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Contaminants of Emerging Concern in Water

Contaminants of Emerging Concern Raise Many Questions

When the news reports on traces of birth control hormones or pain killers found in water, we do not know what to think. Is there any danger? How will these contaminants affect fish and other wildlife? Should we do something? What should we do? Many water contaminants are the subject of regulations that protect water quality, but many more fall into the category of substances for which we do not know the answer to these basic questions. These include substances that have been called emerging contaminants or contaminants of emerging concern (CECs).

What are CECs?

The United States Geological Survey (USGS) provides a useful definition of CECs: "any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects. In some cases, release of emerging chemical or microbial contaminants to the environment has likely occurred for a long time, but may not have been recognized until new detection methods were developed. In other cases, synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of emerging contaminants."

In other words, CECs are any substances that we are beginning to suspect could cause harm. They may be new substances, or they may have been around for a long time but only recently have been found in the environment. We may just be beginning to understand their effect on the environment or human health, or we may only now have the ability to detect them in the environment. Basically, they are substances we use every day for all kinds of purposes, which

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get flushed, washed or otherwise discarded and end up in water and soil.

Because they are so numerous, diverse and ubiquitous, they are frequently lumped into categories that describe their purpose, use or other characteristic. Some common categories are pharmaceuticals (both prescription and over-the-counter drugs), personal care products, plasticizers, flame retardants, and pesticides. Other categories describe their nature, such as surfactants, which can be used in detergents to aid grease removal and in cosmetics as an emulsifier; or synthetic hormones, which mimic the action of natural hormones. Unfortunately, these categories can overlap, leading to some confusion, and there is no standardized set of categories used in the various studies on CECs. Some of the most common terms used to categorize CECs are listed in Table 1.

CECs are continuously entering water sources throughout the world because of their widespread use. Conventional wastewater and recycled water treatment is only partially effective in their removal or degradation, so they are discharged into the environment with treated wastewater effluent, recycled water, and wastewater plant sludge. In Arizona, effluent discharge makes up a large portion of surface water flow in the rivers that provide recreation, habitat for fish, birds and other wildlife, and also provide drinking water.

Effects of CECs on human and ecosystem health are largely unknown, and relatively little is known about the ways they travel through the environment or how they may be transformed or degraded in the course of their travels. Some studies have shown that even very low exposure to certain CECs can have impacts on biological systems. Effects seen in some fish and aquatic species, however, have not been observed in humans.

Table 2 contains examples of CEC categories with associated effects. It illustrates that CECs have many different potential health impacts on humans and other species. The potential to cause cancer or have toxic effects in animals and humans is noted, but the concern most frequently mentioned

Table 1. *Common Classes of CECs*

Class of CEC	Example	Definition
Antibiotics	Tetracycline, Erythromycin	Medications that fight bacterial infections, inhibiting or stopping bacterial growth
Antimicrobials	Triclosan	Biochemicals that kill or inhibit the growth of microorganisms including bacteria and fungi
Detergent metabolites	Nonylphenol	Chemical compounds formed when detergents are broken down by wastewater treatment or environmental degradation
Disinfectants	Alcohols, Aldehydes and oxidizing agents	A chemical agent used on non-living surfaces to destroy, neutralize, or inhibit the growth of disease-causing microorganisms
Disinfection by-products	Chloroform, Nitrosodimethylamine (NDMA)	Chemical substances resulting from the interaction of organic matter in water with disinfection agents such as chlorine
Estrogenic compounds	Estrone, Estradiol, Nonylphenol, Bisphenol A	Natural or synthetic chemicals that can elicit an estrogenic response
Fire or flame retardants	Polybrominated Diphenyl Ethers (PBDEs)	Any of several materials or coatings that inhibit or resist the spread of fire
Fragrances	Galaxolide	Chemical substances that impart a sweet or pleasant odor
Insect repellants	DEET (N,N-diethyl-meta-toluamide)	Chemical substances applied to skin or other surfaces to discourage insects from coming in contact with the surface
PAHs (poly-aromatic hydrocarbons)	Benzo(a)pyrene, Fluoranthene, Naphthalene	A large group of chemical substances usually found in the environment as a result of incomplete burning of carbon-containing materials like fossil fuels, wood, or garbage
Personal Care Products	Para-hydroxybenzoate	Chemical substances used in a diverse group of personal items including toiletries and cosmetics.
Pesticides or Insecticides	Permethrin, Fenitrothion, Bacillus thuringiensis israelensis (B.t.i.)	Chemical substances or microbiological agents that kill, incapacitate or otherwise prevent pests from causing damage
Pharmaceuticals	Fluoxetine (Prozac), Carbamazepine, Diphenhydramine	Chemical substances used in the prevention or treatment of physiological conditions
Plasticizers	Dioctyl Phthalate (DOP)	Chemical additives that increase the plasticity or fluidity of a material
Reproductive hormones	Dihydrotestosterone (DHT), Progesterone, Estrone, Estradiol	A group of chemical substances, usually steroids, whose purpose is to stimulate certain reproductive functions
Solvents	Ethanol, Kerosene	Chemical solutions, other than water, capable of dissolving another substance.
Steroids	Cholesterol, Coprostanol, Estrone, Progesterone	A large group of fat-soluble organic compounds with a characteristic molecular structure, which includes many natural and synthetic hormones
Surfactants	Sodium Lauryl Sulfate	Chemical substances that affect the surface of a liquid

is endocrine disruption.

Although not all CECs have endocrine disrupting effects, concern with the endocrine disrupting properties of CECs is so common that often the terms "Endocrine Disrupting Compound (EDC)" and the more general term "Contaminant of Emerging Concern" are used interchangeably,

Endocrine Disruption

Endocrine disruption, as the term implies, interferes with the proper functioning of the endocrine system, the system responsible for regulating hormones. Endocrine system disruption may lead to cancerous tumors, birth defects and developmental disorders.

Definitions tend to be highly technical. The World Health Organization defines an endocrine disrupting compound as "an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny." The Environmental Protection Agency (EPA) defines environmental endocrine disrupting compounds as exogenous agents that interfere with the "synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior." Endocrine disruption is a well documented health effect of many CECs.

The endocrine system is a system of glands and organs that secrete hormones into the bloodstream. The hormones then travel with the blood to different parts of the body to generate specific responses. It is a complex system that controls important body functions such as growth, metabolism, and reproduction.

