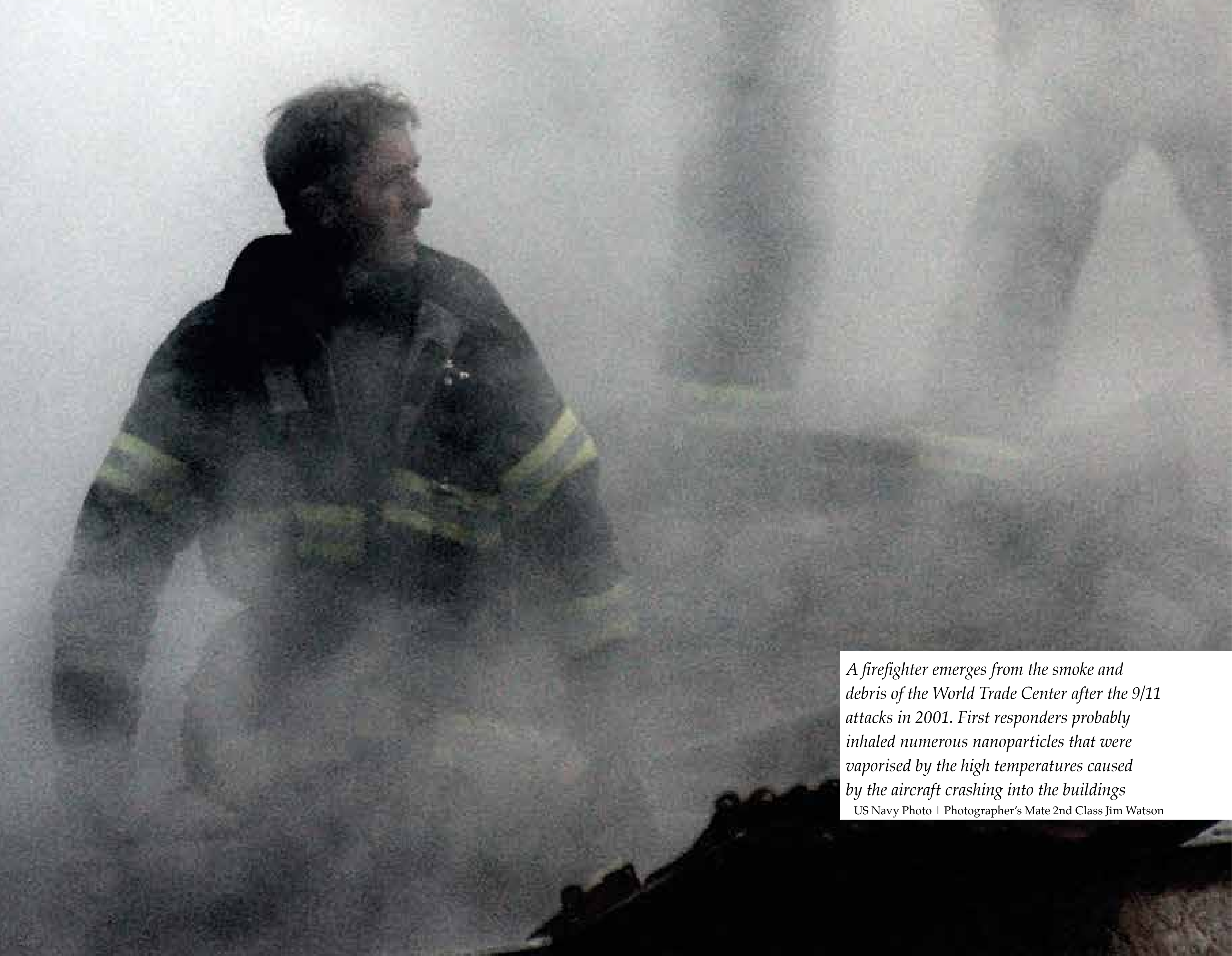
Fighting the nanoparticle war

Nanotechnology is of immense value in a wide variety of applications, but nanoparticles can also be toxic for humans, especially first responders. Here, our authors examine the issue and explain how early detection can protect people working in hazardous environments



