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Out of Sight, but Not Out of Mind: a Look at Nanoparticles in the Marine Environment

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What is the chemical additive that protects our skin from the sun, and where does it go after a swim in the ocean?

J. Evan Ward and John J. Doyle

Out of **SIGHT,** *but* **NOT OUT OF MIND:** *A Look at Nanoparticles in the Marine Environment*



Mussels being exposed to nanoparticles in the feeding bioassay (J.J. Doyle).

FOR MANY PEOPLE, memories of summer evoke thoughts of sitting on the beach, reading a good book with your feet buried in the sand. A typical day in the sun usually requires a few applications of sunscreen to prevent burns, and is repeated after the occasional dip in the ocean to cool off. As splashing children dart in and out of the water, dutiful parents slather on several coats of sunscreen as it gets washed off time and again. Yet, how many of us ever stop

to think about how sunscreen works? What is the chemical additive that protects our skin from the sun, and where does it go after a swim in the ocean?

Manufacturers of some sunscreens and cosmetics routinely incorporate engineered nanoparticles into their products to protect our skin from the sun's potentially harmful UVA and UVB radiation. Some types of nail polish that delight fashionably chic girls and ladies also contain nanoparticles to make removal easier. In addition to cosmetics and sunscreen, nanoparticles are now

Examples of manufactured nanoparticles and their uses

Type of Nanomaterial	Uses
Cadmium Selenide (CdSe)	imaging, biosensor
Carbon nanotubes	composite materials
Cerium dioxide (CeO ₂)	ceramics, catalysts, mechanical and chemical polishing
Nano-silver (Ag)	socks and other clothing, washing machines, refrigerators, air conditioners (anti-microbial)
Titanium dioxide (TiO ₂)	sunscreens, skin care products, paints, whitener in toothpaste
Zinc oxide (ZnO)	paints, industrial coatings (anti-fungal)

included in a diverse range of consumer products such as medications, detergents, paint, electronics and anti-microbial clothing such as socks. The economic worth of products containing nanomaterials is estimated at \$1 trillion dollars. Naturally, one may wonder: what are nanoparticles, and why have they become so sought after in commercial and industrial applications?

Nanoparticles are extremely small fragments of matter having at least one dimension less than 100 nanometers (1 nanometer = one-billionth of a meter). For comparison, one typical hair from a human head or a single sheet of paper has a thickness of approximately 100,000 nanometers. These tiny particles are smaller than the

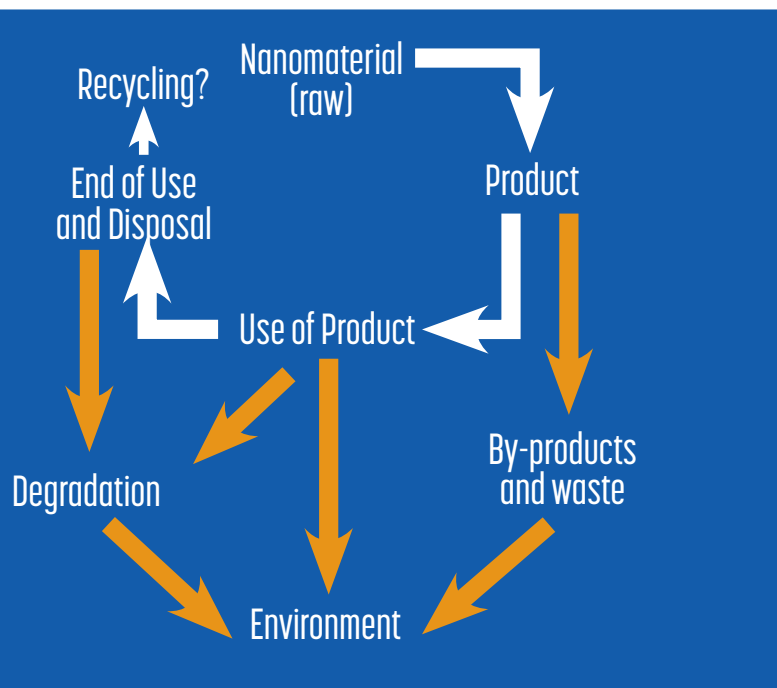
cells of a human body and, in fact, even smaller than the nucleus inside of those cells. Many chemical compounds can be utilized to produce nanoparticles; however, the most common varieties are made from metals (titanium, zinc, iron, gold, silver, and copper), and certain nonmetals (carbon and silicon). Nanoparticles have several unique attributes such as their size and surface chemistry that affect novel thermal, electrical, mechanical, and imaging characteristics which are highly sought-after in the medical, cosmetic, and electronics industries.