Even though it is considered an issue of emerging concern, endocrine disruption is not a new concept. Evidence that several natural and synthetic compounds can cause endocrine disruption has existed since as early as 1930. The issue gained public awareness in the 1950s and 1960s, with the discovery that DDT, a widely used pesticide, had endocrine disrupting properties. In the 1980s and 1990s, evidence began to accumulate that chemicals such as pesticides, surfactants (used in detergents) and synthetic birth control

Table 2. *Examples of CEC Categories and Associated Effects*

Use Category	Where has it been detected?[1]	Suspected health effects from environmental exposure[2]
Antibiotics	Groundwater, surface water, wastewater treatment plant effluent, land applied biosolids, potable water, recycled water	Antibiotic resistance in disease causing bacteria complicating treatment of infections
Disinfectants	Wastewater treatment plant effluent, treated potable water, ground and surface waters, recycled water	Genotoxicity, cytotoxicity, carcinogenicity
Fire retardants	Rivers down gradient of landfills and PBDE manufacturing sites, sewage sludge, natural waterways, sediments, bioaccumulation in fish, whales and other aquatic organisms	Endocrine disruption, indications of increased risk for cancer
Industrial additives	Industrial and household waste, soil	Can be toxic to animals, ecosystems, and humans
Life-style products (Caffeine, Nicotine)	Potable water, groundwater and surface waters affected by sewage or wastewater treatment plant effluent	Can cause cellular stress, negative effects on reproductive activity in animals
Nonprescription drugs	Wastewater treatment plant effluent, surface water, potable water, recycled water	Unknown health effects
Other prescription drugs	Potable water, recycled water, groundwater, surface water, wastewater treatment plant effluent, land applied biosolids	Increased cancer rates, organ damage
Personal care products	Ground-waters, surface waters, sewage, wastewater treatment plant effluent, biosolids, aquatic sediments, biological samples (bioaccumulated in fish tissues)	Bacterial resistance, endocrine disruption
Pesticides	Groundwater, surface water, potable water, recycled water	Endocrine disruption
Plasticizers	Surface water	Endocrine disruption, increased risk of cancer
Reproductive hormones	Surface waters, potable water, recycled water, wastewater	Endocrine disruption
Solvents	Groundwater, soil, potable water	Endocrine disruption, liver and kidney damage, respiratory impairment, cancer
Steroids	Surface waters, groundwater, potable water, recycled water, wastewater, sewage, effluent, biosolids	Endocrine disruption

1. This column indicates locations at which the category of CEC has been detected and/or studied and not necessarily the limit of their distribution.
2. For many of these chemicals, listed effects result from very high levels of exposure.

drugs were causing reproductive disorders, skewed sex ratios and population declines in fish, alligators and frogs.

The fact that natural and synthetic hormones cause endocrine disruption is not surprising, because their original purpose is to interact with the endocrine system. But the recently discovered endocrine-disrupting behavior of numerous other CECs was unexpected. A diverse range of chemicals can cause disruption of the endocrine system in some species, even at very low concentrations on the order of parts per trillion (equivalent of nanograms per liter or ng/L, which is 10^{-9} grams per liter). Because EDCs, like many other CECs, are commonly used chemicals, they can be expected to occur at low concentrations in the environment. In fact, advances in detection techniques and instrumentation are only now creating the ability to detect them where they occur at such low concentrations. Detection tools continue to be developed that can identify CECs at ever lower concentrations.

CECs in the Environment

Because CECs are found in many of the products we use every day, we are continuously releasing them into the environment where they can accumulate over time. For example, sucralose, an artificial sweetener, has been detected in wastewater since it was first approved for use in the United States in 1998. This and other chemicals we ingest in food and drugs are only partially absorbed or broken down. The rest passes through us unchanged.

Many CECs also have chemical properties that make them resistant to natural environmental degradation processes that would break them down. Hence, some CECs can accumulate and persist in the environment, potentially causing adverse effects. Even those compounds that undergo transformation or degradation sometimes form other chemicals that are potentially more problematic than the original chemical. A comprehensive understanding of the sources and pathways of exposure to emerging contaminants is necessary to fully comprehend and evaluate the health risks to humans and ecosystems.

One of the main pathways of CEC exposure is discharge of municipal wastewater effluent. The concern over emerging contaminants is new because they are new chemicals, newly detected chemicals, and chemicals with recently discovered potential health effects. Conventional wastewater treatment plants typically remove organics and pathogens, converting the mass of sewage to common gases and water. These facilities are not designed to remove all CECs. Well operated facilities can reduce the concentrations of many CECs substantially, and some studies have shown that with enhancements, conventional wastewater treatment can further reduce the concentrations.

Basic conventional wastewater treatment, however, is not effective in removing some CECs. Some of these CECs may persist even after advanced wastewater treatment and may be introduced into the environment when the effluent is released to surface water or recharged into groundwater. Or they may be removed from the effluent but remain in the treated sewage sludge produced as a result of the wastewater treatment process. Treated sewage sludge (also known as biosolids) is often applied on agricultural land as soil conditioner or fertilizer. The CECs in land-applied biosolids could leach into and contaminate surface water and/or groundwater. Although CEC breakdown can be facilitated by biosolid composting before application, use of biosolids represents another potential pathway for CECs to enter the environment.

Other sources of CECs include industrial wastewater effluents, untreated wastewater from manufacturing facilities, landfill leachate, effluents from poultry farms and

