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New Mexico Environment Department

State of Knowledge of Pharmaceutical, Personal Care Product, and Endocrine Disrupting Compound Removal during Municipal Wastewater Treatment

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Executive Summary

State of Knowledge of Pharmaceutical, Personal Care Product, and Endocrine Disrupting Compound Removal during Municipal Wastewater Treatment

New Mexico is an arid state and many communities work hard to provide adequate clean water for their citizens. Recycling of wastewater can extend water supplies, and some communities have systems in place to reuse wastewater for non-potable purposes such as industrial process water or irrigation of parks, golf courses, and roadway medians. Some communities, including the Village of Cloudcroft, are planning for more comprehensive reuse of wastewater that will include indirect potable reuse. Indirect potable water reuse can be planned or unplanned. Unplanned potable reuse occurs whenever wastewater effluent is discharged to a river that is a source of supply for a downstream community and is a frequent occurrence throughout the world. Planned indirect potable water reuse recognizes that the wastewater effluent is supplementing a community's native water supply, and may provide a level of treatment that exceeds ordinary wastewater effluent discharge standards in order to protect the water supply.

A consideration in the implementation of a planned indirect potable water reuse project is the potential presence of unregulated or emerging contaminants. While technically the wastewater and water treatment plants are only required to meet state and federal requirements for such facilities, it is prudent to consider the fate of unregulated constituents that may nonetheless have potential impacts on human health. An emerging concern among the public, and thus an appropriate consideration for a planned indirect potable water reuse project, is the potential presence of pharmaceuticals and personal care products (PPCPs) and other endocrine disrupting chemicals (EDCs) in the wastewater.

Pharmaceuticals include antibiotics, analgesics (painkillers such as aspirin, ibuprofen [Advil®], acetaminophen [Tylenol®]), lipid regulators (e.g. atorvastatin, the active ingredient in Lipitor®), mood regulators (e.g. fluoxetine, the active ingredient in Prozac®), antiepileptics (e.g. carbamazepine, the active ingredient in many epilepsy and bipolar disorder medications), and many other medications. Personal care products can include cosmetics and fragrances, acne medication, insect repellants, lotions, detergents, and other products. Ingested pharmaceuticals can be excreted with human waste and enter the wastewater system. Additional pharmaceuticals can enter the wastewater system because of the common practice of flushing unused medication down the toilet. Personal care products can be washed from the skin and hair during washing or showering. Since chemicals can function as both pharmaceuticals and personal care products, PPCPs are typically considered together. Clearly, the number of PPCPs that are used in modern society and can potentially enter the wastewater system is vast.

Endocrine disrupting chemicals are chemicals that have the capability to interfere with the function of the human endocrine system (either stimulating or repressing function). EDCs can interfere with female sex hormones (estrogenic EDCs), male sex hormones (androgenic EDCs),

or hormones that control metabolism and many other systems in the body (thyroidal EDCs). EDCs include actual hormones, such as estrogens excreted from females after use of birth-control pills, or synthetic compounds that mimic the function of hormones, such as bisphenol A.

The purpose of this study was to evaluate and summarize existing knowledge available in technical literature about the ability of common water and wastewater treatment processes to remove PPCPs and EDCs from water, with a focus on the processes that may be used in a planned indirect potable water reuse project such as that currently being constructed in the Village of Cloudcroft. The report is organized according to each of the primary treatment processes, including (1) biological wastewater treatment (activated sludge and membrane bioreactor processes), (2) reverse osmosis, (3) activated carbon adsorption, and (4) oxidation and advanced oxidation processes. Each section starts with a brief description of the process. Following that, each section summarizes key information about each process, including (1) mechanisms of removal and the implications on either the product water or the waste stream, (2) general trends of removal efficiency, (3) trends regarding which micropollutants are poorly or highly removed, and (4) design or operating strategies to maximize removal.

Trends in removal of microconstituents by treatment processes

Membrane bioreactors (MBR) are a modification of the conventional activated sludge (CAS) process in which the secondary clarifier has been replaced with membrane filtration. MBR and CAS systems remove micropollutants by either biological degradation or adsorption to the sludge, which is then physically removed from the wastewater. The technical literature reviewed for this report had evaluated 49 compounds (49 studied in MBR systems and 33 studied in CAS systems). MBRs had similar or better removal than the CAS systems, depending on the study and the compound. The removal efficiency in the MBR systems ranged from slightly better to substantially better than in the CAS systems. Removal efficiencies observed in the articles that were reviewed is summarized in Table ES-1. Ninety percent removal or greater was achieved in at least one study for about a quarter of the compounds by CAS systems and nearly 40 percent of the compounds by MBR systems. Removal of 50 percent or less was achieved for about one-third of the compounds in MBR systems and two-thirds of the compounds in CAS systems. Seven compounds had no removal at all in MBR systems and three compounds had no removal at all in the CAS systems.

Reverse osmosis is a membrane-based treatment process that separates contaminants from water by forcing water through the membrane under pressure. Dissolved contaminants are separated from the water as the water passes through the membrane. Manufacturers sell a wide variety of membrane products that are marketed under a variety of product lines, with two common categories being nanofiltration (NF) membranes and reverse osmosis (RO) membranes. NF membranes are typically operated at lower pressure and used in inland brackish groundwater treatment, membrane softening, and other specialty applications. Many of the studies reviewed evaluated several membrane products and identified them as either nanofiltration or reverse osmosis membranes. Removal efficiencies observed in the articles reviewed for this report are summarized in Table ES-1. Sixty different compounds were evaluated. Eighty-two percent of the compounds exhibited 90 percent or greater removal by both RO and NF. Removal of 50 percent or less was achieved for 17 percent of compounds by NF and 12 percent of

Table ES-1. Summary of Removal of Micropollutants by Selected Water and Wastewater Treatment Processes.

Process	Studies	Compounds	Percent of compounds with no removal	Percent of compounds with removal below 50%	Percent of compounds with removal above 90% or to BDL ¹
MBR	12	49	14	33	39
CAS	12	33	9	64	27
NF	15	57		17	82
RO	15	60		12	82
GAC	10	29	0	0	97
PAC	10	71	6	31	41
Oxidants	20			(see text)	

¹ BDL = below detection limit.

compounds by RO. In general, removal by NF and RO were similar. In some isolated instances, RO performed better than NF.

Activated carbon is an effective adsorbent that is used for removing many dissolved compounds from water. Granular activated carbon (GAC) is used in a fixed-bed process like granular media filtration whereas powdered activated carbon (PAC) is added to water as a suspension, allowed to adsorb constituents from water, and then separated from the finished water. Numerous articles were identified that examined the removal of micropollutants from water by GAC, PAC, or both. GAC was studied with 29 compounds and achieved very high removal in nearly all cases. Removal efficiency is summarized in Table ES-1. The only compound that did not achieve greater than 90 percent removal was salicylic acid. PAC was studied with 71 compounds. Greater than 90 percent removal was achieved for 41 percent of the compounds, and less than 50 percent removal was achieved for 31 percent of the compounds. Low removal results generally corresponded to a low PAC dose (5 mg/L for many of the compounds).

While GAC was able to achieve high removal of nearly all compounds, the capacity of the bed and operating time before breakthrough occurs is an important part of the design and operation of GAC adsorbers. Accepted theory of activated carbon adsorption suggests that compounds not removed well would be the hydrophilic (polar or charged) or large-MW compounds. This trend was generally observed in the studies evaluated for this report. Hydrophilic compounds passed through GAC beds in as little as 2000 to 3000 bed volumes, whereas some hydrophobic compounds did not pass through until 70,000 bed volumes were treated. For a GAC adsorber operating with a 20-minute empty bed contact time (EBCT), 70,000 bed volumes represents 2.7 years of operation. In real operation, however, adsorption capacity and operating life can be dramatically reduced by competitive adsorption between compounds, particularly when natural organic matter is present.

A significant amount of research has been done on the ability of oxidants and advanced oxidation processes (AOPs) to degrade organic constituents in water. Oxidants include chlorine, chlorine dioxide, ozone, permanganate, and UV light, and AOPs used in water treatment include ozone/UV, ozone/hydrogen peroxide, and UV/peroxide. With high enough doses, some oxidants and AOPs can completely mineralize organic chemicals to carbon dioxide and water. Factors that affect the removal efficiency of organic constituents include the specific oxidant or AOP being used, the dose, the contact time, and the water matrix. Because of the wide variety of experimental conditions, it is not useful to summarize removal efficiency in a table as was done for the other treatment processes. In general, chlorine and UV light are not very effective for microconstituents at the doses normally used for disinfection. Insufficient research is available on the ability of chlorine dioxide and permanganate to degrade microconstituents. Ozone can accomplish excellent removal of many compounds, but the research reviewed in this study found some chemicals were less well degraded, including clofibric acid, ciprofloxacin, cyclophosphamide, 2-QCA, and DEET. Ozone-based AOPs such as ozone/UV and ozone/hydrogen peroxide can achieve higher removal of some compounds than ozone can by itself. While AOPs generally can achieve better removal than conventional oxidants, the research reviewed here differed with respect to the best AOP, depending on the experimental conditions and the constituents being targeted.

One limitation of the existing research is that relatively little has examined microconstituent removal by oxidants and AOPs in a wastewater matrix. Only 5 of the 20 articles reviewed here used wastewater as the feed solution; the others used drinking water or deionized water. The organic matter in wastewater may compete for the oxidation potential and lead to the necessity of using higher oxidant doses. Despite this, the potential for ozone or AOPs to be part of the treatment strategy for microconstituents in wastewater is great, and more research is needed in this area.

Although oxidation processes will degrade most organic compounds, it is important to recognize that the products might not be fully mineralized to carbon dioxide and water. Oxidation processes can degrade the compound so that the original compound is no longer biologically active, but may produce degradation products with unknown biological activity. More research into potential oxidation by-products is warranted. However, research has also shown that partial oxidation of many recalcitrant compounds can substantially increase their biodegradability. This effect can be exploited if an oxidation process immediately precedes a biological process to facilitate removal of resistant compounds. Ozone and biofiltration using GAC media is increasingly used in water treatment for control of organics such as disinfection by-products, and the combination of advanced oxidation followed by biofiltration might be a particularly effective method of eliminating PPCPs and EDCs. One study reviewed here found complete removal of all microconstituents for a process train consisting of conventional activated sludge treatment followed by ozone and biofiltration—a very promising result. More research is needed to determine appropriate conditions for combining these processes.

Design and operation strategies to maximize removal

Design and operational strategies to maximize micropollutant removal for indirect potable water reuse applications using biological processes, based on current information, include the following:

- Selection of the MBR process in lieu of the CAS process. The MBR process clearly produces better quality effluent than the CAS process with respect to conventional wastewater parameters such as biochemical oxygen demand (BOD), total organic carbon (TOC), total suspended solids (TSS), and pathogens. Thus, the MBR process provides better feed water quality for subsequent water treatment processes. The MBR process also achieves similar or greater micropollutant removal, depending on the compound.
- Operation of membrane bioreactors at higher values of sludge retention time (SRT).

Design and operational strategies to maximize micropollutant removal using reverse osmosis, based on accepted understanding of the mechanisms controlling the reverse osmosis process, include the following:

- Removal could theoretically be maximized by selection of “tighter” membranes (i.e., seawater RO in lieu of brackish water RO membranes, or brackish water RO membranes in lieu of nanofiltration membranes). Tighter membranes, however, typically operate at lower water flux rates. As a result, it would be necessary to increase the size of the system, which would increase capital costs. Tighter membranes may also require a higher feed pressure, which would increase operating costs.
- Removal could theoretically be improved by operating at a lower recovery. High recovery concentrates the micropollutants on the feed side of the membrane, and the higher concentration increases the mass transfer across the membrane, resulting in lower quality product water. Overall, recovery may have a minor impact on the removal efficiency. For practical and economic reasons, it is desirable to operate at the highest achievable recovery, but it is worth noting that the operating conditions that maximize micropollutant removal may be in conflict with desired operating conditions for cost-effective implementation.

Design and operational strategies to maximize micropollutant removal using carbon adsorption, based on accepted understanding of the mechanisms controlling the adsorption process, include the following:

- Selection of the carbon with the highest adsorption capacity for the compounds of interest. Bench- or pilot-testing is typically required for carbon selection.
- Select GAC adsorption instead of PAC adsorption. GAC uses the adsorption capacity of carbon more effectively and is more appropriate for applications requiring continuous removal.
- If using PAC, increase the carbon dose and/or the contact time. However, carbon dose has a direct effect on the operating cost of the process.
- If using GAC, increase the carbon bed volume with respect to the flowrate being treated (i.e., increase the empty bed contact time). However, bed volume has a direct effect on the capital

cost of the process. Monitor effluent concentrations and regenerate and replace media when breakthrough occurs.

- Couple carbon adsorption with a pretreatment process that will minimize the influent total organic carbon concentration and therefore minimize the negative impacts of competitive adsorption.

Limited information is available on appropriate design and operational strategies to maximize micropollutant removal using oxidants and AOPs in wastewater. Oxidants and AOPs should be applied after biological treatment to minimize competition from wastewater organics (i.e., apply oxidants in the effluent rather than influent of a wastewater treatment plant). Ozone, ozone-based AOPs, or UV/hydrogen peroxide appear to be the best oxidant choices. Higher doses and contact times can achieve better removal, but site-specific studies are needed to determine the appropriate doses and contact times for specific applications. A promising process combination for complete removal of microconstituents is biological treatment to degrade all easily degradable matter (i.e., MBR treatment), followed by advanced oxidation to break down recalcitrant compounds, followed by biofiltration to degrade the products from the chemical oxidation step. This process combination may have benefits over the use of reverse osmosis because of higher water recovery and less waste production, and possibly less energy consumption. This process combination should be investigated further.

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State of Knowledge of Pharmaceutical, Personal Care Product, and Endocrine Disrupting Compound Removal during Municipal Wastewater Treatment

Introduction

A clean and abundant water supply is often taken for granted in the United States. People do not think about their drinking water unless shortages force water rationing or the quality of water becomes the target of reporting in the news media, such as the recent Associated Press story ¹ about trace concentrations of pharmaceuticals and personal care products in the nation's water supply. For the residents of the Village of Cloudcroft NM, issues of water quantity and quality are both daily concerns. In recent years, Cloudcroft has experienced severe water shortages and has had to truck in water to meet demand during the summer tourist season. To meet their drinking water needs, the Village of Cloudcroft is taking an innovative approach to supplementing their supply of fresh water; the village is planning to indirectly reuse its wastewater. State-of-the-art water and wastewater treatment facilities are being built, which may have implications to other communities experiencing water shortages. Wastewater will be treated by a series of advanced treatment processes to produce very high quality effluent. The effluent will be blended with well and spring water (the current source of water for the community) and stored in a covered reservoir. The blended water will then be treated by a water treatment plant, chlorinated, and pumped into the village distribution system. Water from this process is expected to easily meet all Safe Drinking Water Act requirements. In addition, the village, the regulatory agencies, and the design engineers are concerned about the possible presence of unregulated microconstituents in the treated water. The objective of this report is to review the current state of knowledge regarding the presence of these constituents in wastewater and summarize their removal by advanced wastewater and drinking water treatment processes.

Indirect potable water reuse can be planned or unplanned. Unplanned indirect potable water reuse occurs whenever wastewater effluent is discharged to a water body that is a source of supply for a downstream community. Planned indirect potable water reuse has been practiced in the US since the 1970s ². Planned indirect potable water reuse involves treating wastewater to a point where it can be used as a raw water supply, which is then further treated to potable standards ². This practice can be economically feasible for communities with limited water supplies, but several issues must be considered. These include:

- The treated water must be of high quality and must meet, state, and federal drinking water regulations.
- The water and wastewater treatment techniques must be reliable.
- The system must be economically feasible.
- An environmental barrier such as a reservoir or aquifer must be part of the system.
- The treated water must be acceptable to the public. A system may produce the cleanest, safest drinking water in the world but if no one trusts the water or if public sentiment towards the treated water is negative, then there is still a problem.

This last point, public acceptability, may ultimately be the factor that controls whether it is possible to implement a planned indirect potable water reuse system. Public perception may be sufficiently negative to restrict water reuse options even if health and treatment information suggests that a particular reuse strategy will be protective of human health. For instance, an AP story was published in early 2008 reporting that the drinking water supplies for at least 41 million Americans was found to have pharmaceuticals in them¹. The story raised public awareness about the presence of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) in the nation's water supply, and may encourage efforts to regulate the removals of PPCPs and EDCs from drinking water.

