their potential risks, considering:

1. Mass balance approach. Preliminary research suggests the levels of wastewater discharges that may occur from the use of some nanomaterials [2], the extent to which those materials are treated in publicly owned treatment works [3], and the concentrations at which such materials may be toxic to certain test organisms. This paper uses a mass balance approach to synthesize the results of such preliminary research and estimate the magnitude of potential discharges to wastewater treatment plants. It also discusses the toxicological implications of these discharges.
2. 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 paper briefly discusses the regulatory and policy approaches being considered in addressing effluent containing nanomaterials.

2. MASS BALANCE: QUANTIFYING THE DISCHARGE

With reportedly approximately 600 commercial products on the market now [5] and more under development, nanomaterials are beginning to enter municipal wastewater treatment plants. That realization has heightened concerns about the effects of these materials on treatment plants and the potential generally for indeterminate quantities of free nanoscale materials included in discharges released into the environment. Research into the potential amounts of nanomaterial discharges and the consequences of those discharges has just begun; no comprehensive studies on the problem have yet been published.

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; and
- The extent of dilution.

Two case studies illustrate this mass balance approach. They also show the difficulty in closing a mass balance when the details of product manufacture are proprietary. Coincidentally, both examples concern the discharge of silver when washing clothes.

Consider, for example, Samsung's SilverCare™ option on several models of washing machine. While Samsung marketed the antibacterial action of generating nano particles of silver in the rinse cycle as a benefit to customers, some consumers became concerned about the potential consequences of using SilverCare™ products. Initial efforts to market the washing machine met with resistance in Germany. According to news reports, the washing machine was briefly taken off the market in Sweden due to concerns over the potential toxic effects of discharging silver nanoparticles from these machines to wastewater treatment plants [6-7].

A mass balance begins with an estimate of the amount of nanosilver generated in each wash cycle. Samsung has described the technology in several ways. One account [8] indicates that the system electrolyzes pure silver into nano-sized silver ions "approximately 75,000 times smaller than a human hair". The resulting particles would then be approximately 1 nm in diameter. Another description [9] indicates that an electrical current applied to silver plates (each the size of a stick of chewing gum) "nano-shaves" the silver into positively charged silver atoms. Another source [10] states that electrolysis of a silver electrode produces colloidal silver containing both metallic silver particles (1-25 wt%; 5-200 nm diameter) and silver ions (75-99 wt%). The SilverCare™ washing machine may therefore generate a mixture of silver ions and silver nanoparticles.

Samsung has offered several explanations of the amount of silver released when washing a load of clothing. Its product literature notes that electrolysis of silver generates up to 400 billion silver ions during each wash cycle [8, 11]. The two chewing-gum sized plates of silver reportedly last for 3,000 wash cycles [11]. Finally, Samsung reportedly has indicated that using a SilverCare™ washing machine for a year would release 0.05 grams of silver [6].

Completing a mass balance requires several additional assumptions: the manufacturer's data on the amount of water used per wash cycle (12.68 gal [12]); the amount of wastewater generated per day (70 gal/person/day [13]); the number of loads of laundry per household per day (assumed 2 loads on average); and that all the silver generated from the washing machine is discharged to the sewer.

This basis provides a range of estimates of the mass of nano-silver that could be discharged to a wastewater treatment plant. The use of SilverCare™ in washing clothes could result in concentrations of nanosilver in wastewater ranging from 0.001 micrograms per liter (µg/L) to an extreme upper bound concentration of 9 µg/L. The lowest estimate is based on the reported release of 0.05 grams of silver per year and the assumption that only 25% of the mass would comprise nanoparticles (rather than ions) of silver. The highest estimate is based upon complete consumption of the two silver plates during the unit lifetime and the assumption that 75% of the silver was in nanoparticulate form.

Agglomeration and adsorption of nanoparticles would decrease the concentration of nano silver to levels below these estimates. Further, the mass balance calculations do not account for dilution by sources of wastewater other than domestic sewage from homes using SilverCare™ washing machines. Dilution from other sources would also decrease the concentration of silver nanoparticles. Thus, the higher estimate of 9 µg/L is an extreme upper bound.

Several manufacturers market socks that contain nanosilver particles as an antibacterial agent. One study measured the amount of silver that five different brands of socks could release when washed [2]. Four of the test socks initially contained 2.0 to 1,360 micrograms silver per gram sock (µg/g). (One brand did not contain measurable silver.) Between 0 – 100% of the silver washed out of the silver-containing socks after four simulated wash cycles. The concentration of silver in the wash water ranged up to 300 µg/L.

It is difficult to extrapolate from these initial laboratory results to estimate the potential discharge to a wastewater treatment plant. Operating conditions in a typical washing machine could result in lower concentrations than were measured in the experiment, by a factor of 25; additional dilution by other sources of wastewater could reduce the concentration further.