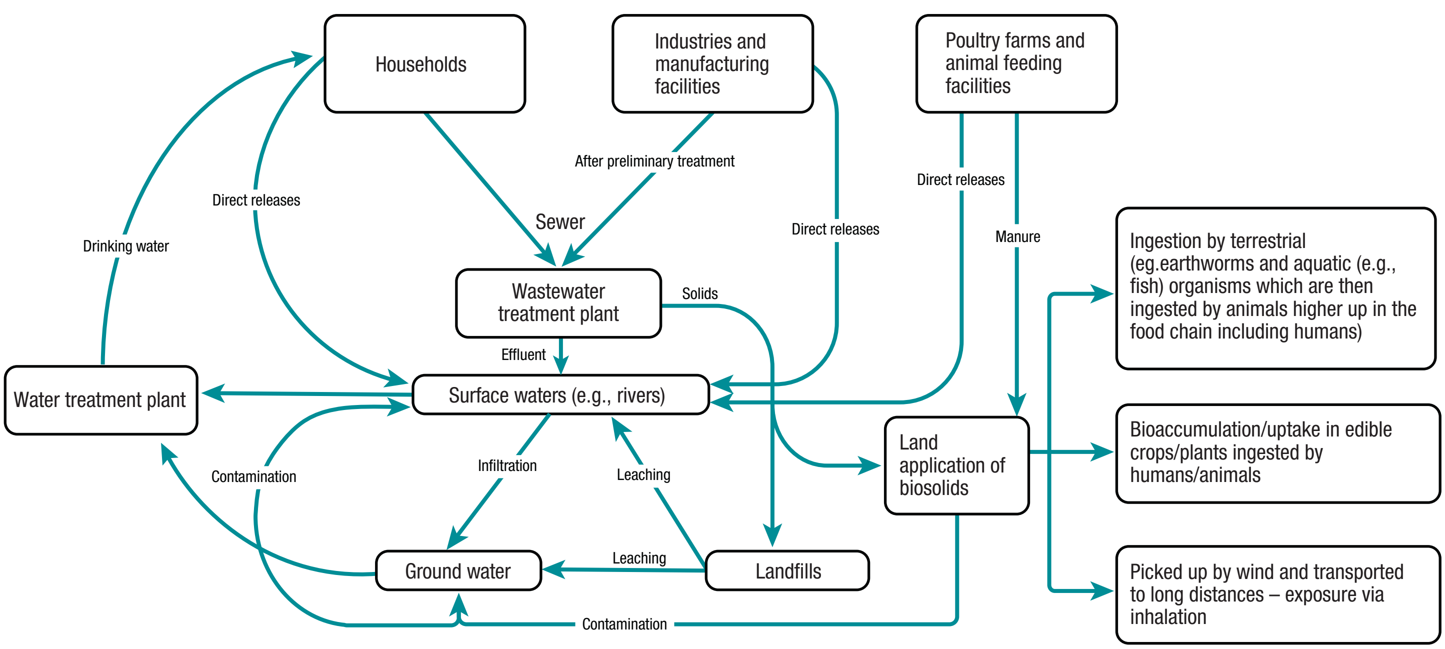


Figure 1: *Pathways of exposure for CECs (Modified from Petrović et al. 2003)*

animal feeding facilities where veterinary antibiotics may be used, and agricultural runoff containing pesticides. Figure 1 gives an idea of the multiple complex pathways through which CECs can enter the environment.

In 1999 and 2000, with the active participation of many

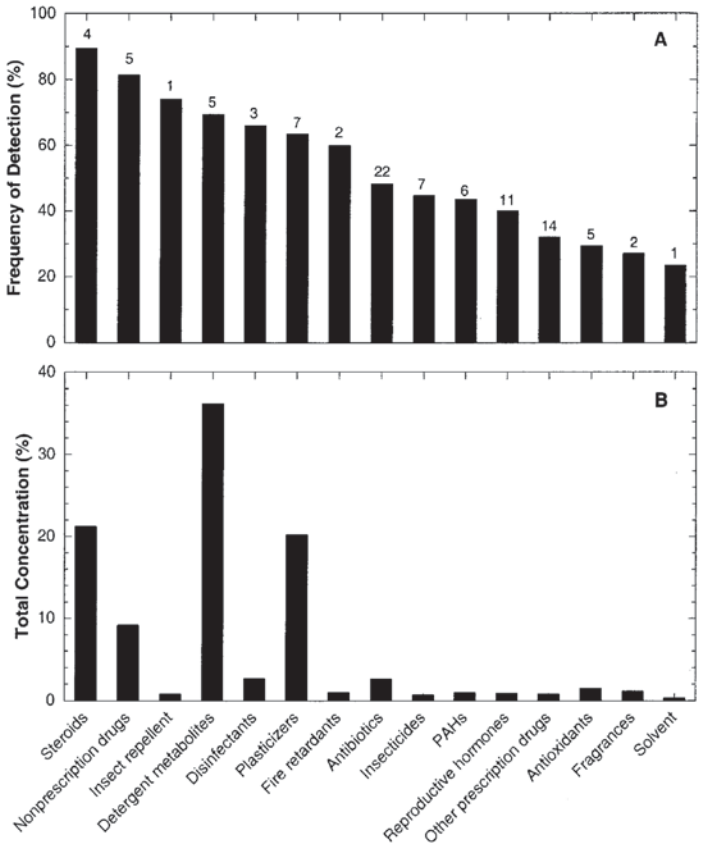


Figure 2: *Frequency of detection of organic wastewater contaminants in streams by general use category (A), and percent of total measured concentration of organic wastewater contaminants by general use category (B). The number of compounds in each category is shown above the bar (Source: Kolpin et al. 2002)*

wastewater treatment plants, USGS researchers conducted reconnaissance studies to look for the presence of CECs in 139 streams across 30 states in the United States. This was the first time such extensive monitoring efforts were undertaken at a national level to look for the occurrence of CECs in the environment. This study looked at 95 organic contaminants from commonly used pharmaceuticals, personal care products and other CECs. All selected sites were known or suspected to be affected by wastewater sources. These included such sources as manufacturing, wastewater treatment plants, residential septic systems, and poultry farms.

One or more of the tested chemicals were detected at 80 percent of the sampling sites. In many cases, these chemicals persisted, albeit at low parts per trillion (ng/L) concentrations, even after secondary treatment at conventional wastewater treatment facilities. Most chemicals studied were detected at low concentrations. Their effects on human and ecosystem health at such concentrations are a topic of research. Also of concern is the unknown potential for synergistic effects when mixtures of these chemicals are present. Mixtures of various chemicals were detected at 75 percent of the sampling sites. In some cases, as many as 38 of the chemicals were detected at a single site.

Many studies since then have looked at the fate and biological impacts of CECs in the environment. The USGS conducted two more reconnaissance studies to test for CECs in groundwater and untreated drinking water sources. These studies confirmed the presence of one or more CECs in samples from the majority of sites.

Figure 2 shows the kinds of CECs the USGS found. Chart A illustrates that steroids were detected in almost 90 percent of the samples. Chart B shows that steroids and detergent metabolites, along with plasticizers, made up the greatest concentrations of contaminants detected. Steroids include hormones such as coprostanol (a fecal steroid) and cholesterol (a plant and animal steroid). Detergent metabolites are compounds created when detergent breaks down through treatment or environmental degradation. Plasticizers are added to materials to make them more flexible; the plasticizers analyzed in this study are most commonly used in polyvinyl chloride (PVC) products.

