

## **Control of Water Terrorism Agents**

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### **Introduction**

With the ongoing war on terrorism comes a heightened sense of concern and anxiety about the threat of water terrorism. While the threat is a real concern, incidents of intentional contamination of a water supply with the intent to harm or kill people are extremely rare.

On the other hand, news of illness and even deaths caused by water contaminated by natural or man made pollutants is common. There are many news accounts of sickness resulting from water supplies contaminated by E. coli bacteria or other pathogenic microorganisms. In 1993, more than 400,000 Milwaukee residents became seriously sick from Cryptosporidium cysts in the municipal drinking water and many deaths were reported. High incidents of cancer and other health problems have been reported from drinking contaminated well water in or near toxic waste dump sites. Outbreaks of typhoid, dysentery and other water borne diseases were common before the introduction of chlorination for disinfection of water supplies. Now, there is strong evidence that even the practice of chlorination is resulting in the formation of carcinogenic byproducts such as trihalomethanes.

The EPA citing such factors as large water dilution ratios, the barrier of water treatment facilities, and stepped-up security measures has stated that it would be very difficult for terrorists to introduce the quantities of contaminants necessary to contaminate an entire water system. In fact, it seems more likely that terrorists would choose to destroy critical water infrastructure such as pump stations, storage facilities, or treatment plants to disrupt supply. Such actions could have a catastrophic effect on the economy in critical areas.

However, there are historical examples of water based terrorism that indicate the vulnerability of water to chemical and biological attack. For example, the Japanese used anthrax as a weapon to contaminate water and food supplies during World War II.

A search on the internet and a minimal amount of money is all that is necessary to build a simple biological fermentation facility capable of producing trillions of deadly bacteria. While most biological warfare agents are more effective when dispersed as aerosols, they can also be deadly in a water supply. Potential biological warfare agents include a number of bacteria, viruses, biological toxins, and cysts.

In fact, there are many sources of cheap and deadly organic and inorganic chemicals on the worldwide market that could be used to poison water supplies. Tanker trucks containing industrial wastes, fertilizers, and chemicals drive on our highways every day providing an easy target for terrorists seeking a supply of deadly chemicals. An abandoned factory or warehouse with a water hydrant or water connection provides a convenient point of entry for such chemicals to be pumped into a water distribution system.

There are some naturally occurring radioactive elements such as radium and uranium that can be found in water. These are primarily found in ground water supplies and are generally present in low concentrations. Contamination of a water supply with man-made radioactive matter would more likely occur from the fallout of the detonation of a nuclear device such as a strategically placed nuclear dirty bomb.

Drinking water standards for the U.S. are established by the Environmental Protection Agency (EPA) under the authority of the Safe Drinking Water Act. The National Primary Drinking Water Regulations are established for contaminants that can adversely affect public health and are known or anticipated to occur in public water supplies. Obviously not all of the agents available to water terrorists will be found in the EPA regulations, but many of these listed contaminants are highly toxic agents that could be used by water terrorists. Go to the EPA web site to find the current maximum contaminant levels (MCLs) for the listed contaminants. ([www.epa.gov/safewater/mcl.html](http://www.epa.gov/safewater/mcl.html))

## **Biological Agents**

A study conducted by the U.S. Army Center for Health Promotion and Preventive Medicine assessed the state of knowledge of biological warfare agents as potable water threats. A number of bacteria, viruses, and biotoxins were assessed in the study. Some of the potential agents that could be used for water terrorism are discussed in the following paragraphs.

### *Anthrax*

Anthrax is a spore forming bacteria, *Bacillus anthracis*, with an incubation period of about 2-7 days. It is a highly infectious disease in hooved animals and can be transmitted to humans. In humans, the disease can take three different forms: cutaneous (most common), pulmonary, and gastrointestinal (from eating contaminated food or water). Manifestations of the disease include severe abdominal pain, fever, vomiting, bloody diarrhea, and shock. Estimates of the infective dosage range from 8,000 to 50,000 spores.

