EMERGING CONTAMINANTS

Key Takeaways

Emerging contaminants are chemicals and substances characterized by a perceived, potential, or real threat to human health or the environment. Contaminants may be considered to be emerging because of the discovery of a new source or pathway that could impact human health. As you will read below, much is unknown about emerging contaminants in Wisconsin, so an important role of the GCC is to provide funding to support research studies that further scientific understanding of these substances and their occurrence, fate and transport in the groundwater environment.

GCC member agencies continue to work on multiple initiatives related to emerging contaminants in groundwater (see groundwater management sections – DNR, DATCP, UW, WGNHS).

For actions to address emerging contaminants contamination in groundwater, see the Recommendations Section.

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What are emerging contaminants and how widespread are they in Wisconsin?

An emerging contaminant is a substance for which there is increasing evidence of environmental occurrence and that the substance may cause adverse human and/or environmental health effects. The term is shorthand for "contaminants of emerging concern". There are two general reasons why concern about a substance can be emerging. The first is technological improvements: some emerging contaminants may have been present in the environment for a long time, but new measurement methods improve our ability to detect them. The second reason is emergence of a compound not previously common in the environment. This could be due to a new substance being manufactured, or recent changes in the use or disposal practices of existing substances. Research on the occurrence and health effects of these contaminants is important to characterize the nature of the risk and decide what actions may be required to protect human and environmental health. Emerging contaminants consist of a range of substances, many of which are produced synthetically. They may enter the environment in a number of ways including wastewater from municipal or industrial sources. Emerging contaminants may also enter the environment from agricultural wastes, which may be solid or liquid. Agricultural wastes are often landspread to make nutrients from the wastes available to crops, but if the wastes contain contaminants, they may migrate toward groundwater as irrigation water, rainwater or snowmelt infiltrate. Some treated municipal and industrial wastes are discharged to groundwater through land treatment/disposal systems. Treatment of municipal and industrial wastes typically lowers the concentrations of emerging contaminants but, in some cases, significant levels may still remain after treatment. Groundwater is impacted if contaminants in treated wastes infiltrate to groundwater.



Pharmaceuticals, including antibiotics and birth control pills, and personal care products are one group of emerging contaminants. *Photo: US Department of Defense*

When waste is discharged through a land treatment/disposal system, or spilled or released onto the ground surface, a number of biogeochemical processes can affect contaminants in the waste material as it leaches downward through the unsaturated soil zone to groundwater. Microbial action, sorption, filtration, ion exchange and precipitation are all processes that can remove, reduce or alter contaminants, including emerging contaminants, as waste material percolates downward through the soil matrix.

Microbial degradation processes, if they occur, can reduce the amount of contaminant that makes it to groundwater. Degradation can be abiotic or biotic, when a microbial organism starts a chemical reaction, in which the organism uses some of the original molecule but the rest - a *metabolite* - is left over. Incomplete degradation, also known as transformation, is when the parent compound transforms into one or more metabolites but not all the way to naturally occurring chemicals. Another process that can reduce the amount of a contaminant in groundwater is *sorption*. Sorption, including both adsorption and absorption, is a physical/chemical adhesion reaction in which substances, dissolved or suspended in water, form a bond with minerals or soil organic matter, attaching them to the solid material.

The occurrence of emerging contaminants in Wisconsin is not easily generalized, but several studies supported by the GCC have investigated the potential for certain emerging contaminants to enter groundwater from specific sources. Information about GCC supported groundwater research projects is available on the UW Water Resources Institute - Wisconsin Groundwater Research and Monitoring Program (WGRMP) web site at www.wri.wisc.edu/wgrmp-repository.

The following sections provide information on some of the types of emerging contaminants that may be found in Wisconsin groundwater.

Pharmaceuticals and Personal Care Products (PPCPs)

Together, pharmaceuticals and personal care products (PPCPs) - including shampoos, detergents and "over-the-counter" non-prescription medicines - make up a category of emerging contaminants that largely enter the environment from domestic wastewater and municipal sources. Sources of PPCP discharge into the environment include wastewater discharged through land treatment/disposal systems, discharge from septic systems, land application of wastewater biosolids and septage, and leakage from older landfills.