Contaminant Removal

There are many factors that can influence how well a wastewater treatment plant performs at removing specific chemicals: chemical properties, level of treatment applied, retention times, pH, temperature, etc. As a result, studies report a wide range of concentrations of common CECs in treated

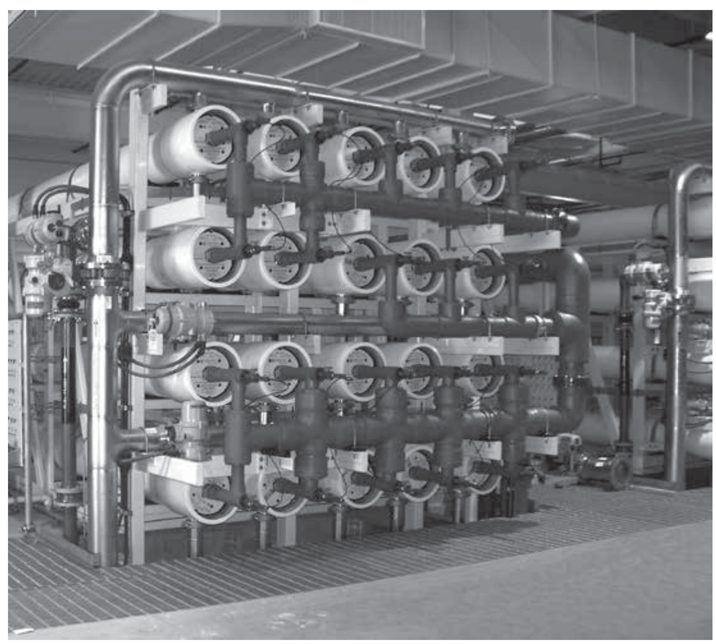


Figure 3*: Reverse osmosis train removes persistent chemicals from effluent at the Scottsdale Water Campus*

wastewater effluent and biosolids. In general, however, there is sufficient evidence that some pharmaceuticals, personal care products and other CECs persist to some degree after conventional wastewater treatment. Although recent studies have shown that conventional treatment plant operations can be optimized to reduce the concentrations of many CECs in effluent, the persistence of CECs has been observed in many studies on wastewater treatment effluents, sewage sludge and land-applied biosolids in the United States and Europe. Some CECs can persist in the treated effluents from wastewater treatment plants even after advanced treatment.

One study, conducted on treated effluents from the City of Mesa Northwest Water Reclamation Plant and Scottsdale Water Campus in Arizona, looked for pharmaceuticals such as carbamazepine and primidone (both seizure drugs) and other CECs known to persist after conventional wastewater treatment. Wastewater at the Mesa facility is treated with a combination of techniques—activated sludge treatment, disinfection and tertiary filtration. The treated effluent is then recharged into the local aquifer through recharge basins. When groundwater wells down gradient of the recharge basins were sampled, some pharmaceutically active compounds were found to persist at locations representative of groundwater travel times of up to six years. By comparison, these persistent chemicals were removed from the effluent at the Scottsdale Water Campus, but only after further treatment by microfiltration and reverse osmosis.

These techniques are highly advanced and expensive. Reverse osmosis is also energy intensive. Because wastewater regulations or standards for these pharmaceuticals and other CECs do not exist, wastewater treatment plants are not required by law to apply these advanced treatment technologies to achieve removal of such chemical contaminants to non-detect levels.

As this study indicates, the extent of treatment in a wastewater treatment plant can be a strong determinant of the concentrations of CECs that remain in the effluent and can potentially enter ground and surface water. Studies have also shown the relationship between wastewater treatment performance levels and CEC bioaccumulation levels in aquatic organisms. Fish and other aquatic organisms living downstream of wastewater treatment plants are exposed to effluents containing varying levels of CECs.

One study compared CECs in five rivers downstream of wastewater treatment plants. Researchers examined bioaccumulation of CECs from pharmaceuticals and personal care products such as norfluoxetine (a by-product of fluoxetine, a widely prescribed antidepressant, also known as Prozac), diphenhydramine (a product commonly used to treat allergies, also known as Benadryl) and galaxolide (used as a fragrance). The study found that fish in Arizona's Salt River showed bioaccumulation of these CECs greater than fish in two rivers—the Little Econlockhatchee River in Florida and Trinity River in Texas, and less than two other rivers, North Shore Channel in Illinois, and Taylor Run in Pennsylvania. All five wastewater treatment plants used some form of advanced treatment as defined by the EPA's National Pollution Discharge Elimination System (NPDES)

Antibiotic Resistance

Some researchers have proposed that certain emerging contaminants can pose a serious threat to human health by enhancing the antibiotic resistance of disease-causing microorganisms. Antimicrobial agents are chemical substances that kill and/or inhibit the growth of a wide range of micro-organisms such as bacteria, fungi, protozoa and viruses. Very generally, there are two kinds of antimicrobial agents: disinfectants, which are used outside of a living body and are found in many soaps and cleaning supplies; and antibiotics, which are compounds capable of destroying or inhibiting the growth of bacteria on or in living tissue.

Concern is growing that humans could be exposed to strains of bacterial pathogens that have developed resistance and therefore cannot be killed by existing antibiotics. The pathogens could even show resistance to combinations of antibiotics. Previously known diseases and infections with well-established means of treatment can re-emerge as significant public health problems because the microorganisms that cause them have become resistant to the currently used drugs. Resistance to established treatments has been observed with respect to malaria and tuberculosis throughout the world.

Genetic mutation leading to antibiotic resistance is a naturally occurring phenomenon. Sometimes genetic mutations happen in genes that encode for resistance to harmful external agents, thus the natural process of mutation leads to antibiotic resistance in some microbes. The widespread use of antibiotics and disinfectants in many products such as detergents and soaps is contributing to the increase in antimicrobial resistance. When an antibiotic is used, a few resistant organisms in the target bacterial population may survive, and the new microbial community may end up containing a higher number of resistant bacteria. The incidence of infections due to drug resistant bacteria in hospitals has increased. Hospitals, which are 'hotspots' for antibiotic and antimicrobial use, have seen the rise of two resistant bacterial species: Methicillin-resistant *Staphylococcus aureus* (MRSA) and Vancomycin-resistant *Enterococcus.* They are known to cause infections originating in hospitals or nursing homes and can be very difficult to treat. This suggests that the concentrated use of antimicrobial agents in such facilities may be causing the rise in resistance.

Even though researchers have found evidence for growing antibiotic resistance in general, they have not been able to show a conclusive cause and effect relationship with CECs in the environment. Some studies found higher levels of antibiotic resistance genes downstream of a wastewater treatment plant compared to upstream. These studies suggest that effluent from wastewater treatment plants can be a significant source for the spread of antibiotic resistance in the environment.