Anthrax spores are very stable with an estimated life of 2 years in pond water and about 40 years in soil. Spores are highly chlorine resistant, but the vegetative form is effectively killed by chlorine disinfection at 5 ppm of free available chlorine and 20 minutes contact time.

The report indicates that Anthrax spores are effectively removed from water by filtration with pore sizes less than 1.0 micron. RO systems, with even smaller pore sizes, are more effective.

### *Tularemia*

Tularemia is a disease caused by the bacillus *Francisella tularensis*. It is more common in small animals such as rodents, but it is transmissible to humans, and there have been some outbreaks of the disease in Europe traceable to contaminated drinking water. It has also been weaponized as an aerosol.

Typhoidal tularemia is the form of the disease associated with direct ingestion of the bacteria. The disease produces flu like symptoms and can result in death if untreated.

The bacteria can survive and grow in water and mud for months and seems to be resistant to cold and freezing temperatures. There is conflicting information in the literature about the survivability of the bacteria at disinfection dosages of chlorine (0.5 to 2.0 ppm chlorine). The bacteria can be removed from water by filtration with 0.1 to 0.2 micron filtration or by RO.

### *Enteric Viruses*

Enteric viruses such as enterovirus 17 and human rotavirus cause severe gastrointestinal disorders and even death in immune stressed people especially infants and elderly people. The incubation period for human rotavirus is about 19 to 24 hours. At least one strain of human rotavirus is reported to survive as long as 64 days in water; however, it is reported that normal disinfection practices with chlorine should effectively inactivate the virus. Also, reports indicate that RO is capable of 99.99 percent removal of rotavirus.

### *Anatoxin A*

Anatoxin A is a neurotoxin produced by the filamentous freshwater cyanobacteria *Anabaena flos-aquae*. Animals poisoned by the toxin have been observed to suffer severe convulsions and death in a matter of minutes to hours. Disinfection dosages of chlorine are ineffective on the toxin, but it does gradually convert to a nontoxic form in water in a matter of several days. Typical water treatment methods including alum flocculation, filtration, and chlorination are ineffective in removing the toxin, but RO effectively removes the toxin.

### *Botulinum Toxin*

Botulinum toxins are lethal neurotoxins derived from the proteins produced by the bacteria *Clostridium botulinum*. The toxin has been weaponized by Iraq and others as an aerosol; however, it is more toxic when ingested than inhaled. The lethal oral dose (LD<sub>50</sub>) is estimated at about 0.006 micrograms per kilogram. Symptoms occur within 24 to 36 hours and include progressive paralysis followed by death from the inability to breathe.

Normal chlorination disinfection practice will likely inactivate most of the toxin. One study showed 84 percent inactivation at 0.4 ppm free available chlorine in 20 minutes contact time. Another study using RO treatment reported greater than 99.988 percent rejection by the RO membrane. Also, activated carbon has been shown to be effective in removing the toxin.

### *Ricin*

Ricin is a waste product from the production of castor oil. It is relatively easy to obtain, but it is not considered a credible water terrorism agent because it is less toxic by oral ingestion. Ingestion can cause gastrointestinal hemorrhage, and tissue and organ necrosis. It is considered a potential aerosol threat (used by Iraq), but it is most lethal when injected.

Normal water treatment practice including coagulation, flocculation, filtration, and disinfection with chlorine is not effective. Activated carbon appears to be effective, and one study shows that RO membranes reject greater than 99.8 percent.

## **Radionuclides**

Some elements are known to exhibit natural radioactivity, and most of these elements have relatively high atomic weights. Radioactivity is the nuclear decay or transformation of an element and is characterized by the emission of energy in the form of alpha particles, beta particles, and gamma rays. The parent substance in the radium decay series is uranium-238 which ultimately decays to stable lead-206. The radioactivity of a nuclide is characterized by the nature of the radiation, energy, and half-life. For example, radium-226 undergoes decay to radon-222 by the emission of alpha particles; the half-life is 1,620 years.

