PROJECT MEMORANDUM

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From:	Eva Steinle-Darling, Ph.D, Curtis Feronti	**Office:**	WCO
Date:	February 3, 2016	**Project No.:**	9963A.00
Subject:	Nanoparticle Literature Review		

This memorandum was drafted in response to a specific request from the Soquel Creek Water District (SqCWD) regarding nanoparticles. The SqCWD wanted to know the latest information on nanoparticles as they pertain to potable water reuse projects. Nanoparticles are not regulated for potable water reuse projects (or potable water projects, for that matter). In conversations with the State of California Division of Drinking Water (DDW) in January 2016, the DDW defined their position on nanoparticles, which is that existing regulations are protective of public health and that there is no intent to regulate nanoparticles. With that said, DDW will continue to evaluate the issue.

1.0 NANOPARTICLE CONCERNS

Nanoparticles originate from a variety of systems: engineered, incidental (e.g., smoke), and natural (Wiesner 2011). Nanoparticles from natural and incidental systems have been present on earth for millions of years (Liu et al. 2014). As for engineered nanomaterials, approximately 60% of the nanotechnology market is for medical, industrial, and chemical applications (Kurwadkar et al. 2014). Therefore the probability of the nanomaterials being released into wastewater is high, and the presence of nanomaterials in biosolids and model wastewater effluents has already been reported (Kiser et al. 2009, Limbach et al. 2008).

The data regarding the concentration and occurrence of nanoparticles in natural and engineered systems is minimal (Li et al 2013). Additionally, there is a multitude of nanomaterials that currently exists and more that could be manufactured. Therefore, it is unattainable to evaluate the ubiquity and toxicity of each individual material (Wiesner 2011). Health risk for nanomaterials is difficult to predict because of the uncertainty surrounding the amount of production, use and characteristics of the materials, exposure pathways, and lack of data connecting the nanomaterials and their effect on organisms and ecosystems (Wiesner 2011). Previously, it has been observed that nanoparticles may produce toxic or developmental effects in the laboratory and are toxic when made of heavy metals or fibers previously known to be toxic (Wiesner 2011). Nanoparticles may be able to penetrate the body and distribute through the body more widely than larger particles (Li et al 2013, Liu et al 2014). Despite this, to date, there are no published cases of a human disease or incident attributed to nanomaterials (Wiesner 2011).

2.0 KEY RESEARCH PROJECTS

In April 2014, the EPA announced research grants to Arizona State University and the University of California, Santa Barbara to gain a better understanding of chemical and nanomaterial impacts over the duration of their life cycle, including their design, manufacture, use and disposal. When complete, the research at Arizona State University will document the trade-offs between incorporating nanomaterials to improve consumer products and the potential risks to humans and the environment. Paul Westerhoff, the LCnano Network director, leads this research team. The University of California, Santa Barbara's research will develop an online tool for academia, industry, and other decision makers to evaluate life cycle impacts of chemicals which they can then use to make more informed decisions about product design.

The WaterReuse Research Foundation (WRRF) funded the "Review of Nanomaterial Research and Relevance for Water Reuse" with Qilin Li as the Principal Investigator. The report identified the scopes and research goals of major national and international research programs on health and environmental impacts of engineered nanomaterials (ENMs). It goes on to summarize research on water reuse applications of ENMs and the potential human health and ecological risks of nanomaterial in relation to water reuse. The report identifies research needs and major knowledge gaps pertinent to water reuse and helps to answer three key questions for utilities:

1. "How can water reuse utilities take advantage of burgeoning nanotechnology?"
2. "How can ENMs be removed by wastewater treatment trains and how can they affect wastewater treatment processes?"
3. "What are the nanomaterial-related regulatory issues that water reuse utilities should be aware of?"

Another WRRF funded study was the "Evaluation of Impact of Nanoparticle Pollutants on Water Reclamation" conducted by Dr. Rajagopalan Ganesh and Dr. Diego Rosso. The study obtained preliminary data on the fate and impact of manufactured nanomaterials in biological treatment, media filtration, and disinfection water reclamation processes. Nanomaterial behavior and the impacts of size were evaluated by bench-scale studies.