PPCPs and EDCs are present in water at very low concentrations and therefore are frequently referred to collectively as microconstituents. PPCPs include but are not limited to fragrances, antibiotics, analgesics, insect repellants, lipid regulators, and antiepileptics. Many PPCPs are also EDCs, which are compounds that can disrupt an organism's endocrine system, often resulting in changes to its hormonal balance³. People have been aware of EDCs since the 1930s and they have been detected in surface and even finished drinking waters since the 1960s and 1970s⁴. There are three general classes of EDCs: estrogenic or anti-estrogenic (female sex hormones), androgenic or anti-androgenic (male sex hormones), and thyroidal compounds (hormones that control metabolism and many other systems in the body)^{5,6}. Although there is currently no comprehensive list of EDCs, efforts are underway to develop one. One problem in forming this list is that a huge number of chemicals are in use in commerce today and most of these chemicals have yet to be screened for endocrine function.

Microconstituents have been detected in wastewater in the US since the 1960s and 1970s and concern has been growing more recently about whether these chemicals pose a risk from an environmental or human health perspective⁶. Much of this concern is fueled not by an increase in the concentration of these compounds in drinking water supplies, but rather by the improved ability to detect them at very low concentrations. Current analytical methods can detect many organic compounds at concentration levels as low as 1 ng/L or 1 part per trillion (ppt)⁴. Another concern is the potential for synergistic effects of mixtures of microconstituents. A recent study has demonstrated that certain compounds that coexist in water pose greater threats than if they were to exist alone⁷. Another concern is that antibiotics found in trace amounts might lead to the formation of resistant strains of bacteria.

Discharge from wastewater treatment plants (WWTPs) have been shown to be a major source of many microconstituents^{3,5,8}. A large portion of PPCPs enters wastewater as human excretions of unmetabolized or partly metabolized pharmaceuticals^{9,10}. Another source is believed to be through disposal of expired medications through sinks or toilets. Untreated animal waste, manufacturing residues⁹, household chemicals, and pesticides are other sources of microconstituents¹¹.

Since wastewater is a major source of microconstituents, it is important to consider this class of potential contaminants when considering a planned indirect potable water reuse project. Specifically, it is important to understand which treatment processes will remove microconstituents from water and wastewater and to what degree. The purpose of this study was to evaluate and summarize existing knowledge available in technical literature about the ability

of common water and wastewater treatment processes to remove PPCPs and EDCs from water, with a focus on the processes that may be used in a planned indirect potable water reuse project such as that currently being constructed in the Village of Cloudcroft. The process train for the Cloudcroft water and wastewater treatment facilities is shown in Figure 1. These processes include membrane bioreactors (MBRs), reverse osmosis (RO), advanced oxidation using ultraviolet light (UV) and hydrogen peroxide (H_2O_2), and adsorption by granular activated carbon (GAC). The Cloudcroft treatment train also includes ultrafiltration, but it is widely recognized that ultrafiltration is not effective for microconstituent removal, so it will not be discussed in detail in this report.

A significant amount of technical literature, encompassing nearly 50 articles, was identified for this study. The literature includes results of research conducted at bench-, pilot-, and full-scale. Studies of removal from full-scale facilities can provide the most reliable indicator of removal efficiency for a specific set of design and operating conditions. The results can also be predictive of removal at other facilities when the design and operating conditions are similar. However, full-scale results can be less helpful for predicting results at other facilities if the design and operating conditions are different, if influent water quality is different, if new processes are to be considered, or if contaminants are not detectable in the influent of existing facilities. Furthermore, the number of studies that evaluate the ability of full-scale facilities to remove PPCPs and EDCs is somewhat limited, particularly in the case of newer technologies like membrane bioreactors. Bench- and pilot-scale studies can be used to evaluate a range of operating conditions that cannot be tested easily at full-scale, the effect of different design and operating conditions, the removal of compounds that are not present in full-scale wastewater influent (via spiking), and the relative ability of multiple and/or new processes. Pilot studies are frequently required by regulatory agencies to verify performance of treatment facilities prior to the construction of full-scale facilities. Thus, the results of bench- and pilot-scale studies can greatly extend our understanding of the ability of treatment processes to remove PPCPs and EDCs. Nevertheless, comparisons between full-scale systems and smaller systems must be made with caution because the scale of a system can affect the performance of a system, particularly in cases where hydrodynamic conditions cannot be scaled easily. For instance, fouling and flux in bench-scale membrane systems cannot be used to predict fouling and flux of full-scale membrane systems because the hydrodynamics of flat sheet bench-scale membranes are significantly different than full-scale membrane modules. Bench testing with synthetic water or single contaminants can provide valuable information about the mechanisms of removal but may not be representative of full-scale performance with natural waters when competitive interactions between constituents in the water may predominate. When water matrix, hydrodynamic conditions, and other factors are consistent between systems, bench- or pilot-scale systems can effectively predict performance that will be achieved at full-scale.

This report begins with a description of how the properties of microconstituents affect their removal during treatment. Following that section, a brief description of membrane processes is provided because MBR and RO both use membranes, but the removal mechanisms are entirely different. The remaining sections deal with each process in sequence. For each process, the section summarizes (1) a brief description of the process key (2) mechanisms of removal and the implications on either the product water or the waste stream, (3) general trends of removal

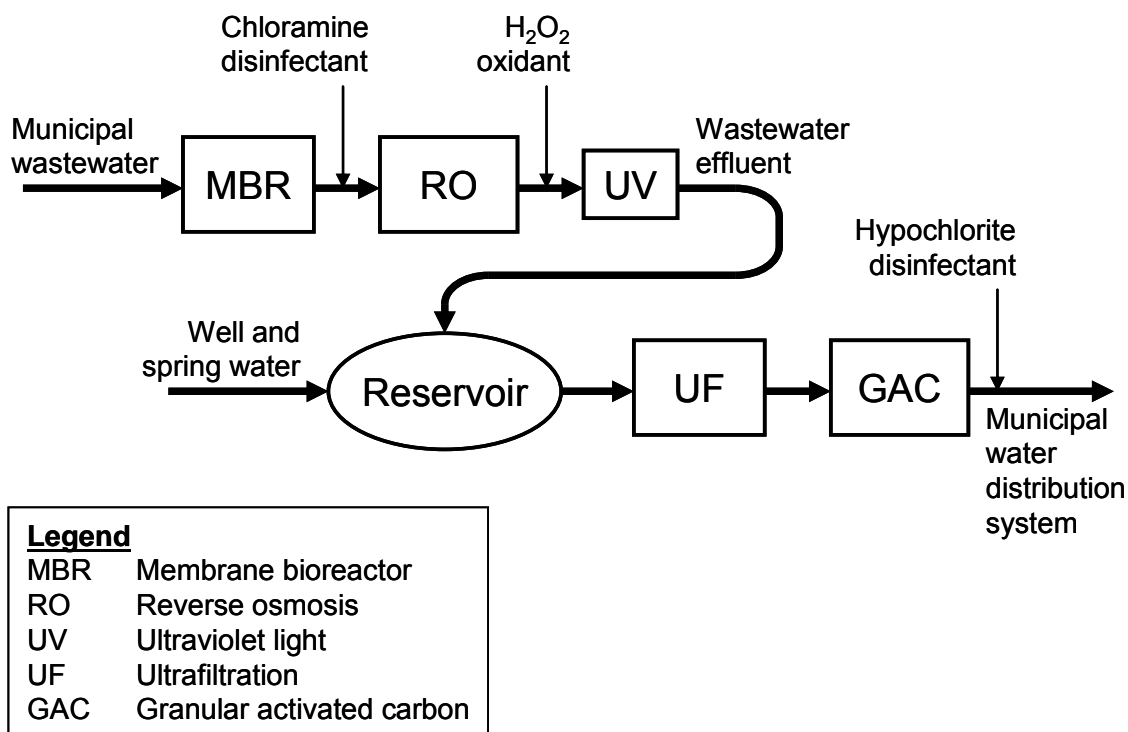


Figure 1 – Process train for the Village of Cloudcroft water and wastewater treatment facilities.

efficiency, (4) trends regarding which micropollutants are poorly or highly removed, and (5) design or operating strategies to maximize removal.

Properties of Microconstituents and Their Effect on Treatment

Separation of contaminants from water or wastewater is accomplished by exploiting differences in physical, chemical, and biological properties between the contaminants and water. These properties include molecular weight, solubility, charge, polarity, volatility, chemical reactivity, biodegradability, and others. Often, groups of compounds with similar properties can be removed by a single treatment process that exploits a specific property. There are thousands of different drugs and chemical compounds in use today that can, and do, end up in water with a correspondingly large variation in their physical, chemical, and biological properties¹². These compounds will respond differently to different treatment techniques.

Another factor for removing microconstituents from drinking water is that many compounds, especially pharmaceuticals, are designed with specific properties that make them resistant to removal by some treatment techniques¹³. These include:

- High chemical stability

- High water solubility
- Low biodegradability
- Low sorption coefficients

Although these characteristics may be desirable for a pharmaceutical and aid in the compound's intended purpose, they can also be characteristics that make the compound harder to remove from water. Of course, different compounds will have different properties that will affect their removal by the treatment processes being used.

Description of Membrane Processes

Membrane bioreactors, reverse osmosis, and ultrafiltration are processes that rely on membranes to separate contaminants from water. Membranes used in water and wastewater treatment are thin synthetic plastics that allow water to pass through while specific constituents in the water are retained. Even though MBR, RO, and UF processes all incorporate membranes, the processes are fundamentally different and the membranes perform different functions. These differences have important implications for water and wastewater treatment processes and their effectiveness at removing microconstituents. For this reason, a basic understanding of membranes and their differences is necessary before specific microconstituent removal technologies can be discussed. A brief description of these membrane processes and the primary differences between them is provided in this section. The book *Water Treatment: Principles and Design* by Crittenden et al.¹⁴ provides a thorough discussion of membrane processes used in water treatment and the following summary is based largely on that source.

Four types of membranes are used in municipal water and wastewater treatment. These membranes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membranes. They are classified by such characteristics as nominal pore dimensions (pore size), operating pressures, and the types of constituents the membranes reject. Figure 2 shows these membrane types in descending order of pore size¹⁴. It is important to note that membrane classification is somewhat arbitrary and that different manufacturers might market similar membranes under different classifications. In water and wastewater treatment, these four membrane classifications belong to either of two distinct physicochemical separation processes. MF and UF membranes are used in a process called "membrane filtration" whereas NF and RO membranes are used in a process called "reverse osmosis." RO membrane manufacturers market their merchandise as being in a variety of product lines, including seawater reverse osmosis (SWRO), brackish water reverse osmosis (BWRO), low-pressure reverse osmosis (LPRO), ultra low-pressure reverse osmosis (ULPRO), and nanofiltration (NF). While older literature sometimes identifies nanofiltration and reverse osmosis as independent processes, they in fact rely on similar mechanisms and NF membranes are generally recognized today as a product line, not a unique separation process.

The objective of membrane filtration is removal of particulate matter and is achieved by straining particles that are larger than the membrane's pore size¹⁴. Thus, the primary removal mechanism is sieving where the larger particles are physically blocked from entering the smaller pores. Membrane filtration is very effective at removing particles larger than 0.1 to 0.01 μm . Membrane filtration is used in membrane bioreactors.

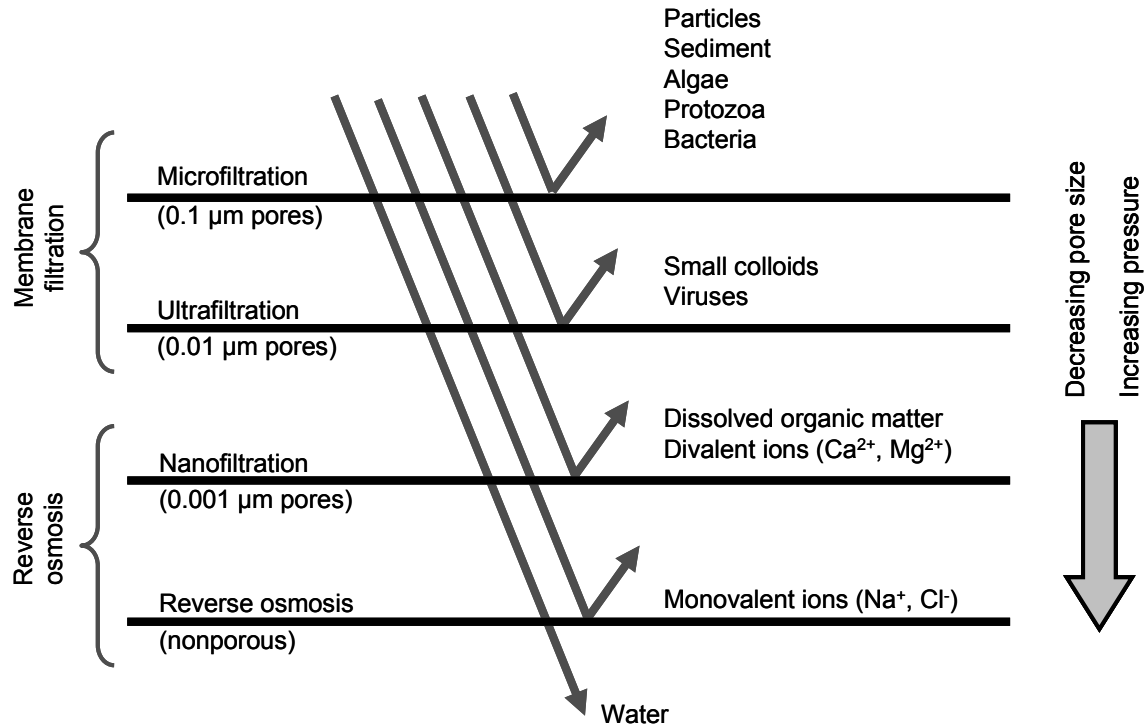


Figure 2 – Membranes used in water treatment ¹⁴.

While membrane filtration relies on separation based on the size of the suspended solids, reverse osmosis separates dissolved constituents from solution ¹⁴. The separation mechanism depends on differences in the rate of diffusion of solutes through the RO membrane rather than mechanical sieving based on membrane pore size. As a result, the removal efficiency for RO is dependent on such parameters as pressure, water flux rate, and influent solute concentration. The removal efficiency varies from about 50 percent to greater than 99 percent and depends on solute charge, polarity, and molecular weight. Even with these lower removal efficiencies, the RO process has shown that it can effectively remove most microconstituents and, as this report will discuss in more detail, can be much more effective than membrane filtration processes at PPCP removal.

RO membranes can be engineered for specific objectives. The uses for RO systems include desalination of brackish water, water softening, and the removal of specific contaminants and natural organic matter (NOM) ¹⁴. This specificity makes a reverse osmosis system ideal for the removal of PPCPs from water. It is also why the EPA has designated RO as a best available technology for the removal of many inorganic contaminants and most synthetic organic compounds. Although the reverse osmosis process can be very effective at removing microconstituents from water, there are some drawbacks to the process that will also be discussed in this report.

Membrane fouling is one of the greatest challenges affecting the design and operation of membrane facilities ¹⁴. Fouling is defined as the “process resulting in loss of performance of a

membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores”¹⁴. Fouling is characterized by a loss of specific flux. Fouling of RO membranes is particularly difficult to manage if the feed consists of treated wastewater because of the high concentration of dissolved organic matter which is hard to clean and can cause rapid fouling.

Most RO plants operate at a constant membrane flux (the rate of flow through the membrane). This constant flux is maintained by increasing the transmembrane pressure to make up for the loss of specific flux, which is caused by fouling on the membrane surface. This matter can be removed during the backwash cycle (for membrane filtration only) and further removal can be obtained during membrane cleaning, which involves the use of chemicals. Depending on the type and extent, most fouling is considered reversible and membrane flux can be re-established by membrane cleaning. The portion of specific flux that cannot be recovered by backwashing or cleaning is considered irreversible. This permanent loss in flux is dependent on both the source water and the type of membrane used.

Activated Sludge and Membrane Bioreactor Processes

Many WWTPs use the conventional activated sludge (CAS) process to treat wastewater. The CAS process is a biological process that involves aerobic biodegradation of suspended and dissolved organics in wastewater. The process involves developing a mixed culture of suspended microorganisms in an aeration basin. The microorganisms are separated from the treated wastewater by gravity settling and recycled back to the aeration basin. The supernatant from the clarifier becomes the treated wastewater effluent. The CAS process is highly effective at removing organic constituents; a well-operated plant will remove greater than 90 percent of both the suspended and dissolved organic material in the influent wastewater. Typical effluent limits on a CAS plant consist of maximum concentrations of 30 mg/L for both 5-day biochemical oxygen demand (BOD₅) and total suspended solids (TSS).