Alpha particles are positively charged ions (+2) of helium with an atomic weight of 4. They do not travel much more than 10 cm in air and can be stopped by a sheet of paper. Beta particles are electrons, negatively charged, which travel at high velocity up to several hundred feet in air; they can be stopped by a thin sheet of aluminum. Gamma rays are electromagnetic radiation with a very short

wavelength, very high energy, and extreme penetrating power. The unit of gamma radiation is the *photon*. Gamma rays are stopped by several inches of lead or several feet of concrete.

The official unit of radioactivity is the *curie* (Ci) which is defined as the quantity of radioactive material with  $3.7 \times 10^{10}$  disintegrations per second; this is nearly equivalent to one gram of radium. This is such a large number that microcurie ( $10^{-6}$  curie) and picocurie ( $10^{-12}$  curie) are more commonly used units. The EPA MCL for alpha emitters is 5 pCi/l for radium-226 and radium-228, and 15 pCi/l for gross alpha activity.

The unit for radiation dose equivalent is the *rem*. The *rem* is defined as the amount of ionizing radiation that produces the same biological damage in man as that resulting from the absorption of one *rad* of gamma radiation. A *rad* (radiation absorbed dose) is the dose of ionizing radiation that results in the absorption of 100 ergs of energy per gram of absorbing material.

Radium is a naturally occurring element that can leach from radium-bearing rock strata primarily into ground water. Studies on the water supplies of municipalities that use surface water show average radium-226 concentrations of less than 0.3 pCi/l (ranging from 0.002 to 3.7 pCi/l). Studies on ground water supplies in areas with radium-bearing deposits show radium-226 concentrations in the range of about 0.5 to 50 pCi/l.

Soluble radium exists as a divalent cation in solution. Studies show that conventional water treatment practice consisting of coagulation, flocculation, settling, and filtration does not effectively remove radium. Efficiently operating ion exchange softeners can remove greater than 95 percent of the feed water radium concentrations. Softeners continue to remove radium even after hardness breakthrough; therefore, regeneration practice to provide consistent hardness removal assures good radium removal. Well operated RO systems can remove greater than 95 percent of the feed water radium, and mixed-bed demineralization can provide greater than 99.5 percent removal of radium.

The EPA anticipates that the MCLs established for radionuclides will not be exceeded in most cases; however, in cases of non-compliance, application of a treatment technique to meet compliance would be required. The EPA has identified the best available treatment (BAT) to achieve compliance. Ion exchange, RO, and lime softening are recommended for removal of combined radium-226 and radium-228. Ion exchange and RO are recommended for control of beta particles and photon radioactivity. RO is recommended for control of gross alpha particle activity.

## **Water Treatment Technologies**

### *Activated Carbon*

Granular activated carbon is recognized as the best available technology for removing a broad spectrum of dissolved organic contaminants in water. It has been used successfully for years in ground water remediation practice to remove organic contaminants in ground water from gasoline spills or leaking underground storage tanks.

Activated carbon removes dissolved organic compounds by a process of adsorption. Adsorption is a physical rather than chemical process. It is a surface phenomenon whereby dissolved organic molecules in the liquid phase (water) adhere to and concentrate on the surface of the solid phase (carbon). Adsorption is caused by weak electrostatic charges known as van der Waals' forces.

Granular activated carbon with a highly porous structure and total surface area of about 1000 square meters per gram is a very effective adsorbent. The porous structure of activated carbon is extremely complex and consists of a massive network of micro and macro pores. Small organic molecules are better adsorbed in the small micro pores, and the larger molecules are adsorbed in the larger macro pores. Activated carbon with a good distribution of pore sizes provides for the adsorption of a broad spectrum of dissolved organics in water.

Activated carbons are made from a variety of materials including hard wood, coconut shells, coal, etc. In the manufacturing process, the raw material is dehydrated and carbonized by slowly heating at a high temperature in the absence of air. The carbonized intermediate product is then treated with an activating agent such as steam or carbon dioxide. The activation process burns off any remaining ash or tar and enlarges the porous structure. The activated carbon is then pulverized and classified.