Pharmaceuticals detected in groundwater worldwide include antibiotics, non-steroidal anti-inflammatory drugs, birth control medications, and many other prescription medicines. Many pharmaceuticals begin to degrade in subsurface soil and groundwater. Pharmaceutical degradation products and metabolites in the subsurface environment are still being discovered. In addition to prescription medicines, stimulants, such as caffeine and nicotine, as well as recreational drugs, may also be found in groundwater.

Pharmaceuticals enter the environment through disposal of unused pills as well as excretion of the compounds or their metabolites from the human body. A metabolite is a compound produced by the body's metabolism from the "parent" compound, i.e. the original pharmaceutical. Metabolites often, but not always, have similar chemical properties as the parent compound.

Antibiotics have been detected in treated wastewater effluent from facilities across the state, with very low concentrations of tetracycline and sulfamethoxazole detected in groundwater directly adjacent to a wastewater treatment facility groundwater discharge site¹. Acetaminophen (Tylenol), paraxanthine (a caffeine metabolite) and the hormones estrone and β -estradiol have been detected in private on-site wastewater treatment system (POWTS) effluent in a Dane County study², and estrogenic endocrine disrupting compounds (EDCs) were detected in POWTS effluent in a southeast Wisconsin study³. Neither study detected these compounds in groundwater. A follow up study at the Dane County site, ten years after subdivision development, however, found a number of contaminants that may have moved from POWTS discharge into groundwater. Artificial sweeteners, often used as an indicator of domestic wastewater effluent, were found in the study in seven of ten monitoring wells and in two water supply wells.

Per- and Polyfluorinated Alkyl Substances (PFAS)

A group of emerging contaminants of much current concern are perfluoroalkyl and polyfluoroalkyl substances (PFAS). These compounds are comprised of organic carbon chains in which some hydrogen atoms (poly-), or all hydrogen atoms (per-), have been replaced with fluorine atoms. PFAS have been used in a variety of industrial and consumer products since the 1940s and are now being detected in groundwater and drinking water supplies worldwide. PFAS gained widespread use in part due to their ability to repel water and oil and withstand high temperatures. They are found in numerous consumer products, such as non-stick cookware, stainand water-repellent clothing and carpeting, grease-resistant liners to food packaging, including microwave popcorn, some spray paints, and Class B firefighting foams, used on flammable liquid fires.

Many polyfluorinated substances that are part of the PFAS chemicals family transform in the environment to other PFAS, especially to perfluoroalkyl acids such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). PFAS are not known, however, to degrade in groundwater or elsewhere in the environment into any non-toxic end products. They may therefore accumulate in environmental settings. PFAS can enter the environment in a number of ways, including placement of PFAS containing products in landfills, use of PFAS containing consumer products resulting in their presence in wastewater, land spreading of wastewater biosolids on cropland, and direct use and lack of containment of PFAS chemicals at manufacturing and firefighting sites.

The two most widely studied PFAS chemicals are PFOA and PFOS, both of which present health risks and are commonly found in groundwater. While these two substances were directly manufactured during the mid-20th century, manufacturing shifted during the late 20th century to polyfluorinated substances (precursors) that sometimes transform to end products, including both PFOA and PFOS. These polyfluorinated precursor compounds may transform slowly in soil and groundwater, and therefore represent possible ongoing sources of PFOA and PFOS to the environment.

In the United States, industry voluntarily phased out the manufacture of PFOA in 2015 and PFOS in 2002. However, because of the extremely stable nature of these compounds they continue to be found in the environment at industrial locations where they were once used. In 2019 more than 180 countries worldwide agreed to ban production and use of PFOA and its salts. In 2023 the Environmental Protection Agency (EPA) proposed to designate PFOA and PFOS as hazardous substances under the Superfund law.

There is concern about the limited number of continuing ongoing uses of PFOArelated chemicals, which are still available in existing stocks and from companies not participating in the PFOA Stewardship Program. Goods imported from countries where PFOS and PFOA are still used might also represent a continuing source of these chemicals in the environment.