Membrane bioreactors (MBRs) have become increasingly popular over the last ten to fifteen years as the technology has improved and the price of membrane filtration units has dropped¹⁵. A membrane bioreactor combines the processes of biological treatment and membrane separation¹⁶. The MBR process is identical to that in CAS except that the suspended microorganisms are separated from the treated effluent by membrane filtration instead of by gravity settling. This modification produces a much higher quality effluent because the concentration of suspended solids is essentially zero. The BOD₅ concentration of an MBR plant is also low because much of the effluent BOD₅ from a CAS plant is due to suspended solids. Diagrams of a CAS and an MBR plant are shown in Figures 3 and 4, respectively.

In an MBR plant, the membranes can be configured inside the aeration basin or externally¹⁶. The membrane of an MBR achieves nearly complete removal of suspended solids¹⁷. Since solids separation does not depend on the settling characteristics of the biomass, separation with a membrane allows for higher concentration of biomass in the aeration basin, which can reduce the size of treatment plant.

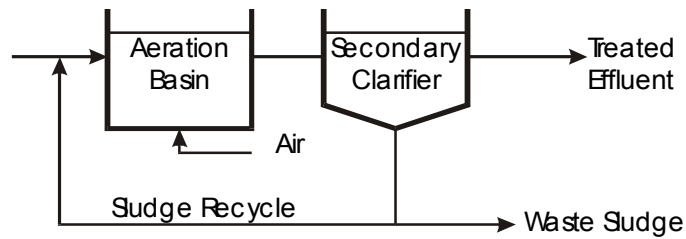


Figure 3 – Flow diagram of the conventional activated sludge (CAS) process.

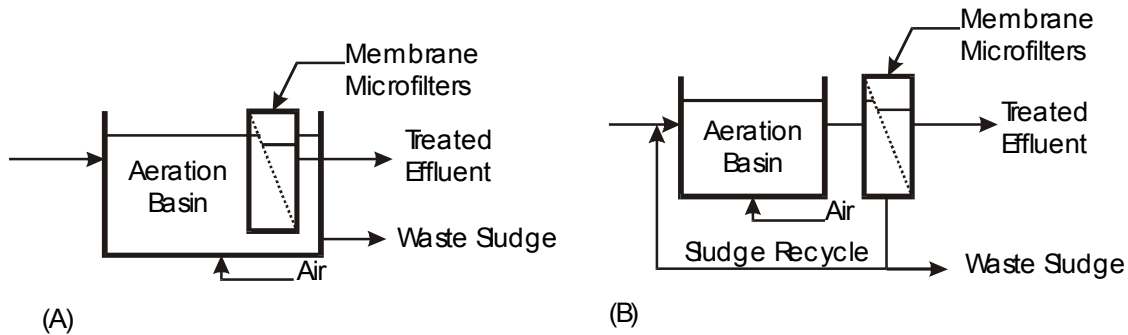


Figure 4 – Flow diagram of the membrane bioreactor (MBR) process with (A) membrane filters located in the aeration basin and (B) membrane filters located outside of the aeration basin.

The performance of the activated sludge process depends in large part on the rate of growth of the microorganisms. This dependence is principally because microbial growth in a treatment plant is substrate limited. Thus, as the food supply is reduced to lower concentrations, the rate of growth of the organisms decreases. A key parameter controlling the activated sludge process is the solids retention time (SRT), which is the average age of microorganisms in the system. SRT is inversely proportional to the rate of growth so that a long SRT corresponds to the presence of a slow growing suspended culture. In the CAS, the SRT is limited by the settling characteristics of the microbial population to a maximum of 15 days¹⁴. Because the MBR process does not depend on settleability, higher SRT values can be used with correspondingly better removal of many trace constituents in the solution^{15,17}. This increase in SRT has many benefits and may be especially important in the removal of microconstituents. The concentration of biomass is an important parameter in the quality of effluent produced both in terms of conventional parameters and in the removal efficiencies of microconstituents¹⁵.

MBRs have many advantages over the CAS process. Four of the most common advantages that MBRs have over CAS processes are¹⁶:

1. The effluent from an MBR plant is better than that from a CAS plant for all conventional wastewater parameters including BOD₅, chemical oxygen demand (COD), total organic carbon (TOC), TSS, and ammonium content^{15,18}. The effective pore size of the membrane (typically <0.1 μm) is smaller than most bacteria found in wastewater^{6,16}. This reduces the

need for disinfection processes that may lead to production of disinfection byproducts (DBPs). There is evidence that some DBPs may act as EDCs ⁴.

2. MBRs produce less sludge because of the longer SRT. Less sludge production decreases the waste that must be disposed of, which also decreases disposal expenses.
3. MBRs can operate at higher mixed liquor suspended solids (MLSS) concentrations. This facilitates growth of nitrifying bacteria, which oxidize ammonia to nitrate (NO₃⁻).
4. MBRs allow for independent control of SRT and hydraulic retention time (HRT). This allows for a decrease in HRT while maintaining a long SRT. CAS processes must allow a long enough HRT for mixed liquor solid particles to grow microbial floc that is large enough to settle well (~50 μm) ¹⁷. For an MBR system, the particles only need to be larger than the membrane pore size. A reduction in the HRT decreases the volume of the aeration tank.

The ability to operate MBRs at a long SRT can increase microconstituent removal in a couple ways. One way is that the hydrophobic organic compounds can accumulate on the sludge. The compounds are then removed from the effluent during the separation of the sludge from the effluent. Another way is the adaptation of bacteria to degrade recalcitrant compounds in the system as other, more degradable substrates, are consumed by the culture ¹⁷.

Some research has shown that the CAS process effectively removes many microconstituents but is ineffective at removing others ⁹. The following section summarizes the results of previous investigations of removal of microconstituents by biological processes.

Mechanisms for microconstituent removal by biological processes

The removal of microconstituents by biological processes can be attributed primarily to two mechanisms, sorption and degradation ^{15,17,19}. Sorption is a term that includes adsorption, absorption, and ion exchange and is used when it is not clear which is occurring ¹⁴. For the MBR process, sorption is the transfer of microconstituents from the water to either the sludge or the membrane ^{19,20}. Sludge in CAS and MBRs have large specific sorption capacities that can be attributed to the high specific surface area of the suspended microbial population ¹⁹. Despite the large sorption capacity, current research is showing that the removal of many microconstituents by the MBR process is mainly due to biodegradation/biotransformation. Better biodegradation/biotransformation of compounds is due to the low concentration of TOC in a slow growing culture with long SRT. This forces organisms to develop degradation pathways for slowly degradable compounds in order to continue to recover energy to support microbial growth. Although there has been some contradicting research about the effect of SRT on some compounds ¹⁹, many reports have shown that a higher SRT increases biodegradation and therefore increases removal ^{15,17,19,20}. Since MBRs can operate at much higher SRTs, they obviously have an advantage over CAS systems.

Another possible mechanism of microconstituent removal by MBRs is the membrane itself. The mechanisms for removal by membranes include size exclusion, charge repulsion, and adsorption ²⁰. Comerton, et al. found that UF membranes were capable of sorbing microconstituents ²⁰. Due to the relatively large pores on UF membranes (microconstituents are at least 100 times smaller than the smallest pore sizes of these membranes), size exclusion does not contribute to the removal of microconstituents by the MBR process. Factors that can influence the adsorption of PPCPs onto the membranes include the characteristics of the chemicals (size, charge,

hydrophobicity) and the membranes (charge, hydrophobicity, roughness), and the properties of the water (temperature, ionic strength, presence of various constituents).

A primary advantage of biological degradation is that the micropollutants are eliminated from the environment rather than being transferred and concentrated in a waste stream. A potential disadvantage is that the contaminants might not be completely degraded to harmless compounds and the degradation products may exhibit toxicity. When adsorption to the sludge occurs, the micropollutants are physically removed from the wastewater without forming degradation products. Wastewater sludge is typically subjected to an additional biological degradation process and then applied to land or landfilled.

Microconstituent removal effectiveness by biological treatment processes

Table 1 summarizes information on 12 investigations of microconstituent removal by MBR and CAS processes. Because the interest in microconstituent removal is recent and MBRs are a relatively new technology, the articles listed are all within the last 5 years. Many of the researchers studied only a small number of target microconstituents, in part because of the analytical challenges associated with measuring these compounds. The target compounds and their removal efficiencies in the MBR and CAS processes in the studies from Table 1 are shown in Table 2. Although many of the studies covered in this literature review have varying ranges of compounds studied, some trends are evident in the findings. These include:

1. The studies confirm that MBRs achieved comparable or better removal of microconstituents than the CAS process. A couple studies found only slightly better performance^{17, 18} while other studies reported much better removal for many more compounds^{15, 19, 21, 22}. A wide range of removal efficiencies is shown in Table 2. The conclusion of most of the investigations was that the MBR process can remove some microconstituents well but other compounds are left unaffected. Only a few microconstituents were removed to below the method reporting limit (MRL)^{6, 15, 17-19, 23, 24}.
2. The investigations confirm that longer SRTs in the MBR process produce a more diverse microbial population that enhances nitrification and removal of poorly degradable compounds^{6, 16, 18-20}.
3. Biodegradation and sorption to the sludge and membrane²⁰ were the main removal mechanisms for microconstituent removal by the MBR process^{15, 17}. Although both of these mechanisms can remove microconstituents, biodegradation was found to be the most effective mechanism for microconstituent removal^{3, 6, 19}.
4. MBRs do an exceptional job in removal of traditional wastewater parameters including TOC, total suspended solids (TSS), ammonium, and COD^{15, 16}.

MBRs did not effectively remove some compounds including diclofenac^{18, 19, 24}. Several studies found that the antiepileptic medication carbamazepine is especially persistent with both the MBR and CAS process having little to no effect^{15, 17, 22, 24, 25}. Seven compounds that were not removed at all in the research by at least one research group included carbamazepine, DEET, diclofenac, EDTA, hydrocodone, TCEP, and trimethoprim.

Table 1: References, information, and comments on PPCP/EDC removal by CAS and MBR processes

Reference	Type of systems	Scale	Source of wastewater	Source of compounds	Number of compounds evaluated	Comments
Kimura, et al. (2007)	MBR	Pilot	Municipal Wastewater	Wastewater	6	MBR with longer SRT (65 vs 15 days) performed better. Longer SRT means more diversity. Elimination in both CAS and MBR primarily due to biodegradation although sorption plays a key role as well. The MBR's generally showed better removal than CAS process.
Radjenovic, et al. (2007)	MBR/CAS	Bench (MBR), full scale (CAS)	Municipal Wastewater	Wastewater and spiked	22	MBR outperformed CAS in removing most compounds with smaller variations in efficiency in the MBR. MBR will not completely remove micropollutants and should be modified for optimization. Modifications could include changes in membranes and inoculation of special microorganisms.
Clara, et al. (2005)	MBR/CAS	Pilot (MBR), full scale (CAS)	Municipal Wastewater	Wastewater	11	Study used MBR with UF membrane operated at different SRTs. UF membranes did not achieve higher removal due to size exclusion. Carbamazepine was not removed by either process while some compounds were removed at >90% for both processes. Only slight differences in compound removal observed between processes. MBRs recommended for reuse of treated wastewater and offer other advantages over CAS. Longer SRT improved performance in both processes.
Kimura, et al. (2004)	MBR/CAS	Pilot (MBR), full scale (CAS)	Municipal Wastewater	Wastewater	7	MBR with MF membrane exhibited much better removal for ketoprofen and naproxen than CAS. The other compounds were observed to receive comparable removal. Increased removal attributed to MBRs with longer SRT so adaptation of microorganisms to less degradable compounds could occur.

Table 1 (continued): References, information, and comments on PPCP/EDC removal by CAS and MBR processes

Reference	Type of systems	Scale	Source of wastewater	Source of compounds	Number of compounds evaluated	Comments
Comerton, et al. (2007)	MBR/RO/NF/UF	Bench	Lake water, wastewater effluent, and DI water	Spiked	22	Study looked at adsorption of PPCPs to membranes with UF>NF>RO. This is due to the membranes with larger pores sizes allowing solutes to access many more binding sites within the membrane. Larger pore sizes also mean less rejection due to size exclusion which has been found to be a major contributor in removing micropollutants.
Wintgens, et al. (2004)	MBR/NF/RO	Full scale	Landfill leachate treatment plant	Non-spiked	2	Removal of BPA by MBR was 99% with CAS process removing 91%. Biodegradation was most effective with higher sludge age and complete retention of solids.
Snyder, et al. (2007)	MBR/NF/UF/RO/NF and combination of systems	Bench/pilot/full scale	Primary and secondary wastewater effluent, groundwater, secondary wastewater	Spiked and non-spiked	36	MBR effective at reducing concentrations of many PPCPs/EDCs although several compounds were unaffected and very few compounds were found to be removed below the MRL. Study also found that MBR's shows promise at removing hormones. Removal is likely due to biodegradability and results were found to vary greatly.
Baumgarten et al. (2007)	MBR/PAC/NF/RO/O ₃ /O ₃ with UV	lab and pilot	Municipal and industrial wastewater	Wastewater and spiked	5	Pilot scale MBRs treated spiked municipal and industrial wastewater. They were run with and without PAC addition (50<PAC<200mg/L). Results for the MBR without PAC addition varied from <LOQ to 27% elimination. Elimination greatly increased with PAC dose with most achieving > 94% elimination. Contributed adsorption rather than biodegradation to elimination but this was with addition of PAC.
Kim et al. (2006)	MBR/GAC/RO/NF & UV in combination with RO and NF	Full/pilot	Wastewater and surface waters	Non-spiked	26	MBR showed limited removal of target compounds but was effective at removing hormones and some pharmaceuticals. Conventional drinking water treatment processes found to be inefficient and CAS showed incomplete removal of 25 tested micropollutants. Recommends multi-barrier approach with MBR followed by RO or NF, and processes including GAC and MF with RO or NF are recommended because of the high removal rates achieved.

Table 1 (continued): References, information, and comments on PPCP/EDC removal by CAS and MBR processes

Reference	Type of systems	Scale	Source of wastewater	Source of compounds	Number of compounds evaluated	Comments
Bernhard, et al. (2006)	MBR/CAS	Pilot/Full	Wastewater	Wastewater and spiked	25	MBR process showed better removal than CAS. SRT was found to have an optimal range with increased time not increasing removal efficiencies. Suggest ozonation and photochemical degradation to increase persistent polar pollutant removal.
Clara, et al. (2004)	MBR/CAS	Pilot/Full	Wastewater	Wastewater	7	No significant removal rates observed between MBR and CAS. Longer SRT increased removal efficiencies for some compounds. Carbamazepine was not removed by either process.
Lesjean, et al. (2005)	MBR/CAS	Pilot/bench/full	Wastewater	Wastewater	9	MBRs were found to remove most compounds better than the CAS process although some non-biodegradable compounds, such as carbamazepine, were found to be very persistent in both process. The less polar steroid compounds were removed very well.