Factors that influence adsorption include the physical characteristics of the carbon, temperature, pH, characteristics of the organic compounds, and the design of the contacting system. Physical characteristics of the carbon that influence adsorption include particle size, pore size distribution, and the total surface area. As the particle size of the carbon granule decreases, the adsorption rate increases. Pore size distribution influences the size of the organic molecules that are adsorbed. Adsorption capacity is proportional to the surface area.

Organic molecules vary in their adsorbability. The greater the solubility of the compound in water, the more difficult it is to adsorb the organic. For example, methanol is very soluble and has negligible loading on activated carbon. More volatile compounds tend to be more adsorbable. The more neutral forms of organic acids and bases may be very adsorbable in contrast to the more ionic form that may be weakly adsorbed; slight changes in pH may affect adsorbability. The contact time in the carbon bed is an important consideration. Generally,

longer contact times in the carbon bed result in more efficient adsorption. Adsorption is also competitive with the more strongly adsorbed compounds pushing the weakly adsorbed compounds down the carbon bed.

Activated carbon has a high capacity for the removal chlorine and chloramines. Removal of chlorine is accomplished by a process of catalytic reduction.

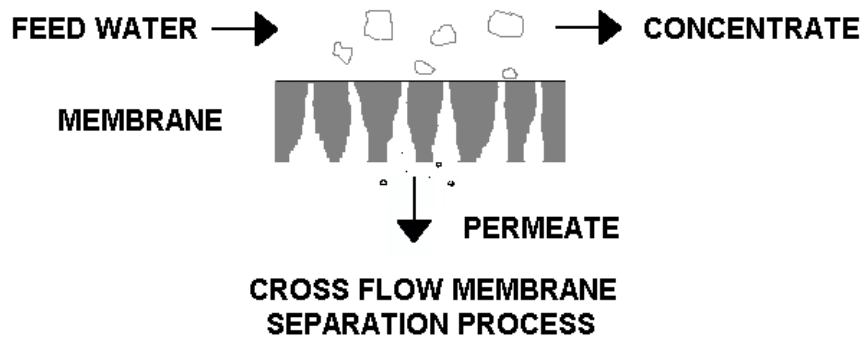
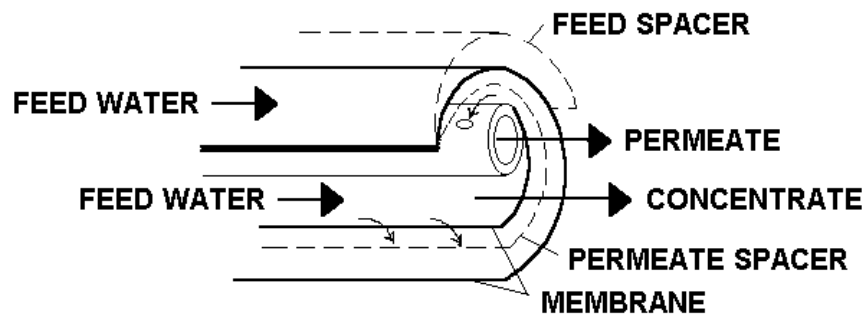
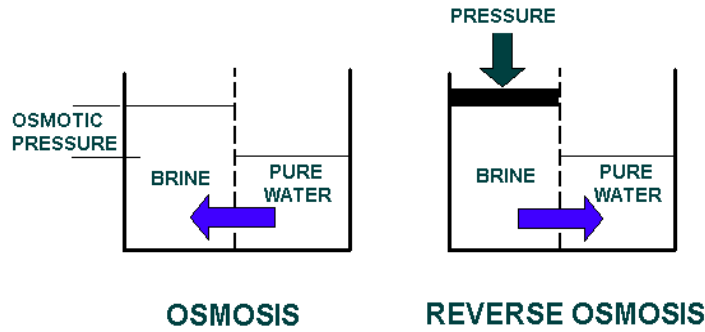
Activated carbon is recognized as the best available technology for the control and removal of the broad spectrum of potentially toxic organic compounds that could be introduced to a water supply either accidentally or intentionally. Granular activated carbon cartridges are available in a variety of styles and configurations that are relatively easy to install and service. They are relatively inexpensive, improve the taste of drinking water, and provide a degree of protection from potentially toxic substances in the water.

