DUMPING NANOPARTICLES INTO A FJORD

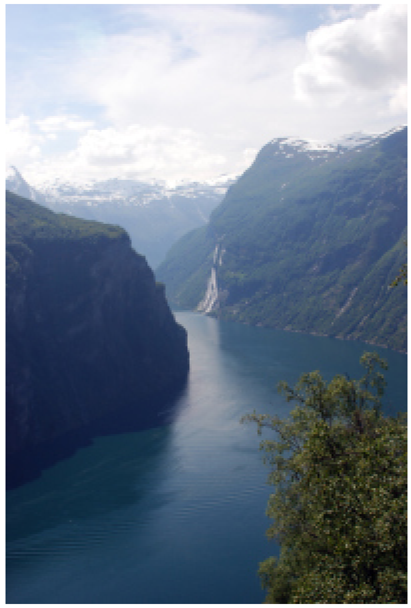
How to think about the potential environmental impacts

Let’s dive in to a real-world nanotechnology problem raised by one of our readers: should waste composed of nanoparticles, let’s call it “nanowaste”, be disposed of differently than regular waste? There are many types of nanowaste that we could discuss, but today we’ll focus specifically on nanoscale titanium dioxide, which Sam discussed in his recent post, generated as a by-product of mining.

Mining for phosphates. Image source.

Our journey into the world of nanoscale titanium dioxide starts in Southwestern Norway, at the Engebø mine. This not-yet-operational mine will extract rutile, the most common structural arrangement of titanium dioxide in nature, from a 2.5 kilometer swath of rock near Engebø Mountain. Extracted material will be sold to producers interested in making pigments and perhaps products that incorporate emerging titanium dioxide nanotechnologies. Most of it will not be nanoscale, but the waste material, also called “tailings”, will contain nanoscale titanium dioxide. Our interest, then, is in how the Engebø mine handles this nanowaste.

According to our interested reader, the mine plans to dump about 6 million metric tons of tailings annually into a nearby fjord (a common marine water body in Norway), 3000 of which will be nanoscale titanium dioxide.



This is a fjord. Image source.

These figures are in agreement with those presented in a 2009 project description presented by Nordic Mining, the company managing this project. Nordic Mining claims that because the tailings contain only naturally occurring materials, no harmful substances will be deposited into the fjord, but our reader raises a valid concern:

Can the disposal of tailings into a fjord be considered a nanoparticle pollution hazard for this marine ecosystem?

After all, we learned in Part I that nanoscale materials have unique properties that can pose unique hazards if they enter the environment. But does this apply to naturally occurring nanoscale materials as much as to those made in the lab? Since I have not been able to find any documented cases of environmental harm from this specific dumping practice, we are left with the much murkier practice of predicting the future. Fortunately, there are scientists doing research in this area that will help paint a better picture for us.

Our picture needs to address two big questions:

First, *what happens to nanoscale materials when they enter natural waters like those in a fjord?* Do they stick to each other and grow larger and larger or do they remain small? Do other things (like bits of soil) stick to them or do they remain clean? These are important questions to ask when trying to decide what forms of life these materials might affect.

Second, *what impact, if any, do these materials have on life in the fjord?* Are they ingested by plants and animals or is there no interaction? If they do interact, are they toxic?

As we proceed, let's recognize that, as with many complex questions, the answer to our reader's concern will not be absolute (i.e. it won't be **yes** or **no**). Instead, our answer will highlight pertinent information generated by scientists studying nanowaste and make conclusions based on this information.

After extraction from Engebø Mountain, nanoscale titanium dioxide should look something like this:

Titanium dioxide powder

But being dumped into a marine water body like a fjord will cause these nanoparticles to look much different. For one, the fjord is composed of seawater, and in this salty environment, the nanoparticles are likely to stick to each other and form larger clumps of nanoparticles. If the water were not salty, the nanoparticles, which have electrically charged surfaces, would be more likely to repel each other and remain separate. But seawater contains many electrically charged ions formed from dissolved salts, and these can interrupt, or "screen", charges that would normally cause neighboring particles to repel each other—in response, the nanoparticles clump together.

It would take only a very simple experiment to determine the extent of nanoparticle clumping: simply take a water sample from the fjord back to a lab, mix in some titanium dioxide nanoparticles, and monitor the particle size over time. If the fjord water is very salty, the particles will clump together a lot and become much larger (the clumps may even be 100 or 1000 times larger than the nanoparticles were originally). If the water is not very salty, the particles will not clump together as much, and may only grow to 2 or 3 times their original size over time. Clumping affects the environmental impact of nanoparticles because many of their unique and potentially hazardous properties are size-dependent: the more that nanoparticles clump together, the more likely they are to behave in commonplace ways that we better understand. The less the nanoparticles clump together, the more likely they are to behave in unique "nano" ways.

I mentioned above that titanium dioxide nanoparticles have electrically charged surfaces, a fact that warrants a bit more attention. Say you are sitting in the center of a nanoparticle that has entered a fjord—all you can see is the particle itself. But if you are on the surface of the nanoparticle, you can see beyond the particle to, in our case, water. The electrical charge that develops on the nanoparticle surface is dependent in part on a property of the water called pH. You may be familiar with pH; it tells you how acidic or basic water is. It also determines whether the molecular building blocks on the surface of the titanium dioxide nanoparticle are more or less negatively charged. So, going back to our experiment where we measure nanoparticle size in a sample from the fjord, the more basic the water, the more negatively charged our nanoparticles will be, and the more they will repel each other and resist clumping.