Table 2: Removal of micropollutants by the CAS and MBR processes

Compound	# of studies	CAS removal range	MBR removal range	MW (b) (g/mol)	Log Kow	Best performing system	Notes
Acetaminophen	2	98.4	99.6 - BDL (a)	151	0.46	About equal	
Alkylphenol	1	~30-95	~75-90	N/A		MBR	
Alkylphenol ethoxylate	1	~75-95	~70-95	N/A		About equal	
Androstenedione	1		BDL	286	2.75		MBR results only
Atenolol	1	No elimination	65.5	266	0.16	MBR	
Atrazine	1		9	215	2.61		MBR results only
Bayrepele acid	1	24	93	N/A		MBR	
Bentazone	1		16	240			MBR results only
Bezafibrate	3	~40-98	~80-95.8	362	4.25	MBR	
Bisphenol A (BPA)	1	91	99	228	3.32	MBR	
Caffeine	1		~99-BDL	194	-0.07		MBR results only
Carbamazepine	6	No elimination-7	No elimination-13	236	2.45		7 & 13 % removal found only in 1 study
Ciprofloxacin	1		73	331			MBR results only
Clofibrac acid	3	27.7-~50	~50-80	215	2.57	MBR	
DEET	2	17	No elimination-62	191	2.18		
Diclofenac	4	~24-50.1	No elimination-87.4	296	4.51		
EDTA	1	1	No elimination	292		About equal	
Enrofloxacin	1		56	359	0.7		MBR results only
Erythromycin	2	23.8	~5-67.3	735	3.06		
Estriol	1		BDL	359	0.7		MBR results only
Flufenamic acid	1		BDL	281			MBR results only
Fluoroquinolonic acid	1		27	N/A			MBR results only
Galaxolide (HHCB)	1	~60-95	~95	258	5.9		
Gemfibrozil	1	38.8	89.6	250	4.39	MBR	
Glibenclamide	1	44.5	47.3	494		MBR	
Hydrochlorothiazide	1	76.3	66.3	298		CAS	
Hydrocodone	1		No elimination	299	2.16		MBR results only
Ibuprofen	6	82.5-~98	~95-99.8	206	3.97	MBR	
Indomethacin	1	23.4	46.6	258		MBR	
Isoproturon	1		25	206			MBR results only

Table 2 (continued): Removal of micropollutants by the CAS and MBR processes

Compound	# of studies	CAS removal range	MBR removal range	MW (b) (g/mol)	Log Kow	Best performing system	Notes
Ketoprofen	2	51.5-~55	91.9->98	254	3.12	MBR	
MCPP	1	13	50	215		MBR	
Meftamic acid	2	29.4-~70	74.8-~90	241		MBR	
Metoprolol	1	No elimination	58.7	267	1.88	MBR	
Moxifloxacin	1		78	N/A			MBR results only
Naproxen	3	~65-85.1	~36-99.3	230	3.18		All but one MBR result shows >95% removal
Ofloxacin	1	23.8	94	361		MBR	
Oxybenzone	1		~41-50	228	3.79		MBR results only
Paroxetine	1	90.6	89.7	329		CAS	
Pravastatin	1	61.8	90.8	425		MBR	
Propyphenazone	1	42.7	64.6	230		MBR	
Ranitidine	1	42.2	95	314		MBR	
Sulfamethoxazole	2	55.6	60.5-~70	253	0.89	MBR	
TCEP	2	30	No elimination-37	286	1.44	About equal	
TCPP	1	13	12	431		About equal	
Testosterone	1		BDL	288	3.32		MBR results only
Tonalide (AHTN)	1	~50-97	~95-97	244		MBR	
Triclosan	1		~66-73	288	4.76		MBR results only
Trimethoprim	1		No elimination	290	0.73		MBR results only

(a) BDL = Below detectable limits. Some studies reported rejection below limits of quantification (LOQ), or not detected in permeate concentrate and not in % removed

(b) MW values of some compounds obtained from chemfinder at www.chemfinder.com.

(c) N/A = not available.

Compounds that exhibit low biodegradability in aerobic wastewater treatment conditions do not appear to conform to any distinct trends in physicochemical properties such as functional chemistry, molecular weight, or charge. Thus, it is difficult to predict which compounds will be poorly removed in a MBR or CAS system without actual testing. However, Snyder et al. evaluated two biodegradation models with 40 microconstituents and found reasonable agreement between predicted and actual results for 33 of the compounds. The researchers noted halogenated compounds as being susceptible to slower biodegradation but did not indicate whether other properties or structural features were useful in predicting biodegradability.

A number of these studies evaluated both CAS and MBR systems, with the CAS system operating at full scale and the MBR system at pilot scale. As noted earlier, results from systems operated at different scale must be compared with caution. In the case of biological systems, the aeration tank is typically a well-mixed system and the performance can be similar when operating conditions such as HRT and SRT are similar. Furthermore, many of the pilot plants in these studies were operated at the full-scale treatment plant site, so the influent water matrix was identical for the two processes. Thus, the comparison between CAS and MBR performance in these studies provides a useful indication of how MBR systems should be expected to perform when operated at full scale.

Challenges for determining microconstituent removal

For some microconstituents listed in Table 2, several researchers found similar results for the removal efficiency by MBR or CAS systems. For other microconstituents, however, the measured removal efficiency varies significantly between studies. Several factors may contribute to this variability. The primary sources of variability may be the low concentrations in the wastewater, the analytical difficulties of measuring these constituents in a wastewater matrix, and differences in experimental procedures.

When dealing with very low concentrations of organic compounds in wastewater there is some variability no matter how careful the researchers are. One large factor in the variability of PPCPs measurements in both treated and untreated wastewater is the low concentrations that must be detected. Recent analytical advances have made detection of these compounds at this level possible. However, different analytical methods have varying ranges of accuracy and at these small concentrations the level of detection (LOD) or quantification (LOQ) becomes very important. Sampling and analytical methods and potential for contamination of samples become especially important when analyzing compounds at very low concentrations. A particular analytical challenge is managing interferences introduced by other organic compounds in wastewater. Microconstituents such as PPCPs and EDCs are of interest in wastewater at concentrations as low as 10 ng/L whereas the concentrations of suspended solids and dissolved organic carbon in the solution are typically present at concentrations > 100 mg/L. This constitutes a difference of seven orders of magnitude. Preparing samples for analysis of microconstituents involves extracting, purifying, and concentrating the analytes in the presence of this overwhelming background matrix. This is a very difficult challenge that is subject to many possible interferences that introduce uncertainty to the final analytical results.

Another factor that may affect the results of these studies is the source water for the tests. The source of water and source of microconstituent for each study cited in this section of the

literature review are listed in Table 1. Some studies spiked laboratory-prepared water²⁰ with different microconstituents rather than taking the water directly from a WWTP^{2, 15, 17, 20}. Both methods offer advantages and disadvantages in determining PPCP removal efficiencies. The advantage of spiking laboratory water with a known amount of a compound and then measuring the removal efficiency is precision. The amount of a given compound is known and the results more accurately represent constituent removal under carefully controlled conditions. The disadvantage is that the spiked water may not accurately reflect how the process will work in a complex system given all the other parameters not accounted for in the spiked water. Parameters such as TSS, NOM, TOC, and other compounds found in municipal wastewater may give completely different results than those found by spiking laboratory water.

Summary of biological effectiveness for microconstituent removal

MBRs are effective for removing many microconstituents. Removal of 50 percent or greater was achieved for about two-thirds of the compounds shown in Table 2. MBRs, however, cannot achieve complete removal of all microconstituents and some chemicals show particular resistance. In particular, no elimination was observed in at least one study for 7 of the compounds in Table 2.

Design and operational strategies to maximize micropollutant removal for indirect potable water reuse applications using biological processes, based on current information, include the following:

- Selection of the MBR process in lieu of the CAS process. The MBR process clearly produces better quality effluent than the CAS process with respect to conventional wastewater parameters such as biochemical oxygen demand (BOD), total organic carbon (TOC), total suspended solids (TSS), and pathogens. Thus, the MBR process provides better feed water quality for subsequent water treatment processes. The MBR process also achieves similar or greater micropollutant removal, depending on the compound.
- Operation of membrane bioreactors at higher values of sludge retention time (SRT).

Additional strategies to maximize the removal of microconstituents by biological processes are the subject of current research. One area of research is the modifying the properties of the membrane¹⁵. Parameters such as molecular weight cut off limits and surface charge on the membrane can be modified to best suit the effluent parameters desired. Modifications may also be made in the treatment process itself. These might include the inoculation of special microorganisms which could be specially suited to remove specific microconstituents¹⁵.

Indirect potable water reuse requires water to be treated to a particularly high quality because of public perception and concern about possible long-term health effects. Many researchers have agreed that a multibarrier approach is the best way to achieve this and an MBR system can be a good first process. Although the MBR process is not effective at removing all microconstituents, they can provide subsequent systems with a high quality feed water that has low TSS and DOC. Of these systems, reverse osmosis, which will be explored further in the next section, is proving to be an effective process.

Reverse Osmosis

Reverse osmosis is a membrane-based treatment process that separates contaminants from water by forcing water through the membrane under pressure. Dissolved contaminants are separated from the water as the water passes through the membrane. The primary treatment mechanism in reverse osmosis is the physical separation of micropollutants from water because of differences in physicochemical properties that allow permeation through the membrane at substantially different rates. RO can effectively remove most microconstituents. Like the MBR process, removal efficiencies depend on properties of the feedwater, membranes, and compounds to be removed²⁰. Unlike the MBR process, though, the RO feedwater must be of high quality to prevent fouling. This means that the feedwater for an RO system cannot be raw sewage and in fact must be nearly free of solids, as discussed below.

Pretreatment requirements for the reverse osmosis process

The RO process requires influent water of high quality and pretreatment is almost always incorporated to prevent scaling, clogging of influent channels, and formation of biofilms¹⁴. There are four fouling mechanisms that may occur on an RO membrane: (1) accumulation of suspended solids (sometimes referred to as colloidal fouling), (2) scale formation from inorganic precipitates, (3) accumulation of organic matter, and (4) biological growth on the membrane surface.

Scaling can be minimized with pH adjustment or/and antiscalant addition to the feed water, while clogging of influent channels and fouling can be minimized by providing a feed water as free from particles as possible. At a minimum, particle removal requires a minimum pre-filtration of 5 µm or less. This is because RO, unlike membrane filtration, does not have a backwash cycle that removes larger particles that build up on the surface of the membrane. For the treatment process train in Cloudcroft, the RO system will receive feedwater from the preceding MBR process. As mentioned earlier, the effluent from the MBR is of high quality and meets or exceeds the particle parameter required for RO feedwater. Membrane filtration has been shown to be an effective pre-treatment technology for RO processes.

The pretreatment to prevent biofouling is disinfection. The type of disinfectant used is of concern because some disinfectants will degrade some RO membranes. Chloramines have been found to be an acceptable disinfection for use ahead of RO membranes, whereas chlorine is not acceptable.

Mechanisms for microconstituent removal by reverse osmosis

Many factors influence the removal mechanisms of microconstituents by the RO process. As noted earlier, reverse osmosis is a diffusion-controlled process. Solute separation occurs when constituents diffuse across the membrane slower than water does. Diffusion, and therefore removal efficiency, is influenced by:

- Physical-chemical properties of the compound: These include the molecular weight, size, diameter, solubility, diffusivity, polarity, hydrophobicity, charge, and protonization of the compound^{26, 27}.

- Membrane properties: These include the membrane's surface charge, molecular weight cut-off (MWCO), pore size, hydrophobicity, and surface roughness^{26,27}.
- Membrane operating conditions: These include such parameters as flux, transmembrane pressure, and the fraction of water to be recovered^{26,27}.
- Feedwater characteristics: The composition of the feedwater can play an important role in rejection efficiencies. These parameters include a feedwater's temperature, ionic strength, pH, hardness, concentration of microconstituents, and total organic matter concentration²⁶.

Water is a small, neutral, polar molecule. Conventional understanding of reverse osmosis dictates that removal efficiency will increase as the physicochemical properties of the micropollutant deviate from those of water. Drewes et al. (2006) developed the diagram shown in Figure 5 to estimate rejection of microconstituents by reverse osmosis^{26,28}. The objective of the diagram is to correlate removal efficiencies with solute and membrane properties. Although the diagram can be useful in the design of water treatment systems to remove certain microconstituents, the accuracy of this diagram has not been confirmed²⁶. Figure 5 summarizes many types of interactions between the membrane, compound, and source water. Three main mechanisms that contribute to PPCP removal by reverse osmosis are adsorption, charge repulsion, and size exclusion²⁰.

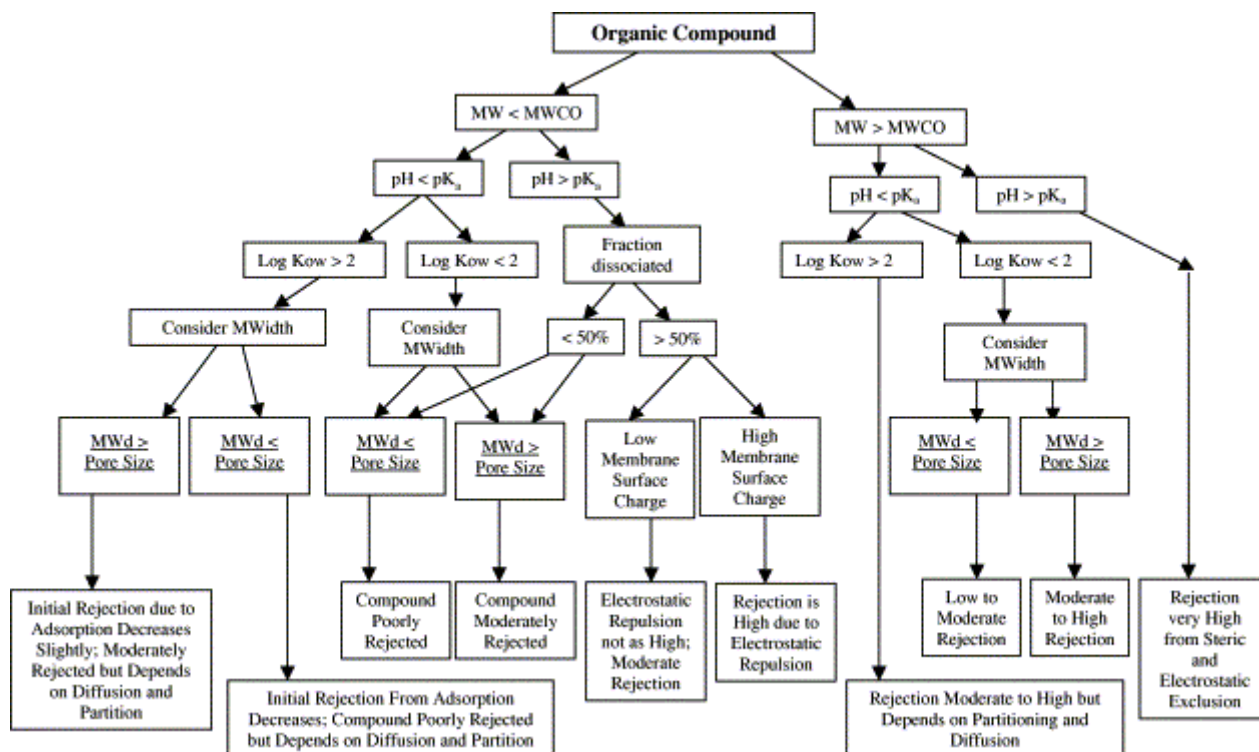


Figure 5 – Rejection diagram for microconstituents using membrane processes as functions of both solute and membrane properties^{26,28}.

Molecular size has been shown to be a major mechanism for solute rejection by RO and NF membranes^{3, 8, 29, 30}. The density and MWCO of the membrane greatly affect removal due to size exclusion, for both ionized and non-ionized compounds and is especially important for solutes that are not charged. Some studies have shown that the RO process removes uncharged organic compounds primarily through size exclusion^{3, 29}. Compounds with a molecular weight greater than 200-300 Daltons (Da) are effectively rejected by RO/NF membranes although some larger compounds can still be detected in the permeate^{27, 29}. For example, Kimura et al. (2004) reported that 17 β -estradiol (MW: 279 Da) was found in RO permeate, although at very low concentrations⁸.

Another important removal mechanism employed by the RO process is charge repulsion or electrostatic exclusion. This mechanism relies on repulsion between the negatively charged membrane surface and negatively charged solutes. Experimental results have shown that negatively charged compounds could achieve high rejection due to electrostatic exclusion^{27, 31}. This was found to be true regardless of other physicochemical properties.

The concentration of microconstituents may also have an effect on how well they are rejected. Kimura et al. suggests that rejection efficiencies decrease with lower feed concentrations although they suggest further research should be done to determine its effects²⁷.

An operating parameter that can have a large effect on microconstituent removal is the fractional feed water recovery. Factors that can limit recovery are osmotic pressure, concentration polarization, and the solubility of sparingly soluble salts¹⁴. Higher recovery will result in increased permeate volume but will decrease its quality¹⁴. This can be important when trying to remove microconstituents. Verliefe et al. showed that at a recovery of 10 percent, a NF membrane was able to remove >75 percent of all target compounds with most achieving >90 percent removal and a few compounds being removed at >99 percent³². At 80 percent recovery, the same compounds were removed less effectively with one compound dropping to ~10 percent removal.

Membrane selection

Because solute removal efficiencies are closely linked to the chemical and physical properties of the membranes, material selection for RO membranes is important. A good RO membrane must meet many characteristics¹⁴. Ideally, an RO membrane material will produce a high flux that will not clog or foul easily while still maintaining high solute removal efficiency. The material should be affordable while being durable and stable. No commercial RO membrane can completely reject all solutes²⁶. Membrane manufacturers have focused their efforts on developing membrane materials that achieve a high solute rejection while producing high water flux at the lowest transmembrane pressure²⁶.