### *Reverse Osmosis*

Natural *osmosis* is the passage of water molecules through a semi-permeable membrane into a solution (brine). The membrane is permeable to the water but not to the solutes in solution. Water molecules permeate the membrane in both directions, but more molecules flow to the brine side of the membrane in an effort to establish equilibrium conditions at the membrane. Water continues to flow to the brine solution until the increase in the height of the brine solution equals the *osmotic pressure* of the brine solution. The osmotic pressure of the solution is a function of the type and concentration of the solute and is generally about 1.0 psi per 100 ppm of total dissolved solids in brackish water.

In *reverse osmosis* (RO), the *feed water* (brine) is pumped across the surface of the membrane at pressures ranging from about 200 to 400 psi above the natural osmotic pressure allowing water to flow in the reverse direction and *permeate* through the membrane. The impurities are rejected by the membrane and flushed from the membrane surface in the *concentrate* flow stream.

*Permeate* is the purified product water from the RO membrane. RO is a cross-flow membrane separation process that generally rejects greater than 97 percent of the feed water total dissolved solids, greater than 95 percent of the feed water total organic carbon (TOC), and rejects most colloids, particles, and microorganisms. The ability of the membrane to reject organics depends on the chemical characteristics and molecular weight of the organics. Also, ions with higher atomic weight and higher ionic valences are rejected more efficiently than smaller, lower valence ions.



Commercial RO membranes are generally available in cellulose acetate, polyamide, and thin film composite construction. The thin film membranes are the most common and offer significant advantages such as higher salt rejection, wider operating pH range, significantly higher permeate production, and resistance to polymer hydrolysis. However, they are not chlorine resistant, and pretreatment consisting of activated carbon for de-chlorination and filtration for particle removal to less than 5 microns is required to optimize membrane life (2 to 3 years).

The most common membrane configuration is the spiral wound membrane module. The spiral wound modules are designed for installation in FRP or stainless steel pressure vessels to operate at high feed water pressure. Standard RO membranes are generally available in modules of about 20, 30, 60, 90, and 350 square feet of membrane area. With flux rates in the range of 20 to 30 GPD per square foot of membrane area, standard modules range in production from about 400 GPD to 10,000 GPD. Single membrane systems operate at recoveries of about 15 to 20 percent, and larger systems with many membrane modules in series and parallel arrays can operate up to about 75 percent recovery.

An RO system generally consists of a high pressure pump, standard RO membrane modules in FRP or stainless pressure vessels, a back-pressure control valve in the concentrate line to regulate membrane operating pressure and recovery, and instrumentation and controls. Some small capacity RO systems operate on normal potable water line pressure; however, production and salt rejection are much lower.

Generally, the production (flux) of an RO membrane is proportional to the applied pressure differential minus the osmotic pressure. An increase in the operating pressure differential will increase the production, and an increase in the osmotic pressure of the feed water will decrease the production. The production of a membrane system is also a function of the feed water temperature. As the feed water temperature decreases, the production of the membrane decreases.

The rated production of an individual RO module is based on standard feed water conditions, normal operating pressure, and module recovery. For example, a standard thin film module (90 sq. ft. membrane area, 4" diameter by 40" length) has a rated clean water production of about 2,700 GPD at 2,000 ppm NaCl feed water concentration, 77°F, pH 7.5 units, operating pressure of 225 psi, and module recovery of 15 percent. This module at an operating feed water temperature of 50°F would only provide about 60 percent of the rated production.

The rate of salt passage through the membrane is proportional to the salt concentration differential across the membrane. Thus, an increase in the salt concentration differential will result in an increase in the salt passage through the membrane. The rate of salt passage is independent of the operating pressure.

For example, the module described above, with an average salt rejection of 98 percent, would provide permeate water with a salt concentration of about 40 ppm ( $2000 \text{ ppm} \times 0.02 = 40 \text{ ppm}$ ). The same module operating on feed water with 200 ppm NaCl would provide permeate water with a salt concentration of 4 ppm ( $200 \text{ ppm} \times 0.02 = 4 \text{ ppm}$ ).