Other studies, however, indicate that the antibiotic resistance from wastewater effluent may be negligible in the context of naturally developing antibiotic resistance. For instance, a study in Arizona compared antibiotic resistance at the Gilbert Riparian Reserve that uses treated wastewater effluent and the Maricopa Agricultural Center (MAC) at the University of Arizona that uses only ground water. When soil samples collected from both sites were compared, the *Enterococcus* strains from the MAC site exhibited higher multi-drug resistance than the strains from the Gilbert site. These results, along with evidence of multi-drug resistant bacteria from pristine environments, like Lechuguilla Caves in New Mexico, have left the scientific community baffled about the mechanisms of antimicrobial resistance in bacteria.

categorization, but the higher level of advanced treatment used by the facilities on the Florida and Texas rivers appeared to produce a higher level of removal effectiveness.

Other researchers have evaluated the treatment efficiency of advanced technologies such as advanced oxidation processes, granular activated carbon, nanofiltration and reverse osmosis in removing pharmaceuticals and other CECs. All these techniques have been shown to provide high levels of removal for most tested chemicals, but some chemicals still may remain and may be detected at trace levels. Also, some disinfection technologies can convert the

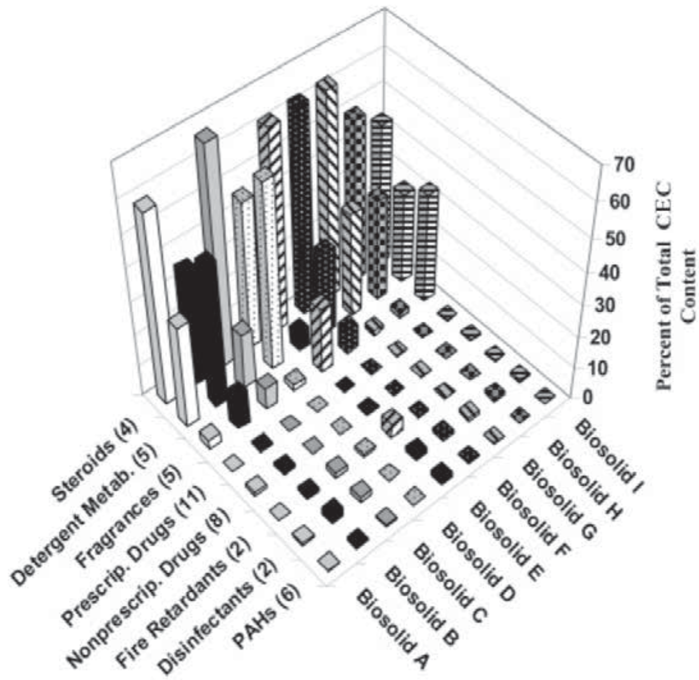


Figure 4: *Percent composition of various CECs found in the biosolids from treatment plants in seven states across the US. Biosolids G and H were from the same treatment plant in Arizona (Modified from Kinney et al. 2006)*

parent chemical into a more toxic by-product. Advanced oxidation processes, which include ultra-violet treatment, ozonation, combined ozone and hydrogen peroxide treatment, and combined ultra-violet and hydrogen peroxide treatment, are examples of processes that can produce toxic disinfection by-products (DBPs).

Removal of all contaminants of concern to below current detection limits is possible using a combination of advanced technologies, but that would result in an expensive, energy-intensive process. Without knowing the long-term health impacts of these CECs, we cannot know whether the expense would necessarily provide any significant improvement in human and ecosystem health. For this reason, research efforts need to focus on understanding the long-term health and environmental effects of these chemicals in order to allow us to assess the real risks and develop appropriate treatment technologies and processes.

Beyond removal at wastewater treatment plants, CECs may be removed by natural attenuation processes in the environment such as exposure to sunlight, biodegradation and adsorption onto sediments in watercourses. The removal efficiency of these processes is highly variable, depending on the properties of the contaminant and the environment. Natural attenuation is a very important mechanism, but is particularly challenging to assess because the process is site specific. A study on an effluent dependent section of the Santa Cruz River in Arizona showed that the estrogenic activity in the river decreased by more than 60 percent at a distance of 25 miles downstream of the wastewater discharge outfall. The study attributed the decrease to the natural processes mentioned above.

CECs in Wastewater Biosolids

As discussed earlier, when contaminants are removed from wastewater in treatment plants, they are frequently transferred to the sludge and finally to the biosolids. Biosolids consist of wastewater treatment sludge that has been further processed to remove water and reduce its pathogen content. The result is a stabilized product, rich in carbon, nitrogen, oxygen, and other nutrients. Biosolids are often applied to land as soil conditioners or fertilizers. From there any CECs in the biosolids may enter the environment through several pathways.

A 2008 study looked at the fate of one class of compounds—poly-brominated diphenyl ethers (PBDEs)—after wastewater treatment at the Roger Road Wastewater Reclamation Facility in Tucson. The Roger Road plant employed conventional biological treatment followed by chlorination. It was observed that 85 to 95 percent of the PBDEs, which are used as flame retardants, were transferred from the wastewater to the biosolids during wastewater treatment. Concentrations of PBDEs at the level of parts per million (or mg/L) were detected in surface soils of agricultural plots where these biosolids were applied. A portion of the effluent from the plant was infiltrated in basins at the City of Tucson's Sweetwater Recharge Facility where concentrations of PDBEs were found in surface sediments. The study estimated that these compounds could persist in the soil for at least a few decades. Laboratory studies have identified neurological and reproductive damage in mice exposed to PBDEs on the order of parts per million.

Another study looked at levels of 87 organic wastewater contaminants in biosolids obtained from wastewater treatment plants from seven different U.S. states, including two biosolid samples from a treatment plant in Arizona. These contaminants spanned a wide range of chemicals such as prescription and non-prescription drugs, detergent by-products, disinfectants, fire retardants and PAHs (polycyclic aromatic hydrocarbons, which are found in grilled meat, smoked fish and other foods cooked at high temperatures). All the treatment plants employed secondary activated sludge treatment and chlorine disinfection. Even though the biosolids studied as part of this work came from different wastewater treatment plants in different parts of the country, similar trends in the type and mixtures of the contaminants were detected (see Figure 4). As was also found in the USGS study of CECs in surface water, the greatest concentrations detected in samples were steroids and detergent metabolites. In every biosolid sample, at least 30 chemicals were detected and 55 chemicals were detected at least once.

Ecosystem Health Effects

Scientists have studied how organisms are affected by exposure to treated wastewater effluent. The responses of different organisms to effluent vary with the susceptibility of the particular species, chemical mixture and characteristics of the effluent. This variability makes it difficult to compare and interpret the results of the different studies. Even so, several studies have consistently observed adverse health and reproductive effects in certain organisms exposed to CECs via wastewater effluent.