The two most popular materials used in RO membranes are cellulose acetate and polyamide. Although both materials have benefits and drawbacks, the polyamide seems to be better suited for the removal of microconstituents. One of the drawbacks of polyamide membranes is that chlorine and other disinfectants damage the membranes. Care must be taken in designing these systems to maintain feed water with proper disinfection while maintaining the integrity of the membrane.

Besides the membrane material, the decision to use either a NF or RO membrane can have important implications on different parameters. As mentioned earlier, the classification of different membranes can be somewhat arbitrary. NF membranes can selectively remove divalent cations (hardness) and anions (e.g. sulfate) and NOM while leaving a greater fraction of the monovalent ions in the permeate. While traditionally many RO membranes removed ions indiscriminately, newer RO membranes have been developed that have improved selectivity.

Although RO membranes will achieve higher removal of microconstituents than NF membranes due to their tighter, denser material, NF membranes have some advantages. RO membranes requires higher pressures and are therefore more energy intensive¹⁴. NF membranes can be operated at lower pressures than RO, resulting in lower operating costs²⁹.

Summary of RO effectiveness for microconstituent removal

Table 3 summarizes information on 15 papers that investigated microconstituent removal by RO. Although results may vary for removal efficiencies of individual compounds depending on the study, a frequent conclusion in these articles is that the reverse osmosis process is effective at removing nearly all microconstituents.

Table 4 lists the removal efficiencies for the compounds studied in these articles. This table also lists some of the compound's physical and chemical properties, how often the compound was studied, and which RO membrane achieved highest removal. It should be noted that various parameters such as pH, the ratio of the permeate flux to concentration polarization mass transfer coefficient, (J/k ratio), and even time can have significant roles in the rejection of these solutes. It is likely that some of the apparent differences in performance are due to differences in experimental conditions and analytical methods between different studies. Because of these differences, some caution should be used when interpreting these results.

As noted earlier, higher molecular weight, charged, more nonpolar, and more hydrophobic compounds should be removed more efficiently by reverse osmosis. The articles reviewed for this report generally indicated that the results followed these trends, although it is difficult to observe these trends in the summary table in this report because of the generally high removal for many compounds and the confounding effects of differences in removal caused by different study conditions. Some trends were evident, such as that charged compounds always achieved very high removal efficiency. Thus, it is theoretically possible to use chemical structure relationships to predict which micropollutants will be harder to remove with reverse osmosis.

In the section on the MBR process, it was noted that seven compounds were not removed at all in at least one study. Of those, carbamazepine, DEET, diclofenac, hydrocodone, TCEP, and trimethoprim were effectively removed by reverse osmosis. EDTA removal by RO was not evaluated in any of the articles reviewed for this report.

Some neutral compounds were not well removed by reverse osmosis. Less than 50 percent removal of bisphenol A and caffeine were found by at least one researcher, but greater than 99 percent removal was achieved by the MBR process for these compounds. Compounds that were poorly removed by RO in some studies like bisphenol A and caffeine tended to be well removed by MBR. Thus, for at least some compounds, compounds that are poorly removed by the MBR

Table 3: References, information, and comments on PPCP/EDC removal by the RO process

Reference	Type of systems	Scale	Water source	Source of compounds	Number of compounds evaluated	Comments
Snyder, et al. (2007)	MBR/NF/UF/RO/ NF and combination of systems	Bench/pilot/ full scale	Primary and secondary wastewater effluent, groundwater, secondary wastewater	Spiked and non-spiked	36	The RO process removed nearly all compounds to below method reporting limits although some were still detectable in trace amounts. Recommends multi-barrier approach for removal of trace contaminants.
Kosutic, et al. (2007)	RO/NF	Pilot	Veterinary pharmaceutical manufacturing wastewater and artificial model waters	Spiked and non-spiked	7	Both RO and NF showed high removal, but loose NF membranes had trouble removing smaller antibiotics. Tight NF membranes performed slightly better than RO and can be operated at lower pressures and less energy. Size exclusion was dominant rejection mechanism for the studied unionizable antibiotics although physicochemical effects can influence rejection of some low molecular organics.
Wintgens, et al. (2004)	MBR/NF/RO	Full scale	Landfill leachate treatment plant	Non-spiked	2	The MBR removal mechanism was biological removal while NF and RO was size exclusion. NF performed slightly better than RO but all treatment techniques achieved between 70-99% removal.
Drewes, et al. (2002)	RO/NF	Full scale	Municipal wastewater	Non-spiked	13	None of the investigated compounds were detected in the RO or NF effluent.
Kimura, et al. (2004)	RO/NF	Bench	DI water	Spiked	11	Evaluated polyamide and cellulose acetate membranes. Polyamide generally performed better but neither achieved complete rejection. Size exclusion was attributed to removal by polyamide membranes, while polarity was the main mechanism by cellulose acetate membranes.
Xu et al. (2005)	RO/NF/ULPRO	Bench	DI water	Spiked	6	Tight NF membranes and ULPRO operate at lower pressures and perform similar to conventional RO. For tight high-pressure membranes, a minimum MWCO is necessary, but the MWCO was not as important for solute rejection as surface charge.

Table 3 (continued): References, information, and comments on PPCP/EDC removal by the RO process

Reference	Type of systems	Scale	Water source	Source of compounds	Number of compounds evaluated	Comments
Comerton, et al. (2007)	MBR/UF/NF/RO	Bench	Lake water, MBR effluent, DI water	Spiked	22	Study looked at adsorption of PPCPs to membranes and found that membranes with larger pore sizes allow solutes to access many more binding sites within the membrane (UF>NF>RO). Although the larger pore sizes increases solute adsorption to the membrane it also decreases rejection due to size exclusion, which has been found to be a major contributor in removing micropollutants by membrane processes.
Kim, et al. (2005)	RO/NF	Bench	DI water	Spiked	8	The membranes (three RO and one NF) achieved good rejection of 5 of the studied compounds and poor rejection of three compounds. Solute with intermediate hydrophobicity saw significant adsorption to the membranes and good rejection of polar/charged compounds was observed due to electrostatically hindered transport. One membrane that was more hydrophilic had less rejection of hydrophobic compounds.
Kimura, et al. (2003)	RO/NF	Bench	DI water	Spiked	9	Both RO and NF membranes achieved >90% rejection of negatively charged compounds regardless of physico-chemical properties. Rejection of non-charged compounds were found to be greatly influenced by the compounds size and rejection was generally lower (<90%). This study also suggests that lower removal efficiencies result from lower solute concentrations.
Drewes, et al. (2006)	RO/NF	Full scale	Water recycling plant	Non-spiked	12	Physical sieving thought to be one of the main mechanisms for rejection of organic solutes although other factors may play a role. These include the charge on the membrane, the hydrophobicity of the solute, and the fraction of the solutes that are ionic. Membrane fouling can also play a large role in solute rejection. The authors conclude that membrane systems are complex and solute rejection is dependent on many factors.

Table 3 (continued): References, information, and comments on PPCP/EDC removal by the RO process

Reference	Type of systems	Scale	Water source	Source of compounds	Number of compounds evaluated	Comments
Baumgarten et al. (2007)	MBR/PAC/NF/RO/ O ₃ /O ₃ with UV	Bench and pilot	Municipal and industrial wastewater	Wastewater and spiked	5	RO and NF membrane processes rejected selected compounds very well. None of the spiked compounds were detected in permeate regardless of recovery and NF permeate recovery was 90%.
Kim, et al. (2006)	MBR/GAC/RO/NF & UV in combination with RO and NF	Full/pilot	Wastewater and surface waters	Non-spiked	26	NF & RO processes achieved >95% removal for all target compounds. NF performed as well as RO with less energy used. No additional improvement was seen by combining UV with RO although high removal rates with RO/NF alone were already achieved. Multi-barrier approach recommended.
A. R. D. Verliedde et al. (2007)	NF & NF/GAC	Bench	Surface water	Spiked	20	At a recovery rate of 80% the NF/GAC worked exceptionally well while NF alone performed poorly with neutral (all 8 removed <20%) and positively charged (4 out of 5 removed <40%) compounds doing the worst. At a recovery of 10% NF achieved >90% for almost all compounds. Size exclusion plays a role in solute removal but main mechanism for NF was solute charge.
Yoon et al. (2002)	Coag/GAC/PAC/AO P/biofiltration/RO/NF/UJF					This literature review gives very broad removal efficiencies for many different treatment processes. They give RO >90% removal on all classes of compounds with NF generally from 70->90.
Snyder, et al. (2003)	Coag/floc/AC/BAC/ Ozone/chlorine/NF/ RO/degradation					This literature review gives removal efficiencies of different types of compounds (EDCs, pharmaceuticals, PCPs) for many different treatment processes. RO is found to remove all micropollutants at >90% (excellent) while NF was found to work well, but not as effectively as RO for many compounds with removal from 70-90% to >90% (Good to excellent). They note removal efficiencies of membrane processes are dependent on both the compounds structure (size, polarity) and properties of the membrane.

Table 4: Removal of micropollutants by the reverse osmosis process

Compound	# of studies	NF Removal range	RO Removal range	MW (b) (g/mol)	Log Kow	Best performing membrane	Notes
17β-Estradiol	1		83 & (29) (c)	272	4.01	RO results only	Hydrophobic neutral
2-Naphthol	2	12	43-57 & (0)	144	2.7	RO	Hydrophobic neutral
4-Phenylphenol	1		61 & (11)	170	3.2	RO results only	Hydrophobic neutral
9-ACA	1	93	96	222	3.85	RO but both do well	Charged
Acetaminophen	1	BDL	BDL (a)	151	0.46	Both do well	
Aminopyrine	1	97-99		231	1	NF results only	Neutral
Androstenedione	2	BDL	BDL	286	2.75	Both do well	
Atenolol	1	90-95		266	0.16	NF results only	Positively charged
Bezafibrate	1	99		362	4.25	NF results only	Negatively charged
Bisphenol A	3	45-99	83-99 & (18)	228	3.32		Hydrophobic neutral
Bromoform (BF)	2	45	45, <20, >80	253	2.4		<20% removal was with virgin membrane
Caffeine	3	BDL	70-BDL & (44)	194	-0.07		Hydrophilic neutral
Carbamazepine	5	88-BDL	91-BDL & (85)	236	2.45		Hydrophobic neutral
Carbon tetrabromide (CTB)	1	92	92	332	3.42	Both do well	
Carbon tetrachloride (CT)	1	77	77	154	2.83		
Chloroform (CF)	2	<5-<50	18	119	1.97		Hydrophobic neutral
Ciprofloxacin	1	>97.9	>97.9	331		Both do well	
Clenbuteral	1	88-90		277	2	NF results only	Positively charged
Clofibric acid	1	98-99		215	2.57	NF results only	Negatively charged
Cyclophosphamide	1	94-99		261	0.63	NF results only	Neutral
DCAA	1	91	95	129	0.92	RO but both do well	Charged
DEET	1	BDL	BDL	191	2.18	Both do well	
Diclofenac	6	54-BDL	>80-BDL	296	4.51	RO	Hydrophilic ionic. All NF but 1 where >93
Dilantin	1		BDL	318	4.51	RO results only	
Enrofloxacin	2	>98.4-99.4	97-99	359	0.7	Both do well	
Erythromycin	1	BDL	BDL	735	3.06	Both do well	
Estradiol	1		BDL	272	4.01	RO results only	
Estriol	2	BDL	BDL	359	0.7	Both do well	Hydrophobic neutral
Estrone	1		BDL	270	3.13	RO results only	
Ethinylestradiol	1		BDL	296	3.67	RO results only	
Fenoprofen	1	96		242	3.9	NF results only	Negatively charged

Table 4 (continued): Removal of micropollutants by the reverse osmosis process

Compound	# of studies	NF Removal range	RO Removal range	MW (b) (g/mol)	Log Kow	Best performing membrane	Notes
Fluoroquinolonic acid	1	>99.7	>99.7	Not found		Both do well	
Fluoxetine	1		BDL	309	4.05	RO results only	
Gemfibrozil	5	65-99	90-BDL	250	4.39		Hydrophilic, ionic
Hydrocodone	1	BDL	BDL	299	2.16	Both do well	
Ibuprofen	5	>92-BDL & 21-33	96-BDL	206	3.97	RO	Hydrophilic ionic
Iopromide	1		BDL	791	-2.05	RO results only	
Isopropylantipyrene	1		78 & (69)	231	1.94	RO results only	
Ketoprofen	2	98-99 & 18-32	97-BDL	254	3.12		Hydrophilic ionic
Levamisole	1	69-99.9	97-99.4	204	2.87		
Mecoprop	1	27-32	97-98	215	3.13	RO	Hydrophilic ionic
Metoprolol	1	90-95		267	1.88	NF results only	Positively charged
Moxifloxacin	1	>99.6	>99.6	Not found		Both do well	
NAC standard	1		79 & (0)	201	2.36	RO results only	
Naproxen	4	BDL & 22-27	>95-BDL	230	3.18		Hydrophilic, ionic
NDMA	1		<50	74		RO results only	Hydrophilic neutral
Nonylphenol	1	70-99		220		NF results only	
Oxybenzone	2	BDL	BDL	228	3.79	Both do well	
Oxytetracycline	1	99-99.2	99.2-99.3	460	-2.87	Both do well	
Pentoxifylline	2	95-99	BDL	278	0.29	RO but both do well	Neutral
Perchloroethylene (PCE)	1	95	95	165	3.4	Both do well	
Phenacetine	3	19-<50	71->95 & (10)	179	1.58	RO	Hydrophilic neutral
Phenazone	1	85-94		188	0.38	NF results only	Neutral
Pindolol	1	75-93		248	1.75	NF results only	Positively charged
Praziquantel	1	98-99	99.6-99.9	312	2.42	RO but both do well	
Primidone	4	87->94 & 10	84-BDL & (85)	218	0.91		Hydrophilic neutral
Progesterone	1		BDL	315	3.87	RO results only	
Propranolol	1	75-87		259	3.48	NF results only	Positively charged
Salbutamol	1	~93		239	0.64	NF results only	Positively charged
Salicylic acid	1	92	92	138	2.26	Both do well	Charged
Sotalol	1	90-93		272	0.24	NF results only	Positively charged
Sulfadiazine	1	89-99.4	99.4	250	-0.34	Both do well	

Table 4 (continued): Removal of micropollutants by the reverse osmosis process

Compound	# of studies	NF Removal range	RO Removal range	MW (b) (g/mol)	Log Kow	Best performing membrane	Notes
Sulfaguandine	1	67-99.1	99-99.3	214	-1.07		
Sulfamethazine	1	96-99.4	99.1-99.3	278	0.76	Both do well	
Sulfamethoxazole	3	BDL	70-BDL & (82)	253	0.89		
TCAA	1	94	96	163	1.33	RO but both do well	Charged
TCEP	2	95	95	286	1.44	Both do well	
Terbutaline	1	90-99		225	0.9	NF results only	Positively charged
Testosterone	1	BDL	BDL	288	3.32	Both do well	
Trichloroethylene (TCE)	1	31	31	131	2.29		Hydrophobic neutral
Triclosan	2	BDL	BDL	288	4.76	Both do well	
Trimethoprim	3	89-BDL	98-BDL	290	0.73	RO	

(a) BDL = Below detectable limits. Some studies reported rejection below limits of quantification (LOQ), or not detected in permeate concentrate and not in % removed

(b) MW values of some compounds obtained from chemfinder at www.chemfinder.com.

(c) Efficiency shown in (paratheses) were for SC3100 cellulose acetate membrane [15]

process are effectively removed by the RO process, and vice versa. For other compounds with poor RO removal, information is not available for effectiveness by the MBR process. For instance, less than 50 percent removal was found by at least one study of RO removal for 17 β -Estradiol, 2-naphthol, 4-phenylphenol, bromoform, chloroform, NDMA, phenacetine, and TCE, but no corresponding information for the removal of these compounds was found in the MBR literature reviewed for this report. All of these are neutral compounds and most are hydrophobic. Based on the trends predicted by Figure 5, the lack of removal of these compounds may be due to the specific shape of the chemicals.