Nowack and Gottschalk have done several modeling studies to obtain information on environmental exposure concentrations of engineered nanomaterials (Gottschalk et al. 2010, Gottschalk et al. 2013, Nowack et al. 2015). Model systems, including those describing fate and transport of nanomaterials, require validation by analytical data, but in this case there are limited measurements available. A wide variety of nanomaterials are present in natural systems, but only some are ENMs. The same systems contain an abundance of other particles of natural origin. Currently available analytical tools cannot distinguish between natural and engineered nanomaterials at the low ENM concentrations predicted in environmental matrices. Together, modeling and analytical studies can provide complementary views on nanomaterials. Estimates of the presence of ENMs in various

environmental bins can be obtained through modeling, while analytics can physically characterize ENMs in these systems with clues towards the total concentration of nanomaterial (Nowack et al. 2015).

3.0 RESEARCH FINDINGS

Currently, very few data points are available on concentrations of nanomaterials in wastewaters. Based on probabilistic material flow analysis, engineered nanomaterials are estimated to be present in sewage treatment plant effluent on the order of ng/L to µg/L (Gottschalk 2010). Environmental monitoring data for assessing release of nanomaterials from the various parts of the nanomaterial life cycle is unavailable due to the limitations of detection methods. For similar reasons, information on the occurrence of nanoparticles in natural and engineered systems is incomplete (Li et al. 2013).

As nanoparticles are materials that possess distinct physical, chemical, optical, and electronic properties compared to their counterparts at macroscale, they behave differently in wastewater treatment (Kurwadkar et al. 2014, Brar et al. 2010). The unique physical and chemical properties of nanoparticles are diverse and existing water and wastewater treatment plants were not originally designed to remove them. The removal efficiencies of nanoparticles by conventional wastewater treatment processes are not well quantified (Li et al 2013, Liu et al 2014).

The results of the WRRF study "Evaluation of Impact of Nanoparticle Pollutants on Water Reclamation" indicated significant differences in the fate and transport behavior of nanomaterials compared to their ionic and molecular forms in water reclamation processes. Many of these differences are due to the colloidal characteristics of nanoparticles. In an evaluation of treatment process performance, the study found nanomaterials to be more readily removed from wastewater and accumulated in biosolids than ionic salts. Media filters removed more nanomaterial than ionic constituents (Ganesh and Rosso 2013).

The most important processes that determine the fate and transport of nanomaterials are aggregation, deposition, and chemical and microbiological transformation (Li et al. 2013). Nanomaterials that are highly negatively charged, functionalized, or coated with macromolecules, giving them low affinity to other particles, are among the most difficult to remove in wastewater treatment (Li et al. 2013). The major pathways for nanoparticle removal are sedimentation of nanoparticle aggregates and adsorption onto coexisting particles, especially biomass. **The greater part of the removed nanomaterials will be associated with biomass** (Li et al. 2013). Most nanoparticles either aggregate or attach to larger particles during primary and secondary treatment. Microfiltration (MF) membranes can then achieve very high levels of nanoparticle removal by efficiently intercepting these aggregates and particles (Li et al. 2013). Due to the high efficiency of membrane filters in particle interception, membrane bioreactors (MBRs) are valuable for nanomaterial removal (Li et al. 2013).

Nanofiltration (NF) and reverse osmosis (RO) membranes are capable of intercepting almost all nanomaterials without any need for pretreatment (Li et al. 2013). Zhong et al. achieved a separation efficiency of 100% by using tubular ceramic membranes to remove nickel catalysts from slurry (2011). Springer et al. evaluated the feasibility of membrane ultrafiltration (UF) for the removal of SiO_2 particles with a mean hydrodynamic diameter of 78 nm (2013). Retention rates over 99.6% were achieved using a 10 kDa membrane, which is in the tight UF range (Springer 2013). Pickering investigated the use of membrane filtration to separate fullerene compounds from a process water (2013). Polyamide nanofiltration membranes (NF200, Dow-filmtec, Midlad, MI) were able to reject approximately 98% of fullerol, an effective photosensitizer nanomaterial, from an aqueous solution (2013). No membrane fouling was observed.