Most studies have focused on the endocrine disrupting effects of these chemicals. A study on English Sole and Hornyhead Turbot exposed to effluent water downstream of the Orange County Sanitation District in California observed masculinization of female fish along with sperm damage and increased vitellogenin levels in male fish. Vitellogenin is a protein related to reproduction that is normally seen only in female fish, amphibians and reptiles. Females of these animals only produce vitellogenin when they begin to develop eggs under the influence of their own naturally produced estrogen. Elevated levels of this protein in male fish likely indicate exposure to external sources of estrogen. Other studies on flounder, fathead minnows and leopard frogs have observed various effects from exposure to wastewater effluent containing CECs, such as gonadal abnormalities, DNA damage and increased incidence of intersex characteristics, including the presence of egg cells in male testes.

Researchers have also observed signs of abnormal health and reproduction in fish and other organisms in the Colorado River Basin. Fish studied in the Gila River, at a sampling site downstream of the Phoenix metropolitan area, showed signs of reproductive changes such as reduced or abnormal gonadal development. Irrigation return flows and wastewater treatment plant effluents are the main contributors to flow in that stretch of the Gila River. Intersex fish and vitellogenin production have been observed at several sampling sites near Phoenix. The study concluded that the presence of pharmaceuticals, personal care products and other CECs in the waters downstream of Phoenix could be causing the adverse health and reproductive effects observed in fish in the Gila River.

Human exposure

Although studies have demonstrated adverse effects on fish and other animals in the environment, the potential effects on human health are still an open question. Very few CECs have been associated with potential adverse human health effects from research on laboratory animals. For example, the EPA has identified Perfluorooctanoic Acid (PFOA), a chemical used in industrial processes, as having a toxicity and bioaccumulation potential that raises concern over their persistence in the environment. However, CECs from pharmaceuticals and personal care products have not raised similar concerns for human health.

For pharmaceuticals, the concentrations detected in the environment are minute compared with prescribed therapeutic doses; a person would have to consume or be exposed to contaminated water for thousands and in some cases millions of years to consume the equivalent of one therapeutic dose (for example one pill) of the drug. This being the case, it is fair to ask how pharmaceuticals prescribed for human consumption could possibly be harmful at much lower concentrations in drinking water.

Concerns about human health effects of pharmaceuticals in the environment reflect the current lack of knowledge about environmental exposure to these chemicals. In some cases pharmaceuticals are used on a short-term basis and the long-term effects of low doses are not as well studied as use of these drugs under therapeutic conditions. Most of these drugs are meant to be consumed by people with specific health conditions and not by the general public. However, if these pharmaceuticals enter potable water systems, they are consumed by all people including children, the elderly, people with compromised immune systems or genetic predispositions that may make them more susceptible, and people with other health conditions.

Figure 5: *Exposure to pharmaceuticals in the environment*
Photos: clockwise from top: © Dgrilla, Pkruger, Salahudin, Vvvladimir | Dreamstime Stock Photos & Stock Free Images

Recently, the WHO released a report and information sheet on the current state of the science on pharmaceuticals with recommendations for guidelines and future research priorities. A working group of experts in water treatment and quality, toxicology and water policy, concluded in the report that at currently detected concentrations and predicted exposure levels, pharmaceuticals do not pose a serious risk to human health. Consequently they recommended against requiring health based guidelines for pharmaceuticals in the *WHO Guidelines for Drinking-water Quality* at this time.

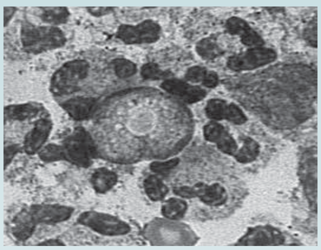
They suggested that concern over pharmaceuticals should not take away focus and resources from more immediate threats to water quality such as disease-causing microorganisms and high levels of arsenic and fluoride.

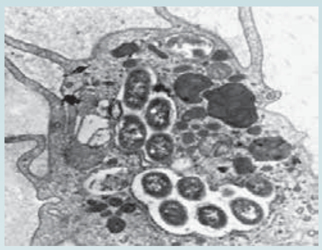
WHO acknowledged that pharmaceuticals in drinking water are an emerging issue and knowledge gaps exist. These include knowledge of the effects of long-term exposure to pharmaceuticals at low concentrations, effects of exposure to complex chemical mixtures, and effects on sensitive populations. WHO also acknowledged that because the science is still evolving, there is a need to constantly review new data and update the guidelines to include pharmaceuticals, if necessary. The use of pharmaceuticals and personal care products is widespread and predicted to increase. Consequently, their presence in the environment will increase. Health risks of chemicals used in these products and their transformation products in the environment require more study.

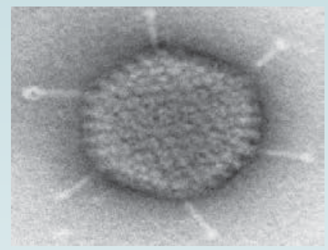
Toward Regulation and Regulatory Guidance

Contaminants of emerging concern, as the name suggests, are a contemporary and evolving issue. Federal and state governments are trying to formulate an approach to address these difficult-to-regulate contaminants. Many of the chemicals are new and there is still much to learn about their actions. They come from a wide range of sources, which makes source reduction efforts difficult. They have very different chemical structures and properties, which produce distinct human and ecological health effects through

Emerging Pathogens







Images of emerging pathogens. From left to right Naegleria fowleri, Legionella pneumophila, Helicobacter pylori, Adenovirus
Source: http://www.cdc.gov/parasites/images/naegleria/HEstain.jpg, http://farm1.static.flickr.com/201/464980384_93408db15c.jpg, http://faculty.ccbcmd.edu/courses/bio141/lecguide/unit2/bacpath/images/helicobacter.jpeg, http://www.virology.ws/wp-content/uploads/2009/01/adenovirus.jpg

The term 'emerging pathogens' is generally used to refer to microorganisms that have been discovered fairly recently, identified in a new area or new mode of transmission, and are known to cause serious human disease. Some of these infectious agents may survive after water treatment and can be introduced into or colonize within distribution systems. Four such hazardous emerging pathogens (Figure 5.1-5.4) are described below. All four are listed on the EPA's third Contaminant Candidate List (CCL3) in 2009.

Naegleria fowleri is a water-based amoeba that was identified as a human pathogen as early as 1965. This pathogen has been found in warm water bodies such as swimming pools, ponds, lakes, and hot springs. If it enters a swimmer's nasal passage, it can travel to the brain where it causes a form of meningitis. Infection usually results in death within a week. Deaths have occurred in Arizona from exposure in lakes and in one unchlorinated potable water system.