RO technology is well suited to remove the broad spectrum of potentially toxic contaminants that could be intentionally introduced into a drinking water supply with the intent of harming people. With a few exceptions, RO effectively rejects most ionized inorganic compounds and most organic compounds with molecular weights over 200 molecular weight. In addition, the membrane pore sizes are so small that virtually all colloids and microorganisms are rejected.

In the pH range of about 6.5 to 8.5, inorganic arsenic ( $\text{As}^{+3}$ ) is present as uncharged arsenious acid ( $\text{H}_3\text{AsO}_3$ ) which is not effectively removed by RO. However, water with oxidizing agents such as chlorine will oxidize arsenic to  $\text{As}^{+5}$  which exists as an anionic radical ( $\text{HAsO}_4^{-2}$ ). In this form, RO effectively removes arsenic. Cyanide compounds are more effectively removed by RO at higher pH levels.

### *Ion Exchange*

Mineral salts dissolved in water dissociate into their respective positively charged *cations* and negatively charged *anions*. Some minerals such as sodium chloride are highly soluble, and other minerals such as calcium carbonate are sparingly soluble. Some substances such as silica and carbon dioxide are weakly ionized. Dissolved salts in water are electrolytes that allow electrical current to pass through water. As the total dissolved solids (TDS) concentration increases in water, the electrical conductivity increases. Conductivity and its reciprocal, resistivity, are commonly used to estimate the TDS concentration in water. TDS can be removed from water by processes such as distillation, RO, and ion exchange demineralization.

Ion exchange is a process where ions electrostatically held on the resin beads exchange for other ions in solution with a higher affinity for the resin. Cation exchange is accomplished with cation resin, and anion exchange is accomplished with anion resin. For example, ion exchange softening is a process for removing hardness ions (calcium and magnesium) by utilizing cation exchange resin in the sodium exchange mode. Unlike ion exchange demineralization that removes TDS from water, ion exchange softening simply exchanges hardness ions with sodium ions. The TDS concentration in the water remains the same.

Cation resin consists of porous plastic beads (polystyrene) with electronegative functional groups chemically attached to the resin; these negatively charged sites associate with an equivalent amount of positive ions (cations) in solution to

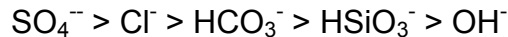
maintain electroneutrality. Similarly, the anion resin is manufactured with electropositive functional groups that associate with anions in the solution. The total number of functional groups per unit volume of resin determines the ion exchange capacity (grains per cubic feet) of the resin.

Cation resin placed in water containing a mixture of calcium, sodium, and hydrogen ions will have most of the exchange sites occupied by calcium, a few sites occupied by sodium, and very few sites with hydrogen ions. This occurs because the resin has a higher affinity for, or is more selective for, ions with higher ionic charge and ionic size. The cation selectivity series is as follows:



The resin will also have a preference for an ion that is present in an overwhelming concentration. Thus, if saturated with a brine (salt) solution, the exchange sites would mostly be occupied by sodium ions. Likewise, if saturated with a strong acid (HCl), the exchange sites would mostly be occupied with hydrogen ions.

The anion resin performs in a similar manner with anions in solution. The anion selectivity series is as follows:



As discussed, cation exchange is used to soften water by removing calcium and magnesium ions from solution. The cation resin in a sodium exchange mode selectively exchanges the sodium on the resin for the calcium and magnesium in solution. When the sodium ions are depleted from the resin, the resin is exhausted and hardness breakthrough occurs. The resin is regenerated (returned to the sodium exchange mode) by treatment with a strong sodium chloride (5-10 percent) solution to reverse the exchange process. The process is not 100 percent reversible, however, and small amounts of hardness remain on some of the exchange sites. This causes a small amount of hardness *leakage* during the normal softening cycle.