A firefighter emerges from the smoke and debris of the World Trade Center after the 9/11 attacks in 2001. First responders probably inhaled numerous nanoparticles that were vaporised by the high temperatures caused by the aircraft crashing into the buildings

US Navy Photo | Photographer's Mate 2nd Class Jim Watson

Nanoparticles have been used for hundreds of years, dating as far back as the 17th century with the forging of Damascus steel swords. The application of nanoparticles is vast and variable, spanning a wide range of theoretical and practical employment, and nanotechnology has become a rapidly growing field this century.

Nanoparticles have unique properties that allow technology to manipulate and incorporate these microscopic particles, making them useful in disciplines such as medicine, consumer products, bioengineering, chemical, material and energy production, defence and warfare – along with many more that have yet to be explored.

While nanoparticles can be used for a multitude of influential effects, they can sometimes inherit toxic properties, which could lead to unintentional – or even intentional – harm.

In warfare especially, it is common for lingering nanotoxic particle exposure to cause many avoidable illnesses. While there are currently no drugs to destroy nanotoxic particles once they enter a person's bloodstream, technology does exist to detect and recognise nanoparticles within the environment, and to identify the potential hazards they may cause.

A nanoparticle is an ultrafine particle with lengths of two or three dimensions greater than one nanometre (one billionth of a metre) but smaller than 100 nanometres. While these particles are extremely small in size, they posses a large surface area per unit volume. As the size of the nanoparticle decreases, the surface area increases greatly, making them suitable for integration, manipulation and/or reaction with the proximate environment. Properties that these particles can take on that affect their physical, chemical and biological behaviours include, but are not limited to: Diffusion; electrical; magnetic; mechanical; optical; and solubility.

Nanoparticles are remarkable for many reasons, one of these being the wide range of compounds they can be composed of. While carbon and metal materials are the most frequently used, metal oxides, lipids, nucleic acids, proteins and polymers are also commonly found in nanotechnology products.

Nanoparticles are also unique architecturally as they can take a vast array of complex forms that alter their function. Nanoparticles can exist as aggregation – particles held together by strong forces – or agglomerations, which is when particles are held together by weaker forces, such as van der Waals or electrostatic forces.

Other structures include, but are not limited to: Coatings; dendrimers; fullerenes liposomes, nanoshells, nanofibres, nanospheres, nanocrystals, nanogels, nanotubes, quantum dots and rods, or polymeric micelles.

As with all technology, risks and dangers exist with the use of nanoparticles. While they can be utilised within a large variety of disciplines, bringing significantly beneficial outcomes for oncology treatments or wound care, they can also be hazardous owing to their toxicity. For over two decades, nanotoxicology research has shown the complexity of interactions among nanomaterials within cells, humans and the environment. Since nanoparticles have such unique properties, like high surface to volume ratios, they are highly reactive and catalytic, causing them to be potentially toxic. According to the National Institute for Occupational Safety and Health (NIOSH), research has proven over the past 20 years that: Small particles, on an equal mass basis, can be more hazardous than larger ones; some incidental nanoparticles (for example, from welding and diesel fumes) can be carcinogenic when inhaled; small and aerosol pollutants have been linked to respiratory and cardiovascular health effects; and certain 'legacy produced' nanomaterials, such as ultrafine titanium dioxide, carbon, black, and fumed silica, are respiratory hazards.

After primary exposure through dermal, inhalation or oral contact, nanoparticles can have detrimental effects on cells, tissues or even organs. Nanoparticles are so tiny that they can easily pass through cell membranes as well as other tight junction, biological barriers such as the epithelial layer of the skin. This allows nanomaterials to be taken up into living organisms easily, leading to the potential for cell dysfunction and destruction.

In a 2009 report from China, it was proven that workplace exposure to polyacrylic ester nanoparticles has caused both pulmonary inflammation and pulmonary fibrosis. Various other studies have associated nanotoxicity with human mortality, causing cardiovascular, pulmonary, neurological and neurocardiac injury.