Since the turn of the century, in applications where PFOS or its precursors were used, manufacturing has shifted to shorter chained PFAS compounds such as perfluorobutane sulfonate (PFBS). Manufacture of PFAS containing additional chemical structures (e.g. ethers) has also emerged, with this category of PFAS being known as "replacements". Examples of replacement PFAS are HFPO-DA (hexafluoropropylene oxide dimer acid, sometimes referred to by the trade name "GenX"), which is a replacement of PFOA, and PFBS, which is a replacement of PFOS. In 2020, for the "Cycle 11" ch. NR 140 rulemaking effort, the WI Department of Health Services (DHS) recommended state public health groundwater quality enforcement standards for 18 PFAS compounds, including HFPO-DA and PFBS. These recommended standards serve as state drinking water health advisory levels (HALs).

PFAS compounds have been detected in Wisconsin groundwater. Much recent work on PFAS in Wisconsin has focused on investigations at contamination sites. As of July 2024, there are 99 open site investigations statewide where one or more PFAS have been identified as a contaminant.

In June 2022, the DNR, in collaboration with the UW-Stevens Point Center for Watershed Science and the WI State Laboratory of Hygiene, sampled the water supplies at 450 homes spread throughout the state. All of the study home's water supplies came from private water supply wells. The objective of the study was to determine concentrations of PFAS present in shallow (from the uppermost 40 feet of an aquifer), ambient (in a location not near any known release of PFAS) groundwater. Collected samples were analyzed for 44 PFAS compounds. At least one PFAS compound was detected in 71% of the study home water supplies, and 22 of the 44 PFAS analytes were detected in at least one of the study samples.

Beginning in January of 2024 public water supply systems began sampling for PFAS. As of March 2024, 1,858 active public drinking water systems had submitted PFAS compliance samples to the DNR. PFAS compounds were detected in 30% of sampled public water supply systems.

For more information on PFAS, see the PFAS section of the report.

Agricultural Contaminants, including Pesticides

In many agricultural practices, pesticides are applied to crops to kill or hinder the effects of "pests", including insects, competing plants (weeds), fungi, and bacteria. On large areas of crops, application is done from small airplanes to distribute the chemicals over a large area. Due to crop irrigation and precipitation events, pesticides may leach into groundwater. There are approximately 500 unique agricultural pesticide active ingredients used in Wisconsin, and about 30 pesticides compounds, including some active ingredients and their breakdown products, have established groundwater quality standards under chapter NR 140.

Most pesticides can sorb to soil and aquifer material, meaning they often travel to and through groundwater more slowly than the water itself. Some are also transformed into metabolites by bacteria. Active methods of destroying pesticides include photocatalytic techniques, which combine use of light and chemicals to "catalyze" pesticide-destruction reactions.

Although pesticides have been in use since the middle of the 20th century, new pesticides continue to come into use. One such pesticide is the herbicide isoxaflutole, which has been approved in Wisconsin for limited use for weed control on corn crops. Field testing, to evaluate potential groundwater impacts from

Isoxaflutole use, was completed in October 2023. Evaluation of the results is currently underway.

Neonicotinoid insecticides are a relatively new group of neuro-active insecticides that are chemically similar to nicotine. Use of these insecticides has been increasing over the last 30 years. They are widely used in Wisconsin agriculture, with more than 500 pesticide products containing neonicotinoid active ingredients registered for use in the state. They're used on corn, soybeans, forage, small grains, vegetables and cranberries. Studies have shown that these pesticides are now found in groundwater-fed streams and DATCP monitoring data shows increased detections of them in samples collected around the state from monitoring wells, irrigation wells, private wells, and surface water.

Though functionally part of the PPCPs category of emerging contaminants, antibiotics and anti-parasitical drugs are also used in agriculture, to prevent infection outbreaks at large livestock rearing operations. The overall amount of antibiotics used in such applications may be similar to or even greater than usage of antibiotics in human medicine, but generally fewer antibiotic substances are used in livestock applications. An example of a livestock antibiotic is sulfamethazine. Sulfamethazine tends to sorb to soil and can be transformed under toxic conditions, but it may not be fully degraded to naturally occurring chemicals. Another type of contaminant from agriculture is hormones. Steroid hormones have been found in a study of dairy wastewater⁴.

For more information on pesticides, see the Pesticides section of the report.