A number of studies reviewed for this report evaluated PPCP and EDC removal at bench or pilot scale. Removal efficiency in these processes is controlled by mass transfer of water and solutes through the membrane. These mechanisms are only slightly influenced by hydrodynamic or water matrix impacts. Mass transfer of solutes through the membrane proceed largely independently of one another. As a result, removal efficiency measured at bench or pilot scale is generally representative of removal at full scale when operating conditions such as recovery are similar. It should be noted that other aspects of membrane system performance, such as fouling of the membrane, are much more dependent on hydrodynamic and water matrix conditions, and therefore do not compare as well between bench scale and full scale.

Design and operational strategies to maximize micropollutant removal using reverse osmosis, based on accepted understanding of the mechanisms controlling the reverse osmosis process, include the following:

- Removal could theoretically be maximized by selection of “tighter” membranes (i.e., seawater RO in lieu of brackish water RO membranes, or brackish water RO membranes in lieu of nanofiltration membranes). Tighter membranes, however, typically operate at lower water flux rates. As a result, it would be necessary to increase the size of the system, which would increase capital costs. Tighter membranes may also require a higher feed pressure, which would increase operating costs.
- Removal could theoretically be improved by operating at a lower recovery. High recovery concentrates the micropollutants on the feed side of the membrane, and the higher concentration increases the mass transfer across the membrane, resulting in lower quality product water. Overall, recovery may have a minor impact on the removal efficiency. For practical and economic reasons, it is desirable to operate at the highest achievable recovery, but it is worth noting that the operating conditions that maximize micropollutant removal may be in conflict with desired operating conditions for cost-effective implementation.

As a treatment process, reverse osmosis has several other negative aspects. These include (1) high loss of product water because of low recovery, (2) high energy consumption, (3) large volume waste stream, which increases disposal costs. These negative aspects should be considered when comparing reverse osmosis to other treatment processes for micropollutant treatment.

Activated Carbon Adsorption

This section examines the adsorption of microconstituents by granular activated carbon (GAC) and powdered activated carbon (PAC). Activated carbon is an effective adsorbent that is used for removing many dissolved compounds from water. GAC is used in a fixed-bed process like granular media filtration whereas PAC is added to water as a suspension, allowed to adsorb constituents from water, and then separated from the finished water. Activated carbon can be used at several scales, ranging from as large as full-scale municipal treatment systems to as small as water filters that can attach to the end of a plastic bottle or faucet. GAC is most commonly incorporated in water treatment facilities for (1) removal of trace contaminants and (2) removal of dissolved organic carbon (DOC)¹⁴. Activated carbon will effectively remove many organic compounds and the USEPA has designated GAC as a best available technology (BAT) for the treatment of many regulated organic pollutants³³.

Charcoal adsorbers were used in the US to treat drinking water as early as the late 1800's. Although the charcoal used was not activated and therefore did not have the extensive porosity characteristic of activated carbon, it was still a useful process for treating water. Activation is a process of treating charcoal or other materials to make them highly porous. In the case of activated carbon, the activation process produces a material with extremely high internal porosity. The internal pores have a large amount of surface area to which contaminants can adsorb. Granular activated carbon can have as much as 100 to 500 square meters of surface area per gram of material. This high surface area is one of the key factors in the effectiveness of activated carbon, since the adsorption capacity is directly related to the amount of surface area available.

Mechanisms for microconstituent removal by adsorption

Activated carbon removes dissolved constituents from solution by adsorption. Adsorption is a process in which compounds in the liquid phase accumulate on a solid surface¹⁴. The adsorption process is used in drinking water treatment to remove synthetic organic compounds (SOCs), disinfection by product (DBP) precursors, taste and odor-causing compounds, and some inorganic compounds. The process involves the adsorbate, the dissolved compound that undergoes adsorption, being transported via diffusion into the porous absorbent, the solid onto which the adsorbate adsorbs to. The solute is attached to the absorbent surface thru either chemical bonds (chemisorption) or physical attraction (physical adsorption).

Physical adsorption is a rapid process caused by nonspecific binding mechanisms¹⁴. It is the most common mechanism by which contaminants are removed from water. Physical adsorption is generally a reversible process meaning that if the concentration in solution decreases, then the contaminant will desorb back into the solution. Chemisorption, on the other hand, is usually an irreversible process where the contaminant is chemically bonded to the surface. Chemisorption is more specific than physical adsorption because the adsorbate shares electron density with the adsorbent, which forms a higher energy bond.

Adsorption is dependent on time and the amount of surface area (capacity) available for adsorption. Adsorption is an equilibrium process, so micropollutants in water will partition between the water and carbon surface until the two are in equilibrium with each other. Thus, presence of micropollutants on the carbon surface will also indicate micropollutants remaining in

the water, although in many cases the remaining micropollutant concentration in the water will be too low to measure.

Adsorption of microconstituents to activated carbon depends on properties of the water, activated carbon, and the microconstituents¹⁴. Physicochemical properties controlling adsorption are similar to those that control removal in reverse osmosis. More nonpolar, more hydrophobic, and lower solubility compounds should be removed efficiently by carbon adsorption. For activated carbon, lower MW compounds are more efficiently removed because of increased accessibility to inner pores of the carbon, which is the opposite of reverse osmosis. In addition, uncharged molecules are more efficiently removed by adsorption (again, the opposite of reverse osmosis), because of the increased aqueous solubility of charged compounds. The pH of the solution affects adsorption for ionic solutes for several reasons. First, the charge on activated carbon is affected by pH. Generally, activated carbon has a negative charge above pH of about 5, and is neutral between a pH of 4 and 5. Adsorption of anionic constituents is thus greater below pH 4, but from an operational standpoint, is not practical. The pH is also an important parameter for the removal of acids and bases where the pH affects the charge of the solute.

Activated carbon has a nonpolar surface at a neutral pH¹⁴. Because water is a polar liquid, nonpolar organics are more hydrophobic and have lower aqueous solubility. Therefore, neutral hydrophobic compounds will have the strongest affinity to carbon surface, and organic compounds that are polar, hydrophilic, or charged will not be adsorbed as strongly due to strong water-adsorbate forces.

An implication of this removal mechanism is that compounds are not degraded or destroyed, just transferred to the activated carbon surface. If carbon were regenerated, compounds would then be destroyed during the regeneration process. If however, the carbon is just discarded when it reaches capacity, PPCPs could be released to the environment from the surface of the carbon.

A second mechanism for micropollutant removal by activated carbon is biodegradation by microorganisms living on the carbon surface. Ozone followed by activated carbon can be an effective removal strategy because the ozone chemically degrades compounds and makes them more biodegradable, and then the microorganisms living in the carbon bed complete the degradation process. This process is commonly called biofiltration and has the advantage that the carbon never reaches capacity and has to be replaced.

Powder activated carbon versus granular activated carbon

GAC and PAC are the two primary adsorption process materials used in drinking water treatment¹⁴. Although this report focuses on the use of GAC, a brief summary of PAC is provided. The only functional difference between the materials is the size of the activated carbon particles—GAC is typically 0.5 to 3.0 mm in diameter and is used in a fixed-bed process like a granular media filter, whereas PAC is 20 to 50 µm in diameter and added to water in powder form. This difference in size leads to a difference in how the material is used in water treatment. Table 5 shows the principal uses, advantages, and disadvantages of both materials.

PAC is added directly to the water in a powder form, so it can be applied at various locations throughout the treatment process. It is removed from solution via sedimentation or filtration¹⁴.

Table 5: Principal uses, advantages, and disadvantages of granular and powdered activated carbon ¹⁴.

Parameter	Granular Activated Carbon (GAC)	Powder Activated Carbon (PAC)
Principle uses	Control of toxic organic compounds present in groundwater Barriers to occasional spikes of toxic organics in surface waters and control of taste and odor compounds Control of disinfection byproduct precursors or DOC	Seasonal control of taste and odor compounds and strongly adsorbed pesticides and herbicides at low concentrations (< 10 µg/L)
Advantages	Can be regenerated Lower carbon usage rate per volume of water treated compared to PAC	Easily added to existing coagulation facilities for occasional control of organics
Disadvantages	Need contactors and yard piping to distribute flow and replace exhausted carbon Previously adsorbed compounds can desorb and in some cases appear in the effluent at concentrations higher than present in influent	Impractical to recover from sludge from coagulation facilities Much higher carbon usage rate per volume of water treated as compared to GAC

As shown in Table 5, one of the main advantages of PAC is that it can be easily added to an existing coagulation facility with minimal capital investment. PAC can also be used only when needed which can reduce costs. Some treatment facilities may use PAC during the spring runoff to remove pesticides and herbicides or during the summer to control taste and odor compounds associated with algal blooms in surface water sources. The method of addition can be a disadvantage if the need to use PAC is more than just seasonal because GAC can be used at lower doses than PAC, which makes GAC more economical if activated carbon is used more regularly or continuously.

GAC is more frequently used in water treatment and is the principal focus of this report. Microconstituent removal by PAC is also provided because the results help explain the performance of GAC ³³.

Granular activated carbon can be used as the upper layer in a dual or multimedia filter. GAC can also act as a substitute for conventional granular filter media ¹⁴. GAC adsorption is usually incorporated with filtration or after filtration and right before final disinfection. When used in an adsorption process after filtration, there are three additional options for GAC contactors: gravity feed contactors, pressure contactors, and upflow and/or fluidized-bed contactors. Gravity feed contactors are similar to granular media filters but deeper.

Adsorption capacity affects the use of PAC and GAC differently. For PAC, a dose of carbon is added to the water and adsorption occurs until the capacity is reached, with the remaining pollutant staying in the water. Removal efficiency can be increased simply by increasing the carbon dose. For GAC, pollutants adsorb to the carbon bed and the pollutant concentration in the effluent can be unmeasurable until the capacity (measured as bed volumes) is reached, at which time the pollutant passes through the bed and the influent concentration of the pollutant is measured in the effluent. Once the adsorption capacity is reached, the media must be replaced or regenerated to restore removal effectiveness.

Summary of activated carbon effectiveness for microconstituent removal

Table 6 summarizes microconstituent removal by the activated carbon process. These studies found that the process is effective at removing many, if not most, targeted microconstituents. The removal efficiencies of all targeted compounds removed by GAC and PAC are listed in Table 7.

Many of the studies identified the conditions related to the effectiveness of activated carbon. For PAC, increased removal efficiency for many compounds is dependent on both the PAC dose^{6, 23, 33} and the contact time⁶. Although many compounds achieve higher removal with increased PAC dose, some compounds that are removed well at low doses do not achieve additional removal with higher PAC doses. For GAC, an important parameter for efficient removal of trace organics is whether the GAC receives regular regeneration or replacement^{6, 34}. One study considered on-site regeneration, but on-site regeneration is costly and would only be feasible if the carbon usage was greater than 150,000 kg/yr¹⁴. Snyder et al. (2007) identified a facility with on-site and regular regeneration as having minimal breakthrough of organic contaminants and improved removal efficiency of selected microconstituents⁶. In contrast, the study found little removal of trace organics in a facility with high levels of TOC that did not provide regular replacement/regeneration. This suggests that the high TOC caused rapid exhaustion of the carbon, thus limiting its ability to adsorb microconstituents.

Westerhoff et al. [35] showed that protonated bases are well removed by PAC. Compounds with low K_{ow} values, as well as deprotonated acid functional groups, appeared to be the most difficult to remove³³, most likely because they have high solubility and are negatively charged. Several studies also concluded that hydrophilic compounds break through the column sooner than the hydrophobic compounds^{6, 34}. Vieno, et al. found that the hydrophobic compound carbamazepine could be effectively removed by GAC even after treatment of >70,000 bed volumes of water³⁴. The same study found that the more hydrophilic compounds could pass GAC treatment after only 2,000 to 3,000 bed volumes of water.

One parameter that affected both GAC and PAC was the NOM concentration (measured as DOC) in the feed water⁶. The presence of NOM can reduce the removal efficiency of microconstituents by activated carbon due to competition for adsorption sites. The NOM can block the pores within the activated carbon structure, leaving less opportunity for the microconstituents to be adsorbed. The quantity and characteristics of DOC in the feed water is an important parameter that can influence removal efficiencies for activated carbon³³. The competition between NOM and microconstituents will have an impact on the effectiveness of GAC for indirect reuse applications since wastewater has higher DOC concentrations than many

Table 6: References, information, and comments on PPCP/EDC removal by GAC and PAC

Reference	Type of systems	Scale	Source of wastewater	Source of compounds	Number of compounds evaluated	Comments
Westerhoff et al. (2005)	GAC/PAC/ coagulation/ oxidation processes	Bench	Surface and DI water	Spiked	64	Coagulation and lime softening removed less than 25% of most EDC/PPCPs while PAC removed 56 out of 64 compounds at >50%, with 37 > 70%, and 9 >90%. Reasonable predictions could be made based on log K _{ow} values. PAC appears to remove protonated bases well while deprotonated acid functional groups seem the most difficult to remove.
A. R. D. Verliefde (2007)	NF & NF/GAC	Bench	Surface water	Spiked	20	High removal efficiencies (>75%) were achieved for all studied compounds when operating at low recovery (10%) for NF. Rejection of neutral compounds attributed to size exclusion while rejection of charged compounds were attributed to both size exclusion and electrostatic forces. Negatively charged compounds had higher rejection than positively charged ones due to negatively charged membrane surface. Rejection of pharmaceuticals decreased with higher recovery for NF alone but when coupled with GAC the rejection was very high even at 80% recovery (>97% for all compounds). Combination of both processes provide "robust" barrier for micropollutant removal. NF removes most organic matter creating less competition for GAC binding sites. Also NF has high removal efficiency for polar compounds while GAC absorbs non-polar compounds more efficiently.

Table 6 (continued): References, information, and comments on PPCP/EDC removal by GAC and PAC

Reference	Type of systems	Scale	Source of wastewater	Source of compounds	Number of compounds evaluated	Comments
Snyder et al. (2007)	GAC/PAC	Bench/pilot/ full scale	Primary and secondary wastewater effluent, groundwater, secondary wastewater	Spiked and non-spiked	36	Both GAC and PAC were highly effective at compound removal. PAC efficiency is highly dependant on dose while GAC efficiency is highly dependant on regeneration. For GAC, water soluble compounds breakthrough much more rapidly than hydrophobic compounds.
Vienno et al. (2007)	UV/Ozone/GAC/ Coag with rapid sand filtration	Pilot	Raw river water	Non-spiked	13	GAC was found to be very effective at removing neutral compounds. Neutral compounds were more effectively removed than ionic, and hydrophobic bed volumes were much greater than hydrophilic before breaching. The key factor is the regular regeneration of carbon.
Kim et al. (2006)	MBR/GAC/RO/ NF & UV in combination with RO and NF	Pilot/full scale	Wastewater and surface waters	Non-spiked	26	GAC was very effective at conventional drinking water treatment with ~99% removal for all target compounds. Multibarrier approach with MBR followed by RO/NF recommended. Low NOM in source water and the hydrophobicity of the compounds were contributing factors.
Yoon et al. (2002)	Coag/GAC/ PAC/AOP/ biofiltration/RO/ NF/UF					This literature review gives very broad removal efficiencies for many different treatment processes. Activated carbon generally achieves 70->90% on most classes of compounds with inorganics at <20 40%. Very wide range without much precision. Sorption capacities reduced with increased DOC.

Table 6 (continued): References, information, and comments on PPCP/EDC removal by GAC and PAC

Reference	Type of systems	Scale	Source of wastewater	Source of compounds	Number of compounds evaluated	Comments
Ternes et al. (2002)	GAC/Ozone	Bench/pilot	River and groundwater	Spiked	5	All compounds effectively removed even at higher concentrations and to a specific throughput of over 70 m ³ /kg except Clofibrilic acid which was less prone to adsorption but removed completely to 15-20 m ³ /kg. Carbamazepine, which is problematic for the MBR process, showed highest adsorption capacity.
Baumgarten et al. (2007)	MBR/PAC/NF/R O/O ₃ /O ₃ with UV	Bench/pilot	Municipal and industrial wastewater	Wastewater and spiked	5	The amount of removal was highly linked to the PAC dose and manufacturer. At 50 mg/L a couple of compounds were <40% removed by one type while the other PAC type removed between 85-95% of the same compounds at the same dose.
Bundy, et al. (2007)	GAC/ Flocculation/ sedimentation/ rapid filtration	Bench	River water	Spiked	4	GAC was found to be very effective with >94% removal for all but aspirin (39-56%). Non-GAC treatment options performed poorly with removal from ~3.4-39%.
Snyder, et al. (2003)	Coag/floc/AC/ ozone/BAC/ chlorine/NF/ RO/degradation					This literature review gives the removal efficiencies of several unit processes for many classes of compounds. Removal due to AC is dependent on properties of both AC and solute with hydrophobic interactions as the dominant mechanism. AC removes most non-polar compounds with log K _{ow} < 2.0. Decreased removal with increased NOM.