In addition to salt content and pH, there is at least one more property that we need to consider in order to understand what will happen to our titanium dioxide nanoparticle entering a fjord: the amount of natural organic matter in the water.

When I say natural organic matter, I'm simply referring to the mix of chemical compounds that result from natural degradation of plant, animal, and microbe material. Present in soil, sediment, and natural waters, it goes unnoticed by most of us. But in the context of nanoparticles entering aquatic ecosystems, natural organic matter should attract our attention because it can interact with nanoparticles and change how they behave.

For example, natural organic matter can stick to the surface of nanoscale titanium dioxide andmake the particles more negatively charged. As we discussed earlier, this makes the nanoparticles less prone to clumping. Not only this, but natural organic matter that sticks to the surface of nanoparticles creates a barrier that makes it harder for neighboring nanoparticles to bump into each other and form clumps. Due to these combined effects, natural organic matter can make nanoparticles resistant to clumping even when other factors, like salt concentration or pH, would promote this behavior. In essence, natural organic matter can make nanoparticles, like nanoscale titanium dioxide entering a fjord, retain their nano-size and perhaps their unique nano-properties.

Let’s recap what we’ve learned so far about nanoscale titanium dioxide that is dumped into a fjord. Three big factors compete for the nanoparticle’s “attention” when it enters a fjord: salt content, pH, and natural organic matter content. The best way to learn what will happen to the nanoparticles is to measure their size over time in a water sample taken from a fjord. But our knowledge also allows us to also predict what will happen to the nanoparticles if some parameter changes. For example, if the water becomes more basic due to a chemical spill or other contamination, we know that the particles are less likely to clump together and will act more like nanoscale titanium dioxide (having uniquely nano-properties) than macroscale titanium dioxide (having common properties).

Our second big question is perhaps a bit more exciting: what impact does nanoscale titanium dioxide have on life in a fjord? If you are thinking ahead, perhaps you are starting to devise an experiment like the one we proposed to address our first question: take a water sample from the fjord, add nanoparticles, and see what happens to the organisms living in that sample. Unfortunately, that experiment is much harder to perform than our previous one. One reason is that your small water sample will not be representative of all the life in the fjord. You will likely have microorganisms and perhaps small worms or insects in your water sample, but you are unlikely to have a fish or a seal. This means that you won’t learn about the effects of nanoparticles on all life in the fjord using this sampling approach. You will also have a hard time actually measuring what happens to the various life forms in your water sample, making it hard to learn anything very specific or concrete (which is what we always seek to do in science). A better approach is to choose just one organism, preferably one that is fundamental to the well-being of the fjord's ecosystem, and see how that organism alone is affected by nanoparticles.

Many researchers have already used this approach. One study that is particularly relevant to us observed the impact of nanoscale titanium dioxide on phytoplankton, very small but very important organisms found in natural waters all over the planet that use the sun's energy to supply aquatic food webs. While this study was not focused on Norwegian fjords in particular, all experiments were performed in seawater, making the results applicable to our situation. The researchers mixed a small amount of nanoscale titanium dioxide (part per million concentration, which falls within the predicted environmental concentration of titanium dioxide nanoparticles not including purposeful dumping) with phytoplankton in seawater and illuminated this mixture with a light that mimics natural sunlight striking the surface of the ocean. Under these conditions, the titanium dioxide nanoparticles clumped together due to the high salt concentration, but also produced a class of very reactive and toxic molecules called reactive oxygen species (see Sam's post for more detail). This resulted in slower phytoplankton growth in the presence of titanium dioxide nanoparticles than in their absence. Because reactive oxygen species are damaging to all types of cells, this result implies that nanoscale titanium dioxide can stress many different types of organisms in aquatic ecosystems, not just phytoplankton. This effect will be more pronounced as the concentration of nanoscale titanium dioxide in the water increases, meaning that greater environmental stress is expected if tailings dumped from the Engebø mining project exceed the low (parts per million) concentration used in this study.

The Engebø project plans to dispose of tailings at a depth of 300 meters below the water's surface, which will limit the amount of sunlight seen by these tailings and reduce their potential to produce reactive oxygen species. However, any tailings that move closer to the water's surface will be more likely to produce reactive oxygen species, increasing their potential to stress the fjord's ecosystem. I have been unable to find any information on the expected movement (or transport) of tailings in a fjord after dumping—this information is critical to determine if the dumping strategy employed by the Engebø project will effectively reduce the environmental risks associated with reactive oxygen species production by nanoscale titanium dioxide.

Now that we've learned about nanoparticle behavior in natural waters and interaction with aquatic life, let's think back to our original question: can the disposal of tailings into a fjord be considered a nanoparticle pollution hazard for this marine ecosystem? Given the large quantity of material in question (3000 metric tons annually), its potential to persist in nano-form, and its demonstrated stress on aquatic environments, nanoscale titanium dioxide tailings cannot be considered inherently safe simply because they are naturally occurring. This is not to say that the dumping practice of the Engebø mine is guaranteed to harm the aquatic ecosystem of a fjord, but simply that the potential for harm exists. Given this potential for harm, it is prudent to pursue alternate forms of disposal that do not involve direct entry of nanoscale material into aquatic ecosystems.

Source : http://sustainable-nano.com/2014/06/03/dumping-nanoparticles-into-a-fjord-how-to-think-about-the-potential-environmental-impacts/