Microbial Contaminants, including viruses and bacteria

Microbial contaminants such as viruses and pathogenic bacteria can be contaminants in groundwater. Most bacteria that exist in the natural environment are thought to present little if any human health risk and some bacteria can also improve water quality by degrading other emerging contaminants (e.g. PPCPs). However, some bacteria are pathogenic (disease causing) and can cause human health impacts. Areas where soil is thin and groundwater supplies are drawn from a carbonate (limestone/dolomite) bedrock aquifer may be especially susceptible to microbial contamination.

Two possible sources of microbial contaminants are livestock manure and human sanitary sewage. Pathogenic microbes from these sources may cause gastrointestinal illnesses, sometimes severe. A common type of enteric bacteria (bacteria that reside in the gut of humans and other animals) is *Escherichia coli* (commonly referred to as *E. coli*). Most strains of *E. coli* bacteria are harmless, but pathogenic strains do exist, for example the Shiga toxin-producing strain *E. coli* O157:H7. Water tests for *E. coli* detect a strain of *E. coli* that itself is harmless, but which is an indicator that pathogenic microbes may be present.

Viruses that have been detected in groundwater include norovirus, adenovirus and enterovirus. Viruses generally cannot reproduce without a host, but they can infect bacteria. A virus that infects, or replicates within bacteria is referred to as a "bacteriophage" (or simply "phage"). This usage of bacteria as hosts may enable viruses to survive longer in groundwater.

Antibiotic resistance is considered by the World Health Organization to be a major threat to health, food security, and development. After usage of an antibiotic, there is a tendency for bacteria that survived previous applications of the substance to become a larger part of the overall bacterial population—this phenomenon results in antibiotic resistance.

Antibiotics are used in both human and veterinary medicine; a greater number of antibiotic compounds are thought to be used by humans. As a consequence of antibiotic use in human medicine, multi-resistant bacteria (i.e., bacteria resistant to more than one antibiotic) have been found in clinical settings. Antibiotic resistance has been found in municipal wastewater discharge in studies in Europe, with patterns indicating that the resistance developed in clinical settings is spreading into the environment⁵. In another study, a strain of *E. coli* resistant to multiple antibiotics was found in hospital wastewater, although community wastewater appeared to be a greater overall contributor of antibiotic resistance⁶. In a study of groundwater impacted by dairies in California⁷, antibiotic resistant bacteria to be present in groundwater.

Human enteric virus indicators and pathogenic bacteria indicators have been found in groundwater supply wells in the Madison area⁸. Studies also suggest human enteric viruses from wastewater sources may be present in private and public drinking water wells across the state^{9,10,11,12,13}.

For more information on microbial pathogens, see the Bacteria, Viruses and Other Pathogens section of the report.

Microplastics

Microplastics are small pieces of plastic, often less than 1 millimeter in size. The name "micro" broadly refers to the size range of micrometers—a micrometer is one one-thousandth of a millimeter. Some microplastics are produced at this size for specific (industrial) purposes, while others are breakdown products of larger plastics¹⁴. Microplastics have been found in marine environments for decades¹⁵, but more recently are being discovered in terrestrial environments, including Lake Michigan¹⁶.

A study published in the journal *Science* found atmospheric deposition of, on average, 132 plastics per square meter every day on western U.S. protected lands¹⁷. Microplastics appear to accumulate in soils, including ones used for agriculture¹⁵. Another study found microplastics—possibly leaked from septic systems—in karst groundwater in Illinois¹⁸. While infiltration of water through soils might slow, minimize, or prevent the spread of microplastics into groundwater due to the filtering effect of soils, karst groundwater is particularly susceptible to contamination because water often flows through open fractures with minimal

filtering. Wisconsin has vulnerable Karst terrain groundwater aquifers but, to date, no studies of microplastics in state groundwater have yet been conducted.

Other Emerging Contaminants

There are other emerging contaminants that have the potential to impact groundwater in Wisconsin. Emerging contaminants not discussed above but which have been studied worldwide include flame retardants, phthalates and other plasticizers, and nanomaterials.

Flame retardants are substances that are added to household, commercial building or other products to reduce flammability. A subset of flame retardants of particular concern are brominated compounds, such as polybrominated diphenyl ethers (often abbreviated "PBDEs") and polybrominated biphenyls (often abbreviated "PBBs"). Brominated flame retardants have been detected in shallow groundwater at municipal biosolids land application sites¹⁹. No sampling for these compounds has yet been done in Wisconsin groundwater.