Table 7: Removal of microconstituents by PAC and GAC

Compound	# of studies	PAC Removal range	GAC Removal range	MW (b) (g/mol)	Log Kow	Notes
a-BHC	2	71		288	3.8	
Acenaphthene	2	92		154	3.92	
Acenaphthylene	2	91		152	3.94	
Acetaminophen	2	72, ~53-97		151	0.46	low range is 5 mg/L PAC
a-Chlordane	2	67		410	6.1	
Aldrin	2	68		365	6.5	
Aminopyrine	1		>99	231	1	Neutral
Androstenedione	3	80, none~92	BDL (a)	286	2.75	low range is 5 mg/L PAC
Anthracene	2	93		178	4.45	
Atenolol	1		~99	266	0.16	Positively charged
Atrazine	2	60, ~41-95		215	2.61	low range is 5 mg/L PAC
b-BHC	2	74		288	3.78	
Benz[a]anthracene	2	86		228	5.76	
benzo[a]pyrene	2	83		252	6.13	
Benzo[b]fluoranthene	2	85		252	5.78	
benzo[g,h,i]perylene	2	77		276	6.63	
benzo[k]fluoranthene	2	82		252	6.11	
Bezafibrate	1		>99	362	4.25	Negatively charged
Caffeine	4	70, ~45-95	>94-BDL	194	<0	low range is 5 mg/L PAC
Carbamazepine	4	74, ~36-97	>99, BDL	236	2.45	Neutral, low range is 5 mg/L PAC
Chrysesin	2	89		228	5.81	
Ciprofloxacin	1	~70-95		331		large range due to type of PAC and Dose
Clenbuteral	1		>99	277	2	Positively charged
Clofibrac acid	1		~99	215	2.57	Neutral
Cyclophosphamide	1		~98	261	0.63	Neutral
d-BHC	2	77		288	4.14	
DDD	2	84		320	6.02	
DDE	2	61		316	6.51	
DDT	2	69		355	6.91	

Table 7 (continued): Removal of microconstituents by PAC and GAC

Compound	# of studies	PAC Removal range	GAC Removal range	MW (b) (g/mol)	Log Kow	Notes
DEET	3	49, ~18-94	BDL	191	2.18	low range is 5 mg/L PAC
Diazepam	2	67		285	2.82	
dibenz[a,h]anthracene	1	83		278	6.75	
Diclofenac	3	39, ~4-92, none~85	>99	318	0.7	Negatively charged, low range is 5 mg/L PAC
Dieldrin	2	68		381	5.4	
Dilantin	3	49	BDL	252	2.47	
Endrin	2	56		381	5.2	
Enrofloxacin	1	~60-96		359	0.7	large range due to type of PAC and Dose
Erythromycin-H2O	2	54, ~16-86		734	3.06	low range is 5 mg/L PAC
Estradiol	3	84, ~42-98	93-95	272	4.01	low range is 5 mg/L PAC
Estriol	2	60, ~40-96		288	2.45	low range is 5 mg/L PAC
Estrone	2	76, ~62-100		270	3.13	low range is 5 mg/L PAC
Ethinylestradiol	2	77, ~36-96		296	3.67	low range is 5 mg/L PAC
Fenoprofen	1		>99	242	3.9	Negatively charged
Flufenamic acid	1	~40-78		281		large range due to type of PAC and Dose
Fluoranthene	2	94		202	5.16	
Fluorene	2	94		166	4.18	
Fluoroquinolonic acid	1	~28-98		Not found		large range due to type of PAC and Dose
Fluoxetine	2	92, ~32-95		309	3.82	low range is 5 mg/L PAC
Galaxolide	2	56		258	5.9	
g-BHC	2	74		288	3.72	
g-Chlordane	2	68		410	7	
Gemfibrozil	3	37, ~4-85	>99	250	4.77	Negatively charged, low range is 5 mg/L PAC
Heptachlor	2	70		373	6.1	
Heptachlor epoxide	2	52		389	5	
Hydrocodone	2	67		299	2.16	
Ibuprofen	4	16, none~77	~97, BDL	206	3.97	Negatively charged
indeno[1,2,3-cd]pyrene	2	80		276	6.7	

Table 7 (continued): Removal of microconstituents by PAC and GAC

Compound	# of studies	PAC Removal range	GAC Removal range	MW (b) (g/mol)	Log Kow	Notes
Iopromide	3	30, ~3-68	BDL	791	-2.05	low range is 5 mg/L PAC
Ketoprofen	1		>99	254	3.12	Negatively charged
Meprobamate	2	33, ~20-100		218	0.7	low range is 5 mg/L PAC
methoxychlor	2	81		344	5.08	
Metolachlor	2	51		284	3.13	
Metoprolol	1		~99	267	1.88	Positively charged
Mirex	2	54		546	7.18	
Moxifloxacin	1	~75-95		Not found		large range due to type of PAC and Dose
Musk ketone	2	67		294	4.31	
Naphtalene	2	84		128	3.3	
Naproxen	2	52, ~3-90		230	3.18	low range is 5 mg/L PAC
Nonylphenol	1	~51		220		
Octylphenol	1	~67		206		
Oxybenzone	3	93, ~79-100	BDL	228	3.79	low range is 5 mg/L PAC
Pentoxifylline	3	77, ~36-97	>99	278	0.29	Neutral, low range is 5 mg/L PAC
Phenanthrene	1	95		178	4.46	
Phenazone	1		~99	188	0.38	Neutral
Pindolol	1		>99	248	1.75	Positively charged
Progesterone	2	86, none~93		253	0.89	low range is 5 mg/L PAC
Propanolol	1		>99	259	3.48	Positively charged
Pyrene	2	95		202	4.88	
Salbutamol	1		~98	239	0.64	Positively charged
Sotalol	1		>99	272	0.24	Positively charged
Sulfamethoxazole	2	36, ~24-89		253	0.89	low range is 5 mg/L PAC
TCEP	3	52, ~15-93	BDL	286	1.44	low range is 5 mg/L PAC
Terbutaline	1		~98	225	0.9	Positively charged
Testosterone	2	79		288	3.32	

Table 7 (continued): Removal of microconstituents by PAC and GAC

Compound	# of studies	PAC Removal range	GAC Removal range	MW (b) (g/mol)	Log Kow	Notes
Triclosan	2	89, ~72-83		290	4.76	low range is 5 mg/L PAC
Trimethoprim	2	83, ~72-100		290	0.91	low range is 5 mg/L PAC
Trovaflaxacin mesylate	1		>95	Not found	1.9	
Salicylic acid	1		39-56	138	2.26	

(a) BDL = Below detectable limits. Some studies reported rejection below limits of quantification (LOQ), or not detected in permeate concentrate and not in % removed.

(b) MW values of some compounds obtained from chemfinder at www.chemfinder.com.

(c) Best performing process not listed due to similar results and lack of data for both processes

surface water sources used for municipal water supplies. For this reason, it is important to use wastewater treatment processes that remove as much DOC as possible prior to use of GAC.

Many studies have found that combined use of GAC or PAC with membrane processes is highly effective at removing microconstituents^{14,32}. Crittenden et al. (2005) listed some benefits of combining UF membranes with PAC¹⁴. One of the reported advantages is that this combination of processes effectively removes both DOC and DBPs. Verliefde et al. (2007) reported the combination of NF and GAC can provide a robust dual barrier for the removal of organic microconstituents³². This is attributed to the NF membrane's ability to effectively remove high-molecular weight polar solutes, while activated carbon is more effective at removing non-polar solutes. Similarly, use of RO to remove NOM would reduce the competition between NOM and microconstituents in a subsequent activated carbon process.

A number of studies reviewed for this report evaluated PPCP and EDC removal at bench or pilot scale. Removal efficiency in these processes is controlled by the time the water and carbon are in contact with each other and the adsorption capacity of the activated carbon. The time is relatively easy to scale between systems and is controlled by the empty bed contact time (EBCT) and loading rate for GAC adsorption and the contact time for PAC adsorption. The adsorption capacity, however, can lead to significantly different results when the scale of the system or the water matrix is different. The water matrix is particularly important because compounds compete for the same adsorption sites. Adsorption studies of single solutes in distilled water provide an upper limit to the adsorbability of a compound. Presence of other compounds and particularly the presence of NOM can significantly reduce the removal efficiency. These effects may be particularly important in wastewater applications because the concentration of adsorbable natural organic matter in waste water may be orders of magnitude higher than the concentration of the target PPCPs and EDCs. Bench-scale tests known as rapid small scale column tests (RSSCTs) can provide good prediction of full-scale performance, but again, the water matrix must be largely identical to the full-scale conditions. As a result, removal efficiency measured at bench or pilot scale may not be representative of removal at full scale unless the water matrix and operating conditions are very similar

Thus, although activated carbon adsorption can effectively remove many microconstituents, the process is influenced by competition by DOC and other constituents. Successful application of the process will require methods of monitoring performance to determine when the breakthrough occurs and how contaminant removal deteriorates.

Design and operational strategies to maximize micropollutant removal using carbon adsorption, based on accepted understanding of the mechanisms controlling the adsorption process, include the following:

- Selection of the carbon with the highest adsorption capacity for the compounds of interest. Bench- or pilot-testing is typically required for carbon selection.
- Select GAC adsorption in lieu of PAC adsorption. GAC uses the adsorption capacity of carbon more effectively and is more appropriate for applications requiring continuous removal.

- If using PAC, increase the carbon dose and/or the contact time. However, carbon dose has a direct effect on the operating cost of the process.
- If using GAC, increase the carbon bed volume with respect to the flowrate being treated. However, bed volume has a direct effect on the capital cost of the process. Monitor effluent concentrations and regenerate or replace media when breakthrough occurs.
- Couple carbon adsorption with a pretreatment process that will minimize the influent DOC concentration and therefore minimize the negative impacts of competitive adsorption.

As well as these processes work, they are not 100 percent effective and several compounds are still detectable in the activated carbon effluent^{6,35}. Some of the important parameters that influence the removal efficiency of microconstituents by the activated carbon process are the carbon type, contaminant solubility, contact time, and competition from NOM²⁴. In addition, the ability of a facility to regenerate or replace the GAC is essential to maintaining high microconstituent removal rates^{6,34}. Nevertheless, activated carbon can provide an additional barrier in a treatment train that, when combined with other effective processes, should offer a multi-barrier approach for PPCP and EDC removal.

Oxidation and Advanced Oxidation Processes

The last category of treatment processes considered in this report is oxidation processes. Oxidation and advanced oxidation processes (AOPs) achieve removal by chemical destruction rather than just separating chemicals from solution¹⁴. The most desirable outcome is the complete oxidation of toxic organic compounds into carbon dioxide, water, and mineral acids, but as this section will discuss, few AOPs achieve total mineralization.

The oxidation process

A variety of water quality problems is amenable to treatment by chemical oxidation. These include disinfection, taste and odor control, and the removal of hydrogen sulfide, color, iron, and manganese, to name a few¹⁴. Oxidation processes have also been used to oxidize organic compounds. This section reviews three types of oxidation processes: conventional chemical oxidation, oxidation by photolysis, and advanced oxidation processes (AOPs).

Conventional oxidation processes use oxidants such as chlorine gas (Cl_2) and its dissolution products hypochlorous acid (HOCl) and hypochlorite (OCl^-), ozone (O_3), hydrogen peroxide (H_2O_2), permanganate (KMnO_4), and chlorine dioxide (ClO_2). The driving force behind all oxidation processes is the exchange of electrons between constituents and the corresponding decrease in the overall electrical potential¹⁴. In conventional oxidation processes, the oxidants are generally selective regarding which compounds they degrade. Although the use of oxidants such as chlorine is common in drinking water treatment, there are disadvantages. One of the largest concerns is the production of disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs).

Advanced oxidation processes combine a chemical oxidant with UV radiation or use combinations of oxidants to increase the rate of the oxidation process. Common AOPs include UV/ozone (UV/O₃), UV/hydrogen peroxide (UV/H₂O₂), UV/titanium dioxide (UV/TiO₂), and Fenton's reagent (H₂O₂ and an iron salt). Other processes such as wet air oxidation, supercritical oxidation, and catalytic oxidation require large amounts of energy in the form of high temperature and pressures. Because contaminant concentrations in drinking water are so low and the daily volume of water to be treated is so large, the latter processes are not used for drinking water treatment.

Oxidation may occur through direct chemical oxidation of susceptible bonds in the target molecule or through generation of highly reactive free radicals such as the hydroxyl radical (OH[•]). AOPs are especially effective at generating free radicals, which is the principal mechanisms responsible for their enhanced performance³⁶. Hydroxyl radicals are reactive electrophiles that react with almost all electron-rich organic compounds¹⁴. For most compounds, their reaction rates are orders of magnitude faster than conventional oxidants.

The effectiveness of disinfection and oxidation processes is determined by a number of factors including the concentration of the oxidant or intensity of UV radiation, the reaction time, temperature, and the presence of competing reactants or free radical scavengers. For most oxidation reactions, there is a direct relationship between oxidant concentration and reaction time. In other words, similar destruction can be achieved using a high oxidant concentration and short reaction time, or low oxidant concentration and long reaction time. Thus, design of disinfection processes are usually based on the parameter CT where CT is:

$$CT = \text{Oxidant Concentration} \times \text{Time}$$

CT usually has units of mg-min/L. The equivalent dose for UV oxidation is the product of light intensity (watts/m²) and time (seconds) to give an exposure measured in Joules/m². Note that the energy of light is inversely proportional to its wavelength so that short wavelength light (i.e. UV light) has more energy than visible light.

Chemical reactions are accelerated by higher temperatures, hence better oxidation or disinfection is achieved in warmer water. However, because of the large volume of water processed in a treatment plant it is not possible to control the temperature of water in a disinfection or oxidation process. Instead, the CT product is increased for lower temperatures to give similar removal.

Most oxidants and especially free radicals are not specific to particular solutes and will react with any oxidizable compound in solution. This includes suspended solids and dissolved organic carbon, whether these compounds are natural or not. Therefore, it is important that the feed water have as low a concentration of DOC as possible to maximize destruction of microconstituents. Further, because suspended solids absorb light, it is important that the suspended solids concentration be as low as possible for oxidation processes that utilize UV light.

Photolysis

Photolysis is a light-induced oxidation process that uses the energy from absorbed photons¹⁴. The compound to be oxidized must have the capacity to adsorb photons of the incident light³⁷. To provide enough energy, light in the UV range of 200 to 400 nm is usually used¹⁴. For photolytic reactions, an unstable compound is formed when a photon is absorbed by an electron in the compound's outer orbital. This causes a reaction that can cause the compound to split apart. The photonic energy needed for the reaction depends on the compound's specific electron structure.

An advantage to oxidation with UV light is that it works well for disinfecting a wide range of waterborne pathogens without creating any of the regulated disinfection byproducts³⁷. This also helps treatment facilities meet part of their overall disinfection demand while reducing the chlorine dose. This reduction in chlorine also decreases the concentrations of halogenated DBPs³⁷.

UV can degrade organic compounds in a couple ways. One method is direct photolysis of photolabile compounds by light absorption³⁷. The other method is indirect photolysis, which can occur in surface water through UV photolysis of NOM that can create hydroxyl radicals. Although NOM can be a source of hydroxyl radicals, it can also decrease degradation of organic compounds through competition for UV light. H₂O₂ can also degrade organic compounds through indirect photolysis. This occurs when UV light, combined with H₂O₂, produce hydroxyl radicals³⁷.

Types of UV Lamps

Three major types of UV lamps are used in water treatment¹⁴. These are (1) low pressure, low intensity, (2) low pressure, high intensity, and (3) medium pressure, high intensity lamps. For the purpose of this paper, the first two types will simply be referred to as low pressure lamps.

Low pressure (LP) mercury lamps are frequently used for UV disinfection³⁸. They emit quasi-monochromatic UV light at 254 nm and have been shown to remove some contaminants, such as ketoprofen and ciprofloxacin. Other compounds are removed to a lesser degree, while the degradation of carbamazepine is found to be negligible. Although the LP lamps have been found to be two to three times more efficient at deactivating microbes than the medium pressure (MP) polychromatic mercury lamps, MP lamps can still be a good choice.