Ladner et al. performed a series of experiments to measure the retention of a class of functionalized nanoparticles (NPs) on porous (microfiltration and ultrafiltration) membranes (2011). The NPs studied consisted of silver, titanium dioxide, and gold; ranged from 2 to 10 nm in diameter; and had organic coatings to yield either positive or negative surface charge. Solutions of NPs were applied to microfiltration and ultrafiltration polymeric membranes of varying materials and pore sizes (ranging from ~2 nm to 0.2 μm). Negatively charged membranes achieved over 99% rejection of positively charged NPs despite pore diameters being up to 20 times the NP diameter. Thus, sorption caused rejection in this case. Membrane rejection of negatively charged NPs was not as high, but behavior was dependent on NP core material (Ag, TiO2, or Au) along with surface functionality. For the five UF membranes with molecular weight cut-offs (MWCOs) from 3 to 100 kDa, rejection of all NPs tested was between 90 and 100%, with the exception of Ag(−). The rejection of Ag(−) averaged 90% for 3-, 10-, and 30-kDa membranes, but dropped to 84% for the 50-kDa case and 60% for the 100-kDa case. The 50 kDa and 100 kDa cases approach the looser end of UF pore sizes. Ladner et al. drew the following conclusions about the interactions of this class of functionalized NPs with polymeric MF and UF membranes (2011):

1. "All of the functionalized NPs were well rejected by membranes with pores smaller than the NP size, but some were well removed by membranes with larger pores. This occurred when NP-membrane adsorption affinity was high, as in the case of positively charged NPs being electrostatically attracted to the negatively charged membranes."
2. "Even though NP-membrane adsorption affinity was similar for two NPs [TiO2(−) and Au(−)] their rejection behavior with MF membranes was quite different. This could be due to differences in the NP–NP self-adsorption affinity, or aggregation potential. Au(−) appeared to have a higher NP–NP self-adsorption affinity, resulting in capture of incoming NPs by already deposited NPs and thus increasing the overall removal."
3. "Five different polymeric membranes (polysulfone, polyethersulfone, cellulose acetate, polyvinylidenefluoride, and nylon) behaved very similarly in terms of rejection. The NP properties appeared to be more important for determining transport behavior than the membrane properties."

4."The behavior of these functionalized NPs can be described by four categories or scenarios: (a) membrane pores smaller than the membrane leading to complete NP retention, (b) pores larger than the NPs and NPs with low adsorption affinity leading to NP passage, (c) pores similar in size to the NPs and adsorption leading to pore blockage and NP retention, and (d) pores being large enough that even when adsorption occurs the pores remain open and NPs eventually break through. The four categories of interactions are not mutually exclusive."

As an aside, nanoparticles have been shown in two instances to impact treatment plant operational performance. Brar et al. found that the discharge of high levels of nanoparticles (seeded into the process, in this case) into wastewater may negatively impact treatment performance by inhibiting microorganisms and secondary treatment processes, fouling membranes, increasing turbidity, and decreasing disinfection efficiency (2010). Safarik and Phipps report that suspended particles in nanoscale size are able to enter membrane pores and lead to fouling during membrane-based water reclamation processes (2006).

4.0 SUMMARY AND RELEVANCE

The following key takeaways were obtained from this preliminary literature survey:

1. Nanomaterials are ubiquitous in the environment and it is currently difficult to distinguish those of natural origin from manufactured (or engineered) nanomaterials.
2. The fate and transport of nanomaterials are determined mainly by aggregation, followed by deposition or sorption to macro-sized particles.
3. Thus, most nanomaterials are effectively removed in processes that focus on particle removal. They will partition significantly into biosolids produced during wastewater treatment with the remainder effectively removed by microfiltration membranes.
4. Any remaining monodisperse nanomaterials are effectively removed by nanofiltration and reverse osmosis membranes.

As previously stated, the State of California Division of Drinking Water (DDW) in January 2016, the DDW defined their position on nanoparticles, which is that existing regulations are protective of public health and that there is no intent to regulate nanoparticles. With that said, DDW will continue to evaluate the issue.

5.0 REFERENCES

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