Oxidative stress

Owing to the gross diversity of nanomaterial make-up, structures and functions, the specifics of their toxicity are not completely understood, although various studies have been performed to identify what makes them so dangerous. While shape and conformation are important, biological assay profiles, cell proliferation, activation of pro-inflammatory signalling, gene expression, and tissue localisation have all been taken into account when evaluating their risk.

One major mechanism of nanotoxicity is the production of the reactive oxygen species (ROS), which typically are highly reactive and have an extremely short half-life, therefore making it a challenge to isolate them for structural evaluation. Overproduction of ROS can lead to oxidative stress, which causes cells to lose their ability to maintain normal physiological redox-regulated functions. Ultimately, this leads to DNA degradation, unregulated cell signalling, change in cell motility, cytotoxicity, apoptosis and cancer initiation.

Nanotoxicology research has shown the complexity of interactions among nanomaterials within cells, humans and the environment

The rapid exponential growth and utilisation of nanotechnology, as well as the high risk of nanotoxicity, escalate the importance of taking precautions when dealing with these highly reactive species. The Environmental, Health and Safety (EHS) department in the US has established a list of factors to consider when assessing the risk of nanotechnology, such as nanomaterial synthesis and use, nanomaterial lifecycle stages, and environmental concentrations. Safety when dealing with nanoparticles has been further assessed by the CDC's National Institute for Occupational Safety and Health, which, in recent years, has been primarily focused on nanotechnology safety for the general population, as well as in the workplace.

Risk is an equation that consists of hazard multiplied by exposure time, so minimising exposure is therefore the key to reducing the risk of nanotoxicity. Effective risk management identified by NIOSH includes identifying potential safety and health hazards, characterising the opportunities for human or environmental exposure and designing a plan to control potential exposure. In 2007, NIOSH created a national initiative called prevention through design (PtD), ▶

▶ which includes identification of hazards, methods, operations, processes, equipment, tools, products, materials, new technologies and the organisation of work. PtD facilitates strategy development to reduce or eliminate risk exposures that can be applied throughout all stages of the lifecycle of an engineered nanomaterial.

While many procedures have been taken into effect to mitigate exposure to nanotoxic particles, it certainly does not eliminate their negative effects, especially in a war environment. After the Gulf War between the years 1990-1991, soldiers came home with atypical post-war symptoms; they were returning with cancer. Most of these cancers were leukaemia and lymphomas, among others. However, many of these disorders were initially dismissed as not having any correlation to the war environment.

In the early 2000s however, it was found that high-potential bombs such as depleted uranium or tungsten – which explode at extremely high temperatures – generally solidify as hollow nanoparticles, which have potentially nanotoxic properties. This discovery was made by a team of researchers, which placed passive sensors to collect dust particles from the core of an explosion outside an Iraqi war field. Numerous nano and microparticles were gathered, with a variety of chemical compositions, some of which proved to be nanotoxic.

It is easy to see how direct exposure to nanotoxic particles could have a significantly negative impact on soldiers on the frontline. But soldiers leave the theatre of war once a conflict is over, whereas civilians can be exposed to these pollutants for an infinite amount of time.

Numerous tissue samples and other biological materials were collected and evaluated from soldiers when they returned from war zones. Tissue samples indicated a variety of particles, ranging in size from 15 microns to 0.1 microns, with structures that were typically spherules; this indicated they had originated from high temperatures and their chemistry had a wide range of elements. Many of these samples were contaminated by inorganic, biopersistant micro and nanosized particulate matter, which explains the cancerous effects on the soldiers.

In order to examine the ill effects of nanotoxic particles resulting from a war-like environment, research teams have been studying both rescue workers and civilians affected by the collapse of the World Trade Centers (WTC) in New York for the past decade. While the towers' collapse on September 11, 2001, was not primarily a result of an explosive, the impact of the aircraft into the massive buildings caused temperatures high enough to vaporise a plethora of nanoparticles. The wind then carried these vaporised particles from what is now Ground Zero, across the whole of New York City and, it is suspected, even further beyond the city's borders. Nanoparticles were discovered in air conditioners, as well as coating pipelines.