As described above, concerns have arisen over the possible effects of discharging silver nanoparticles to wastewater treatment plants. Silver has well-known antimicrobial properties, and wastewater treatment plants typically use microbial cultures to degrade organic wastes.

No published benchmarks allow for a direct comparison of the estimated discharges of silver nanoparticles to levels that are either "safe" or "toxic" to microorganisms at a sewage treatment plant. The acute ambient water quality criterion for silver, which was not derived specifically for nanoparticles, is 3.2 µg/L [14]. This concentration is comparable to the conservative upper bound estimate of the discharge of silver nanoparticles into wastewater from using the SilverCare™ system. Research on the toxicity of silver nanoparticles, as summarized in Table 1, provides further relevant information. In general, the test solutions – and the concentrations at which effects were observed - were more concentrated than the discharge estimates above.

These examples demonstrate the difficulty of estimating the discharge of nanomaterials from the use of commercial products, or to assess the consequences of the discharge. Few data are available on the amount of nanomaterials in commercial products, the amount used, and the concentrations in discharges. Further, research into the toxic effects of nanomaterials is in its infancy. This uncertainty underscores the importance of Life Cycle Analysis in developing new nanotechnology products.

3. REGULATORY CONTROLS

The Clean Water Act (CWA) governs discharges of "pollutants" into "waters of the United States." The statutory definition of a "pollutant" is expansive and there is no credible basis to conclude that it excludes engineered

Table 1: Toxicity Tests on Silver Nanoparticles

Ag Solutions	Test	Results	Ref.
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"	[16]
10 to 50 µg/L Ag nanoparticles (15 nm)	PC-12 neuroendocrine cells from *Rattus norvegicus*	Decreased mitochondrial function	[17]
25, 80, 130 nm Ag nanoparticles	Rat liver cells	Cells internalized nanoparticles; agglomeration limited cell penetration	[18]
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	[19]

nanoscale materials and engineered nanoscale material-containing wastewaters. In its Nanotechnology White Paper, 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." [20] EPA points out that "[a] variety of approaches are available under the CWA to provide protection, including effluent limitation guidelines, water quality standards . . ., best management practices, [point source discharge] permits, and whole effluent toxicity testing." [20]

The centerpiece of the CWA regulatory program is the National Pollutant Discharge Elimination System (NPDES) established under CWA Section 402. Key features of the NPDES program include: 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 that either are technology-based or water quality-based; routine and frequent monitoring of effluent (*i.e.*, wastewater) through sampling and analytical methods to determine compliance; and routine and frequent reporting to the permitting authority of the permittee's effluent monitoring results. Under CWA Section 301(a), it is unlawful for a person to discharge any pollutant "except as in compliance with" a NPDES permit [21].

Wastewater containing nanoscale materials is subject to effluent limitations, whether technology-based or water quality-based, set forth in a NPDES permit. To date, EPA has not publicly released how it intends to develop effluent limitations specifically for engineered nanoscale material-containing wastewaters. Presumably, EPA is internally considering how best to apply its authority under the CWA to address these issues. Similarly, EPA has given no indication as to whether engineered nanoscale materials constitute conventional, non-conventional, or toxic pollutants, a distinction that bears directly on the technology that a permitted discharger must employ to achieve a particular effluent limitation. Little currently is known about the availability and economic feasibility of technology to control wastewater discharges containing engineered nanoscale materials.

The NPDES permit program applies to so-called direct dischargers – facilities that discharge pollutants directly to waters of the United States. It does not apply to what are known as indirect dischargers – facilities that discharge wastewater to publicly owned treatment works (POTWs) rather than directly to waterbodies [22]. EPA's pretreatment program, mandated by CWA Section 307(b), establishes pretreatment standards for this latter category of dischargers [23].

As with effluent limitations, EPA reportedly is considering these issues, but has not yet released any information on its conceptual approach to applying CWA authorities to nanoscale materials, and whether or how pretreatment standards might apply to nanoscale material-containing wastewater streams. It bears noting, however, that 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 in large part by concerns expressed to OPP by the National Association of Clean Water Agencies (NACWA) and an organization representing California POTWs. NACWA and the POTWs expressed significant concern with the effects on wastewater treatment plants from silver ions.

4. 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 Clean Water Act provides protection 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 at present little information is available publicly on how EPA intends to use its CWA authority in this regard, or whether EPA will consider other measures under the CWA.

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.

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[21] CWA § 301(a), 33 U.S.C. § 1311(a).

[22] 40 C.F.R. §§ 122.2, 122.3(c).

[23] 40 C.F.R. Part 403.