Ion exchange demineralization is a process that utilizes cation resin in the hydrogen exchange mode and anion resin the hydroxyl exchange mode to remove TDS from water. The process can be done in a two-bed process where the water is first treated in a cation resin bed then the anion resin bed. The cation resin selectively exchanges the hydrogen on the resin for other cations in solution; water exiting the bed is strongly acidic causing a small amount of residual sodium leakage from the resin (1 to 2 ppm sodium). The anion resin selectively exchanges the hydroxyl ions on the resin for other anions in solution. The small amount of sodium hydroxide leakage determines the resistivity of the demineralized water (about 200,000 to 500,000 ohm-cm). After the resin exhausts, the cation resin is regenerated with hydrochloric acid to return the resin

to the hydrogen exchange mode, and the anion resin is regenerated with sodium hydroxide to return the resin to the hydroxyl exchange mode. Thus, in the demineralization process, the TDS is removed from the water and replaced with  $H^+$  and  $OH^-$  (water).

The mixed-bed demineralization process is much more efficient than the two-bed process. In the mixed-bed, the cation and anion resins are thoroughly mixed together in one resin bed. Cation and anion exchange occurs simultaneously in the resin bed; this prevents the sodium hydroxide leakage that occurs in the two-bed process. Water quality from mixed-bed demineralizers is typically 17 to 18 megohm-cm resistivity. This is close to the theoretical resistivity of absolutely pure water at 18.2 megohm-cm.

### **Point-of-Use Treatment Systems**

A number of suppliers provide point-of-use water treatment systems for consumer use. Some of these systems are portable and designed for field use by the military for removal of chemical and biological contaminants to provide purified drinking water. These integrated systems generally utilize combinations of treatment technologies including activated carbon, RO, ion exchange, ultraviolet, and submicron filtration.

As discussed previously, RO is a proven technology for the removal of a broad spectrum of potential contaminants including chemical, biological, and radionuclides. Pretreatment with a granular activated carbon cartridge can remove potential organic contaminants that are not effectively removed by the RO membrane. A polishing activated carbon cartridge after the RO membrane provides additional assurance of the removal of organic contaminants not rejected by the RO membrane. A polishing ion exchange cartridge can remove residual ionized inorganic contaminants in the RO permeate water. Post filtration with a 0.2 micron membrane filter, ultrafilter cartridge, or ultraviolet system provides a final barrier for potential biological contaminants.

While we can never be absolutely safe from potential threats, point-of-use systems can serve as a final barrier and provide a degree of protection from potential contaminants, either accidentally or intentionally added to a water supply.

### **Environmental Technology Verification**

In October 1995, the U.S. EPA established the Environmental Technology Verification (ETV) Program to develop testing protocols and verify the performance of innovative technology for use in monitoring and controlling potential contaminants to protect public health and the environment. NSF International entered into an agreement with the EPA to establish the Drinking Water Systems Center to provide independent evaluations of drinking water

technologies. Go to the EPA web site ([www.epa.gov/etv](http://www.epa.gov/etv)) and NSF web site ([www.nsf.org/etv/dws](http://www.nsf.org/etv/dws)) to find updated lists of protocols, test plans, verification reports, etc.

### **Future Research**

In conjunction with technology verification, there is a need for future research to develop new technology to provide simple and effective monitoring techniques for potential terrorism agents. Although current technology does provide a means for control for most of these potential contaminants, the need for new technology and innovative solutions for mitigation and effective control of these and other potential contaminants is critical in the war on terrorism.

Based on existing research, current technology can effectively control these contaminants in dilute concentrations. Considering the large dilution factors in most water supplies, this would be the most likely scenario. However, research is needed to investigate the limits of these technologies and to develop new and innovative technologies. In addition, issues relating to decontamination, protection during system servicing, and safe disposal of expendable items need to be investigated.

### **Mitigation of Water Terrorism**

As required under the Bioterrorism Act, suppliers of drinking water serving more than 3,300 persons are required to conduct vulnerability assessments. The EPA is working with government entities and water suppliers by providing technical support and training to conduct the vulnerability assessments and develop emergency response plans. The assessments are designed to evaluate susceptibility and identify actions to mitigate the risks.

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