The unique properties of engineered nanoparticles which are sought after by manufacturers of consumer products might also pose problems for plants and animals

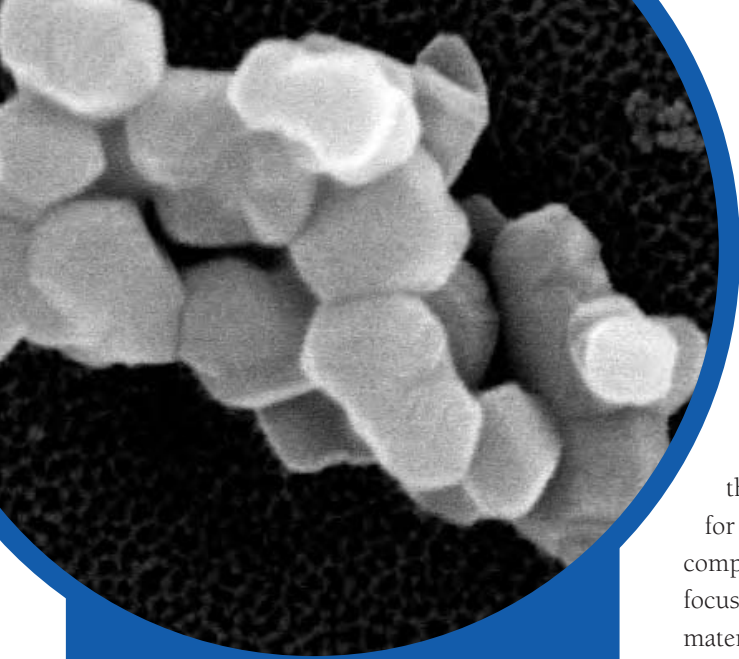
in the environment. Most research on the toxicity of nanoparticles has focused on mammals, and various effects have been reported and debated. Several types of nanoparticles have been shown to have toxic effects on cells in test tubes, including mitochondrial damage and cell death. Even particles made of low-toxicity material (e.g., polystyrene) can be harmful when delivered in their nano form, presumably due to their high surface area. Surface chemistry, physiochemical properties, and reactivity of nanoparticles, as well as environmental factors, can affect interactions with vertebrate cells and tissues. Consequently, particulate material from nanotechnology has come under scrutiny as a potential problematic pollutant, and the need for regulation is now being debated.

With an ever-increasing presence in household goods, it is almost certain that nanoparticles are being released into the

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Production flow chart for products that contain nanomaterials (white arrows) and potential pathways by which these materials can enter the environment (gold arrows).



Individual crystals of titanium dioxide. Crystals are stacked on top of each other and have a width of about 100 nm. Micrograph taken using a scanning electron microscope (J.E. Ward & V. Palumbo).

ABOUT THE AUTHORS

Evan Ward is an experimental biologist at the University of Connecticut's Department of Marine Sciences. He studies the dynamic interactions between marine animals and their environment, particularly bottom-dwelling invertebrates.

John Doyle is a PhD. candidate who is working with Evan. He has also studied forensic science.

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environment via direct use or through more indirect routes such as leaching from septic tanks and landfills, or outflow from wastewater treatment facilities. Despite the overwhelming demand for nanoscale technologies, comparatively little research has focused on the effects of these materials on marine ecosystems, and there is growing concern that nanoparticles could pose a potential ecotoxicological hazard to aquatic organisms.