Mitigating exposure

There were many immediate symptoms experienced by first responders who probably inhaled these nanoparticles. Symptoms included persistent coughing, nasal irritation, shortness of breath, throat irritation, wheezing and asthma, as well as headaches.

These acute symptoms for many victims of nanoparticle exposure were precursors to more chronic and/or serious illnesses in the future. Mount Sinai Hospital's World Trade Center Health Program reported in 2014 that more than 2,500 rescuers and first responders had been diagnosed with cancer, a significant increase from the 1,140 cases reported in 2013.

Currently, no drugs or technologies are available to destroy these non-biodegradable, inorganic particles embedded in tissues.

A large explosion of more than 1,500 pounds of confiscated mortar rounds, grenades, guns and other explosive devices set up by Army explosive ordnance disposal technicians on Contingency Operating Base Q-West, Iraq

US Army | Spc. Eric A. Rutherford

A UH-60 Black Hawk helicopter stirs up dust from a burnt field while approaching to land to pick up US Army Soldiers as coalition forces conducted raids on anti-Iraqi forces near the city of Samarra, Iraq. Direct exposure to nanotoxic particles could have a significantly negative impact on first responders in civilian situations, as well as soldiers in combat

US Army | Sgt. Armando Monroig

Certain technologies, however, do exist to mitigate exposure by immediately detecting and identifying nanoparticles within the environment. One example is the new Rapid Area Sensitive Sight and Reconnaissance (RASSR) robot. This robot is controlled by a remote and a laptop and it is designed to identify current conditions without unnecessarily exposing humans to any dangers that may be present. The RASSR robot has an extending claw, which picks up debris and gathers samples while, at the same time, using a camera to give a 360-degree view of the environment. RASSR is also fitted with a laser to identify the chemical compounds of unknown substances.

The US military is currently using this technology to drill its personnel in managing nanotoxicity exposure. Marines and sailors from the Assessment and Consequence Management team underwent environmental training at the Marine Corps Air Station at Kaneohe Bay, Hawaii on May 13, 2014. By practising nanotoxic particle exposure and response drills, according to the 3rd MarDiv CBRN Chief and ACM team incident commander, Staff Sgt Jesse Bramer, military personnel can: "Discover our own shortfalls so we can fix it and not let it happen in the future." The RASSR robot may prove to be a critical adjunct for soldiers during war to assist in abating nanotoxic exposure to personnel in the field.

Although it has a significant effect on how first responders protect themselves within certain environments that they must work within, the robot does not eradicate nanotoxic particles.

Many first responders at Ground Zero reported that they did not wear respirators and consumed exposed food on site without proper precautions, thus allowing inhalation and indigestion of fine dust particles that contained a high quantity of organic nanoparticles, with a high risk of nanotoxicity. As a result, many of these first responders working at the scene of the collapsed towers developed serious illnesses, which began as an uncontrollable persistent cough in addition to chronic fatigue.

Again, while RASSR does not eliminate the dangers of nanotoxic particles, especially to the permanent residents of these areas, this type of early detection robot is an excellent way of working on particulate identification and limitation/elimination strategy development for nanotoxic particle risk management.

With early detection by the RASSR robot, first responders can take proper precautions such as wearing respirators and not consuming contaminated food; as well as warning bystanders of the potential dangers by identifying airborne particulate matter.

The RASSR robot is a modest start towards mitigation, minimisation and defence against nanotoxic warfare, until future advancements in technology and drugs are developed that will, conceivably, annihilate nontoxic particles. CRJ

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The Rapid Area Sensitive Sight and Reconnaissance robot examines an aircraft leaking chemical agents in the environment during a Chemical, Biological, Radiological and Nuclear training exercise at Westfield, May 13, 2014

US Marine Corps | Lance Cpl. Matthew Bragg

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