Legionella pneumophila are water-based bacteria first identified in 1978. Since then, *L. pneumophila* has been found in swimming pools, cooling towers and water distribution systems of large buildings like hospitals. It has been estimated that this deadly pathogen has caused more than 39,000 deaths in the 22 year period between 1998 and 2005. *L. pneumophila* must enter the lungs to cause disease, so two primary pathways of exposure to this pathogen are inhaling contaminated airborne water droplets (aerosols) and accidental aspiration of contaminated potable water. It is known to cause Legionnaires' disease and Pontiac Fever. Legionnaires' disease, the more serious of the two, has pneumonia like symptoms and has been reported to be fatal in almost 15 percent of hospitalized cases. This pathogen persists in water and can survive in a wide range of temperature and pH conditions.

Helicobacter pylori are water-borne spiral-shaped bacteria discovered in 1982 and are known to cause stomach cancer and ulcers. A primary exposure pathway for *H. pylori* is water contaminated by fecal matter. *H. pylori* can persist in a water supply after incomplete water treatment. The pathogen is also detected frequently in surface waters. *H. Pylori* were first listed on the EPA's Contaminant Candidate List 1 in 1998. Antibiotic resistant strains of this bacterium have been isolated recently.

Adenovirus is a water-borne virus that was first identified during World War II. It is known to cause respiratory infections and gastroenteritis in humans. This species of virus is highly resistant to advanced water treatment techniques like UV-disinfection. Adenoviruses have been detected in sewage, in surface waters receiving sewage, and in some cases, in treated potable water in South Africa and Korea. There is a lack of information about its occurrence in surface and ground-waters in the United States, although its ability to persist in potable water after advanced treatment is well established. Point of use treatment such as filters and reverse-osmosis systems have been shown to provide an additional safety factor and reduce risk of exposure to these microbial contaminants.

different pathways. They are in wide use in a multitude of products, which makes it challenging to find a control group of people (not exposed to the contaminants) for health risk assessments and epidemiological studies.

In the United States, the EPA periodically releases the Contaminant Candidate List, or CCL, a list of unregulated chemicals and microbes that may need to be studied further. The CCL is mandated by the Safe Drinking Water Act. The list was first published in 1998 and since then three lists have been released Listing is trending toward inclusion of more pharmaceuticals, hormones and emerging pathogens. The third list, CCL 3, which was released in 2009, contains some of the CECs described here, including the antibiotic erythromycin, the sex hormone estradiol, and the four micro-organisms highlighted on page 9. The EPA took public nominations for candidate contaminants during the creation of these lists, which both illustrates and addresses the general public's growing concern over the potential health effects of these contaminants.

In another action reflecting concern over the issue, the EPA set up the Endocrine Disruptor Screening Program in 1998, to screen and test chemicals for potential endocrine disruption activity. Methodologies for screening and testing were first developed and validated. The program has two tiers: Tier 1 identifies chemicals that potentially have an impact on the endocrine system, and Tier 2 studies the effects of each identified endocrine disruptor to determine what dose produces those effects.

The EPA plans to use this approach to identify endocrine disruptors and take appropriate regulatory action as required by the Food Quality Protection Act and the Safe Drinking Water Act Amendments passed by Congress in 1996. As part of this program, EPA released the first list of 67 chemicals to be tested for potential endocrine disrupting effects in 2009. A second Endocrine Disruptor Screening Program List of Chemicals for Tier 1 Screening, containing 134 chemicals, was released in 2010.

At the state level, in December 2012, the Arizona Department of Environmental Quality (ADEQ) held the first meeting of its Advisory Panel on Emerging Contaminants, a panel of experts and professionals working with CEC issues. For this panel, ADEQ invited nominations and appointed 35 people, including many from water utilities, engineering firms, universities, and state and local government. The objective of this panel is to prioritize contaminants of emerging concern in Arizona, identify research needs and provide guidelines for the protection of Arizona's water supplies from CECs, including pharmaceuticals, personal care products, and pathogens.

The California Model

The State of California undertook a similar effort in recent years. By initiating statewide discussions, it took the lead in developing a regulatory framework for CECs. Two panels were convened to develop a protocol for prioritizing these contaminants – a Recycled Water Panel and an Ecosystems Health Panel. These panels summarized current understanding, identified knowledge gaps, and made recommendations for future research.

The Recycled Water Panel convened in 2009 to propose a framework to assess CEC exposure risk from water reuse projects to prioritize monitoring. Figure 6 shows their conceptual framework. The first step is data collection on environmentally relevant CECs that may be present in treated wastewater destined for reuse projects. The endpoint of this step is a list of CECs to be screened.