Phthalates are used in bendable plastics as softening agents but are not chemically bound to the plastic and can leach out into water. Research indicates that they might not bioaccumulate (unlike many other synthetic organic compounds), but they have been found to be endocrine disrupting compounds, or substances that disrupt endocrine systems of humans and animals. State groundwater quality standards, in ch. NR 140, have been established for Dibutyl phthalate and Di (2–ethylhexyl) phthalate/DEHP.

Nanomaterials are industrially produced physical particles that are between approximately 1 and 100 nanometers in size (there are one million nanometers in one millimeter). They have diverse uses in industry and commercial products, such as electronic components, paints and coatings, ultraviolet blockers in sunscreens, telecommunication, packaging materials and auto parts.

What are the human health concerns?

Health effects of emerging contaminants vary and are not always well understood. Some emerging contaminants, including some pesticides and PPCPs, act as endocrine disrupting compounds (EDCs), which adversely affect the behavior of natural hormones in animals and humans. EDCs include both anthropogenic chemicals, such as pesticides and plasticizers, and naturally occurring compounds like steroids and plant-produced estrogens. Scientific studies suggest toxic endpoints varying by compound, with possible health effects including developmental, reproductive, neurologic and immune problems, as well as cancer²⁰. In many cases, more research is needed.

How are emerging contaminants trending over time?

In Wisconsin law, there is an established process for regulated facilitates to review groundwater monitoring data and identify contaminants of emerging concern (WI 160.27). A fundamental component of this process is the long-term groundwater monitoring data itself, so maintenance and expansion of current networks is an ongoing priority for the GCC.

Periodic groundwater monitoring in areas known to be vulnerable to emerging contaminants is another way in which GCC agencies coordinate efforts to understand



Nested piezometers installed for monitoring groundwater levels and sampling for groundwater contaminants near Spring Green. Photo: Blake Russo-Nixon.

emerging contaminants. DATCP's regular statistical survey of agricultural chemicals and targeted monitoring programs in agricultural areas are examples of this. The DNR also regularly reviews groundwater monitoring data collected near active and closed landfills, mining operations and hazardous waste remediation sites to gather information on potential sources of emerging contaminants.

The US EPA has a process for regularly gathering data on emerging contaminants and assessing potential risks nationwide. The Unregulated Contaminant Monitoring Rule (UCMR) provides for monitoring of unregulated contaminants every five years, in all large (serving > 10,000 people) and a sample of small (serving < 10,000 people) public water systems. The Third UCMR (UCMR3) monitoring period was completed in 2015. Monitoring for the Fourth UCMR (UCMR4) began during 2018 and focused on select pesticides and several naturally occurring compounds. The Fifth UCMR (UCMR5) began in 2023 and focuses on PFAS, with an expanded analyte list and lower detection limits compared to UCMR3. Data collected at Wisconsin public water supply systems during UCMR monitoring along with GCC-supported monitoring and occurrence study results provide valuable information on the occurrence of emerging contaminants in Wisconsin's groundwater resources.

The US EPA also maintains a <u>Contaminant Candidate List (CCL)</u> of physical, chemical, biological and radiological substances that might potentially be found in drinking water. Potential contaminants listed on the CCL are substances not currently subject to federal Safe Drinking Water Act (SDWA) regulation but are known, or anticipated to be present in public water supply systems. The US EPA evaluates occurrence data on these unregulated contaminants and this information assists with identification of potential emerging contaminants in Wisconsin groundwater.

Further Reading

DNR overview of pharmaceuticals and PCPs in the environment

- DNR overview of per- and polyfluoroalkyl substance (PFAS) contamination
- <u>Wisconsin Remediation and Redevelopment Database (WRRD)</u>
- DATCP Groundwater Quality Reports
- <u>NIH factsheet on endocrine disruptors</u>
- US EPA Third Unregulated Contaminant Monitoring Rule (2012-2016) fact sheets
- US EPA Third Unregulated Contaminant Monitoring Rule (2012-2016) data summary
- US EPA Fourth Unregulated Contaminant Monitoring Rule (2017-2021) information

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