Coastal ecosystems near densely populated, industrialized regions are particularly vulnerable to the infiltration of man-made materials such as nanoparticles. Of course the quantity of nanoparticles released into the environment depends on a number of factors including proximity to a source, and the physical and chemical characteristics of the soil and water in which they are released. Currently, there are no tests to detect nanoparticles in

natural waters, mainly due to their minute size, and the overwhelming volume of water in which they are diluted upon entering coastal environments. However, recent improvements in the sensitivities of analytical equipment have allowed environmental researchers to identify the presence of ever-smaller concentrations of pollutants such as antibiotics, flame retardants, and heavy metals. These technological improvements are helping researchers understand the fate, transport and environmental loads of these contaminants, and someday may allow scientists to detect engineered nanoparticles in the environment.

Organisms that are plentiful in coastal waters, have a sedentary lifestyle, and feed on material suspended in the water, such as bivalve shellfish, may be particularly susceptible to released nanoparticles. Bivalves such as clams, oysters, and mussels, filter large quantities of water in their quest to capture and ingest



John Doyle (left) and Professor Evan Ward (right) . Photo by: Peg Van Patten.

food particles. They play a critical role in cycling nutrients between the sediments and overlying water column, and thus have a profound influence on local water quality. These characteristics make bivalves ideal “canary-in-the-coal-mine” species, and an important group of organisms to study with respect to potential negative impacts of engineered nanoparticles.

With funding provided by the Connecticut Sea Grant program, the Center for Environmental Sciences and Engineering (CESE, UConn), and Connecticut’s Interdisciplinary Research and Training Initiative on Coastal Ecosystems and Human Health, we (authors Professor Ward and graduate student John Doyle) are conducting research at the University of Connecticut’s Avery Point campus on the effects of nanoparticles on bivalves.

With our collaborators, Professor Robert Mason and and Bryan Huey, we are focusing on two commercially relevant species that are common in near-shore waters: the eastern oyster (*Crassostrea virginica*), and the blue mussel (*Mytilus edulis*). The eastern oyster lives on or partially in the sediments and feeds at the water-sediment interface, a region likely to be impacted by nanoparticles that accumulate on the bottom. On the other hand, the blue



mussel prefers to live attached to hard substrates such as rocks and pilings, and is more likely to contact nanoparticles suspended in the water column. Bivalves are some of the most abundant molluscs along the eastern seaboard of the United States, making them among the most likely species to be consumed by humans.

To date, our laboratory research has shown that oysters and mussels can take up titanium nanoparticles by capturing large agglomerations of this material that form in the water,



Bivalves are important members of aquatic environments, so determining the impacts of nanoparticles on this group of animals is important for a full understanding of how these engineered particles might affect near-shore communities. Additionally, if nanoparticles accumulate in bivalve tissues, they may be transferred to higher trophic level organisms including humans.

or by capturing natural particles that have nanoparticles adhering to them. In short-term exposures (2 hrs) the bivalves accumulate significant quantities of titanium nanoparticles, but eliminate the particles in feces over a 6 to 12 hour period. In test tubes, exposure of the “blood” cells of these two bivalves to titanium nanoparticles for two hours causes damage to the DNA. Future studies will examine different types of nanoparticles and longer term exposure (days) to determine if the bivalves accumulate the particles in their tissues for longer periods of time.

Bivalves are important members of aquatic environments, so determining the impacts of nanoparticles on this

group of animals is important for a full understanding of how these engineered particles might affect near-shore communities. For example, deleterious effects on bivalves would compromise their capacity for benthic-pelagic coupling and, in turn, greatly impact the surrounding

environment. Additionally, if nanoparticles accumulate in bivalve tissues, they may be transferred to higher trophic level organisms including humans.

The promise of nanomaterials for science, technology and the economy is great, but their ecotoxicological effects on aquatic organisms and pathological risks to humans may be equally large. Our research results will inform the debate regarding the potential impact of nanoparticles on the environment.

As a result, we can expect more safely engineered nanoparticles in the future, when we slather on the sunscreen.