The next step is exposure screening to determine whether

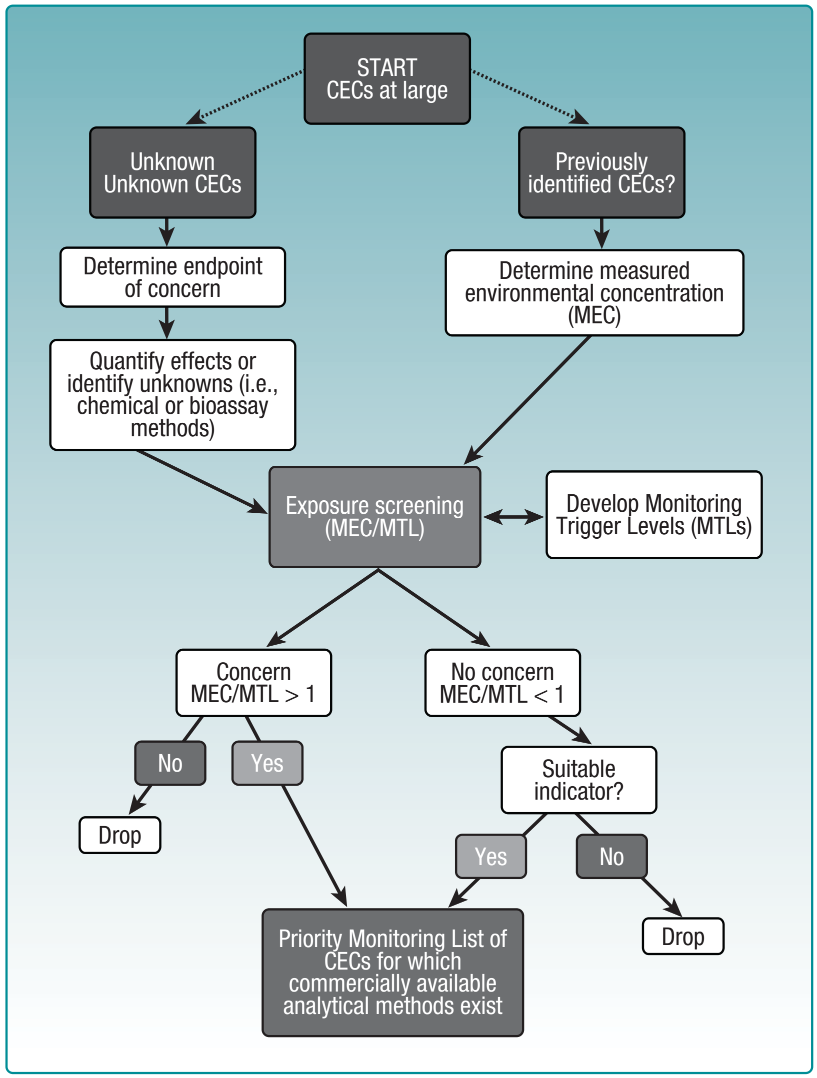


Figure 6: *Conceptual framework for CEC prioritization proposed by the CEC Recycled Water Panel convened by the California State Water Resources Control Board. Source: CEC Recycled Water Panel Final Report 2010*

there is an exposure of concern. For each CEC, a threshold concentration level in water is set to trigger monitoring. When concentration of a CEC greater than the monitoring trigger level is detected, the CEC should be designated as a high priority for regular monitoring. To be considered a high priority CEC, commercial analytical tools must be available to analyze the contaminant at the threshold concentration.

Given the lack of toxicological data, threshold setting will be a particular challenge.

The panel recommended that the prioritization process be repeated at least once every three years.

In addition, the panel recommended that there be frequent monitoring of the CECs during the initial stages of a water reuse project. CECs that consistently occur at concentrations below the monitoring threshold can be removed from the list. Monitoring frequency can be reduced as the project proceeds. CECs that consistently exceed the monitoring trigger levels should be more rigorously monitored. If monitoring confirms the presence of the CEC in the environment at elevated levels, sources of the CEC should be identified and treatments or other strategies for their removal should be developed.

The more recently convened Ecosystems Health Panel developed a framework for identifying, prioritizing and monitoring CECs that are most likely to have an impact on California's receiving waters. A risk-based screening framework similar to the recycled water panel's framework was developed. The panel then applied the framework to representative exposure scenarios in receiving waters, such as streams receiving wastewater discharges from treatment plants. In this way, the panel identified CECs for monitoring. The panel also identified knowledge gaps in the currently available information on sources, fate and toxicity of CECs. They recommended comparing the risks posed by CECs with risks from other regulated contaminants so that research and monitoring efforts can be prioritized and resources directed toward the more severe environmental stressors.

Future Priorities

A great deal of progress has been made in the development of analytical methods to detect CECs at low concentrations (e.g., nanograms per liter). These analytical tools have led to monitoring and assessment studies that have rapidly advanced our knowledge of the occurrence of CECs as individual compounds and mixtures and their distribution in the environment. The long-term health effects of exposure to low levels of CECs and mixtures of CECs are still poorly understood. Conducting controlled risk assessments and epidemiological studies is a major challenge because CECs are ubiquitous in the environment and often occur in complex mixtures. Questions regarding human health effects have not been satisfactorily resolved after many years of study, nor have issues relating to ecosystem effects and species responses. Because multiple, continuous sources of exposure exist in the environment, source reduction will be particularly challenging.

At the University of Arizona, the Arizona Laboratory for Emerging Contaminants is working to detect, identify and measure organic and inorganic micro-pollutants. The laboratory has examined these substances in many media, from our water sources to the fish we eat. Recent and current research projects at the laboratory include evaluating drinking water filters for pollutant removal, determining how trace pharmaceutical compounds act in soils irrigated with treated wastewater, and identifying sources of contamination of perfluorinated compounds in Arizona groundwater. Perfluorinated compounds (for example, PFOAs) are another important CEC category. They are in widespread commercial and industrial use because of their ability to make material stain- or stick-resistant, and there is some evidence that they may cause cancer. ALEC also has participated in research on the Santa Cruz River, evaluating the fate of CECs during river transport and percolation to groundwater.

Looking toward the future, knowledge of CEC occurrence and fate in the environment and human and ecosystem impact is needed. Research in universities, such as that being done by ALEC, and policy development efforts like the recent establishment of the Advisory Panel on Emerging Contaminants in Arizona, are crucial steps. Continued screening and monitoring will provide early warning on potential threats, while research and development to improve monitoring and analysis capabilities will advance our understanding of the nature and extent of potential exposure.

Scientific research alone, however, cannot be expected to determine acceptable levels of risk associated with CECs in the environment. What is acceptable depends on agreement on social values, public understanding of the issues involved, and assessments of the risks to the environment and to humans. Yet lack of information hampers traditional methods of risk assessment. While adverse effects on certain species have been documented, for the most part more

2012 Summer Intern Passionate About the Environment

The 2012 Montgomery & Associates Summer Writing Intern at the WRRC, Madhumitha Raghav, is a PhD student in Environmental Engineering at the University of Arizona working on the last stages of her dissertation. She has always been passionate about environmental issues and believes that in order to develop feasible solutions to most of the problems we face today, it is important to have a holistic approach to understanding the problem and formulating solutions. She enjoys researching and writing about current environmental topics. A class on 'Translating Environmental Science' piqued her interest in effective science communication. During her internship at the WRRC, she communicated extensively with experts in the field from both academia and regulatory agencies as part of her research for the Arroyo. She plans on completing her PhD this summer and is currently looking for positions in environmental consulting.

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general impacts on ecosystems and specific human health effects have not. Our ability to detect traces of contaminants at ever lower concentrations may be raising concerns greater than warranted by the risks. Only an assessment of the real risks will allow us to make the necessary tradeoffs among our various options for addressing CECs. New risk assessment methodologies may be needed along with more public education and discussion in order to develop appropriate responses to this emerging challenge.

This Arroyo began with a series of questions: How important is concern over CECs? What is realistic and what is hype? What, if anything, should be done? Definitive answers to these questions are elusive. There is much we still do not know, and the search for answers is fraught with difficulties. The preponderance of studies, however, indicates a measured response. Concern for CECs should reflect their risks relative to better known threats. Water professionals, regulatory agencies and academics will continue to carry out research, planning, and technology development activities to increase our understanding of the distribution, effects and control of this broad a varied group of chemicals. Reasoned public response to detection of CECs in water will depend on the information provided by these efforts.

Cover photo: Pima County Wastewater Treatment Plant outfall at Roger Road. **Source:** Pima County Regional Wastewater Reclamation Department

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