MP lamps emit a broadband spectrum (205 to 500 nm) of light that is used for disinfection and degradation of photolabile compounds³⁸. When combined with H₂O₂, MP-UV produces hydroxyl radicals that can oxidize a wide range of organic compounds. Although LP lamps produce much better light output per unit of electrical energy, the MP lamps are still considered more important for industrial processes because they can produce a much higher total UV-light output³⁹ and have a much higher radiation density⁴⁰. These factors can be advantageous in larger UV disinfection units and facilities where space is a limiting factor because fewer lamps are needed, which reduces the reactor size.

Types of AOPs

Advanced oxidation processes include various combinations of H₂O₂, Ozone, UV, TiO₂, and other oxidants. Table 8 lists three of these processes and their advantages and disadvantages. The table is taken from Crittenden et al. (2005) and lists only these three because of their full scale feasibility and that they were cited as AOPs used to degrade micropollutants by the sources used in this literature review.

Although most AOPs that have commercial applications are actually a combination of two or more other processes, ozone is sometimes considered an AOP due to its ability to form hydroxyl radicals¹⁴. Ozone forms a variety of free radical species through a sequential decay cycle in water. Ozone also forms hydroxyl radicals when it reacts with NOM. This reaction is considered an important mechanism in destroying target compounds. At high pH (> 8.3) free radical scavengers such as carbonate ions (CO₃²⁻) compete for these radicals with organic compounds, thus the effectiveness of ozonation processes diminishes at high pH.

Summary of oxidation process effectiveness for microconstituent removal

Water utilities have begun using oxidation and AOPs as a way to remove micropollutants due to the success of these processes in disinfecting drinking water⁴¹. Recently, significant advances in the understanding of the aquatic photochemistry of certain single compounds or classes of pharmaceuticals has been made, although specific data in this area is still needed⁴⁰.

Table 8: Advantages and disadvantages of various AOPs¹⁴.

AOP Process	Advantages	Disadvantages
H ₂ O ₂ /UV	<ul style="list-style-type: none"> H₂O₂ is quite stable and can be stored on site for long periods prior to use 	<ul style="list-style-type: none"> H₂O₂ has poor UV absorption characteristics and if the water matrix absorbs a lot of UV light energy, then most of the light input to the reactor will be wasted. Special reactors designed for UV illumination are required Residual H₂O₂ must be addressed.
H ₂ O ₂ /Ozone	<ul style="list-style-type: none"> Waters with poor UV light transmission may be treated. Special reactors designed for UV illumination are not required 	<ul style="list-style-type: none"> Volatile organics will be stripped from the ozone contactor. Production of O₃ can be an expensive and inefficient process. Gaseous ozone in the off-gas of the ozone contactor must be removed Maintaining and determining the proper O₃/H₂O₂ dosages may be difficult. Low pH is detrimental to the process.
Ozone/UV	<ul style="list-style-type: none"> Residual oxidant will degrade rapidly (typical half-life of O₃ is 7 min). Ozone absorbs more UV light than an equivalent dose of H₂O₂ (~200 times more at 254 nm) 	<ul style="list-style-type: none"> Special reactors designed for UV illumination are required. Ozone in the off-gas must be removed. Volatile compounds will be stripped from the process.

Table 9 summarizes information from 20 investigations of micropollutant removal by oxidation and advanced oxidation processes. These studies used a wide range of doses, times, water matrixes, and process combinations. As a result, it is not possible to summarize the removal efficiency of all compounds used in these studies in a single comprehensive table as was done for other treatment processes. Instead, specific results are discussed in the following paragraphs.

Most conventional oxidation processes are not very effective at removing many micropollutants⁴². This is largely because lower oxidant concentrations and less powerful oxidants are needed to achieve disinfection than are needed to destroy trace concentrations of microconstituents. As a result, most studies have found relatively poor micropollutant removal by oxidation processes designed to achieve disinfection. In contrast, AOPs rely on higher oxidant doses, longer reaction times, and employ processes that maximize the production of highly reactive free radical compounds that will attack a wide variety of chemical bonds to destroy nearly all organic compounds^{43, 44}.

Although UV light irradiation can be effective for drinking water disinfection, it achieves limited degradation of many micropollutants^{7, 24, 34, 40, 42, 45}, especially at doses used for disinfection (120-400 mJ/cm²)^{40, 43} (although one source cited typical disinfection doses of <5-30 mJ/cm²⁵). Either much longer exposure times or higher intensity UV light is required to destroy micropollutants^{7, 34, 36, 43}. One author cited that the UV dose required for treating micropollutants would be orders of magnitude higher than that needed for disinfection⁵, while another author cited the appropriate dose is about five times higher⁴³.

The combination of peroxide and UV light has been shown to be quite effective at degrading many micropollutants^{37, 38, 41, 43, 44, 46}. This is believed to be due to enhanced production of free radical compounds. The studies by Muller and Jekel (2001) and Muller, et al. (2001), found that the UV/H₂O₂ process had the highest degradation for atrazine (up to 99 percent), but it also used a lot of energy^{36, 39}.

Ozone and ozone-based AOPs are effective at removing many micropollutants^{7, 46}. Ozonation by itself can reduce both the concentration and number of compounds detected after treatment^{34, 44}. For example, Okuda, et al. (2008) found that ozone coupled with a biological activated carbon process reduced all residual pharmaceuticals to below quantification limits⁴². Although O₃ oxidation of microconstituents is highly effective, special considerations are needed for source waters with high bromide concentration to limit formation of brominated compounds^{14, 43}. Also, O₃ oxidation of microconstituents requires longer contact times and/or higher doses than that used for disinfection, which increase process costs^{44, 47}.

Muller et al. (2001) found that the H₂O₂/O₃ process produced the best microconstituent removal in terms of energy use³⁹. The energy used for this process was an order of magnitude lower than the UV based processes (UV/H₂O₂ and UV/O₃). Kim, et al. (2008) found this process to be very promising but did not pursue a full scale version due to the high bromide concentration in the source water⁴³. Instead, the plant was built using the UV/H₂O₂ process. This system has been operating since 2004 and provides good destruction of both organic micropollutants and microorganisms.

Table 9: References, information, and comments on PPCP/EDC removal by oxidation processes

Reference	Type of systems	Scale	Source of wastewater	Source of compounds	Number of compounds evaluated	Comments
Westerhoff et al. (2005)	GAC/PAC/ coagulation/ oxidation processes	Bench	Surface and DI water	Spiked	64	Ozonation significantly reduced concentrations of many compounds, but not clofibrac acid. When combined with peroxide, which produces hydroxyl radicals, removal was increased. Adding small amounts of hydroxide generally increases removal rates by 5-15% with some increasing >20%. Oxidation does produce byproducts. While some chemicals pose a serious risk to human health (e.g. oxidation byproduct of atrazine) others show less activity than parent compound.
Kim et al. (2006)	MBR/GAC/RO/ NF & UV in combination with RO and NF	Pilot/full scale	Wastewater and surface waters	Non-spiked	26	Combination of RO/NF with UV irradiation did not improve removal. Could be due to already high removal efficiencies of RO process.
Yoon et al. (2002)	Coag/GAC/PAC/ AOP/biofiltration/ RO/NF/JF					This literature review gives a very broad range of removal for many processes. UV generally removes from 40->90% & Ozone ranges from 20->90% on most compounds. Not very precise.
Ternes et al. (2002)	GAC/Ozone	Bench/pilot	River and groundwater	Spiked	5	Ozone effectively oxidized carbamazepine and diclofenac at low doses (0.5 mg/L), and reduced bezafibrate and primidone but was limited in reducing clofibrac acid, even at high doses (3.0 mg/L).
Vieno, et al. (2007)	UV/Ozone/GAC/ Coag with rapid sand filtration	Pilot	Raw river water	Non-spiked	13	Coagulation with rapid sand filtration not very effective at PPCP removal. Ozone removes most compounds at >73% with 6 out of 11 being removed at >92%. Ciprofloxacin presented the most trouble with 16% elimination. Warns of risks of oxidation products. UV disinfection doses often to low to transform compounds.
Pereira, et al. (2007)	UV & UV/H ₂ O ₂	Bench	DI water & surface water	Spiked	6	Low pressure (LP) & medium pressure (MP) mercury lamps can degrade a wide variety of compounds although some compounds may need much more energy. Carbamazepine degraded poorly by UV alone and did better with peroxide/UV as did other compounds. MP lamps outperformed LP in both UV & UV/H ₂ O ₂ experiments. Photolysis byproducts found for naproxen only, but recommends future studies to both find byproducts and their health impacts.

Table 9 (continued): References, information, and comments on PPCP/EDC removal by oxidation processes

Reference	Type of systems	Scale	Source of wastewater	Source of compounds	Number of compounds evaluated	Comments
Kruijthof, et al. (2007)	UV & UV/H ₂ O ₂	Bench/pilot/full	DI water & surface water	Spiked	19	Compounds degraded by a combination of either UV photolysis, OH radical reactions, or both. Priority pollutants, in pilot test, showed a degradation between 17-70% by UV at 1000 mJ/cm ² . No pollutants achieved >80% removal by UV alone. An optimal peroxide dose of 6 mg/L was found to correspond to a UV pose of 0.45 kWh/m ³ (540 mJ/cm ²). Dose required for micropollutants is much higher than for disinfection (120 mJ/cm ²). A full scale UV/peroxide plant operating since 2004 has shown to provide a very robust and reliable barrier for both organic micropollutants and microorganisms. Because of bromide rich source water, Ozone/peroxide treatment was not used although research found it very promising. UV alone has relatively low potential for PPCP removal unless given a lot of time or high doses. UV/peroxide performed much better. Ozone/UV performed the best and Ozone and other AOPs showed that they can effectively degrade many PPCPs although some (DEET, 2-GCA, and cyclophosphamide) were persistent. Mentioned study that shows combination of some compounds coexisting in water being more toxic than if they exist alone.
Kim et al. (2008)	Ozone & UV & AOPs UV/peroxide, Ozone/UV, & Ozone/peroxide	Bench	DI water	Spiked	30	
Muller & Jekel (2001)	UV/Ozone, UV/peroxide, Ozone/peroxide, UV/TiO ₂ , & Fentons reagent	Bench	Tap water	Spiked	1	The Ozone/peroxide process achieved 90% removal of atrazine at an order of magnitude less energy than UV, UV/peroxide, & UV/Ozone. The UV/peroxide process had the highest observed results with up to 99% degradation of atrazine.
Muller et al. (2001)	UV/Ozone, UV/peroxide, & Ozone/peroxide	Bench/pilot/full	DI, tap, and ground water	Spiked	4	Ozone/peroxide performed the best and UV/peroxide used the most energy. LP lamps give much better output per energy consumed but MP lamps are better in industrial settings due to their total UV-light output. Ozone/peroxide has the advantage of being able to investigate removal efficiencies at small scale due to the effectiveness of up-scaling without any loss in effectiveness.
Andreozzi, et al. (2004)	Ozone, peroxide/UV, & TiO ₂	Bench	DI water	Spiked	6	Suggests a significant reduction in micropollutants could be achieved by upgrading existing WWTPs with tertiary treatments based on AOPs. TiO ₂ had poor results. Ozone and peroxide/UV showed reduction of toxicity after 2 to 3 minutes of treatment. Shorter times were optimal for algae (1 minute). Suggests more research should be done into more complex water matrices.

Table 9 (continued): References, information, and comments on PPCP/EDC removal by oxid

Reference	Type of systems	Scale	Source of wastewater	Source of compounds	Number of compounds evaluated	Comments
Ternes et al. (2003)	Ozone, UV, Ozone/peroxide & Ozone/UV	Pilot	Wastewater effluent	Non-spiked	25	Previous study found PPCPs well removed by ozone and AOPs during drinking water treatment so study was done to look at ozone processes in treating wastewater. Ozone doses of 10-15 mg/L reduced all but three target compounds to below the LOQ. Study showed high potential for ozone processes to remove trace pollutants from wastewater. For AOPs, the formation of OH radicals enhances oxidation capacity although additional removal was not significant and the increased costs way not warrant these AOPs for wastewater treatment.
Chen, et al. (2007)	UV/peroxide	Bench	DI water & natural river water	Spiked	4	Looked at removing EDCs by UV/peroxide. The combination of UV with 10 ppm peroxide did decrease both in vitro and in vivo estrogenic activity but could not completely remove in vivo estrogenic activity even at a UV dose of up to 2000 mJ/cm ² .
Okuda, et al. (2008)	Ozone, CAS, BNR, and traditional water & wastewater treatment techniques	Full	Wastewater effluent	Non-spiked	66	The process of coagulation, sedimentation, and sand filtration, followed by UV and chlorination disinfection could not remove pharmaceuticals sufficiently. Ozonation was found to significantly lower both the concentration and number of compounds detected. Ozonation followed by a biological activated carbon process was shown to reduce all residual pharmaceuticals to below their quantification limits. Total concentrations of individual compounds were reduced to less than 20% for a CAS process followed by Ozonation.
Pereira, et al. (2007)	UV & UV/H2O2	Bench	DI water & surface water	Spiked	6	The degradation of carbamazepine and naproxen by LP/UV photolysis is very low although much higher rates were found for all compounds with the addition of 10 mg/L of peroxide (at a UV dose of 40 mJ/cm ²). All compounds reduced to below levels of detection at a higher UV dose (1700 mJ/cm ²) with peroxide added. Generating hydroxyl radicals did not enhance degradation of clofibrin acid and iohexol. Very effective direct photolysis of compounds by UV could be the reason.

Table 9 (continued): References, information, and comments on PPCP/EDC removal by oxidation processes

Reference	Type of systems	Scale	Source of wastewater	Source of compounds	Number of compounds evaluated	Comments
Vogna, et al. (2004)	Ozone & UV/peroxide	Bench	DI water	Spiked	1	Both ozonation and UV/peroxide systems were effective in inducing diclofenac degradation. After 90 minutes of treatment the ozone process showed complete conversion of chlorine to chloride ions with a mineralization of 32% while the UV/peroxide showed 52% chlorine conversion and a mineralization of 39%.
Cicek, et al. (2007)	UV	Full	Wastewater effluent	Non-spiked	3	Looked at the removal of 3 estrogenic compounds in full scale WWTPs. The UV process showed that it did not reduce the amount of any of the estrogens.
Canonica, et al. (2008)	UV	Bench	DI water	Spiked	4	Looked at degradation of 4 drugs using LP and MP lamps at standard disinfection treatment doses (400 J/m ²). Showed a pH dependence related to speciation with acid/base equilibria. A relevant degree of degradation was found (<1% to ~50%) depending on compound.
Baumgarten, et al. (2007)	MBR/PAC/NF/RO/O ₃ /O ₃ with UV	Lab and pilot	Municipal and industrial wastewater	Wastewater and spiked	5	Ozone and Ozone/UV were found to be very effective methods in eliminating persistent targeted pharmaceuticals. UV and UV/peroxide performed poorly and the authors found their results were not worth mentioning. There was no mention of the techniques, procedures, and even doses used for the UV processes and since the results for the AOP of UV/peroxide contradict others, their is some question as to their findings.
Snyder, et al. (2003)	Coag/floc/AC/BAC/Ozone/chlorine/NF/RO/degradation					This literature review covers many processes and gives a very broad range of removal efficiencies for each. Ozone is more reactive than chlorine or chlorine dioxide. For these conventional oxidants, reactivity increases with pH and reactivity is greater in thiols > amines > hydroxyl > carboxyl and aromatic compounds are more reactive than aliphatic compounds. Other oxidants are also selective. For UV, disinfection doses are orders of magnitude lower those required for treating micropollutants making it unlikely to be economically feasible. UV based AOPs may be practical in some situations, but at the time of this article, few reports of micropollutant removal by UV processes were available.

Few AOPs systems have been built solely for removal of microconstituents; most have been designed to provide disinfection. One benefit to using an ozone or UV/H₂O₂ system is that they are widely used, have a high level of technical development in industrial applications, and their effectiveness is well established⁴⁶. Ozone and UV/H₂O₂ have shown that they can destroy microconstituents and appear to be promising techniques although, like other oxidation processes, longer treatment is required for micropollutant removal than for disinfection⁴⁴.

Problem compounds and special considerations

Ozone, ozone-based, and UV-based AOPs can effectively degrade most microconstituents but researchers have found some compounds are slowly oxidized. One study found that 2-QCA, DEET, and cyclophosphamide were poorly removed by these processes⁷. A couple studies found that ozonation could not effectively remove clofibric acid^{33,47}. One study found that Ciprofloxacin was the most persistent target compound with only 16 percent degradation by ozone³⁴. Carbamazepine^{37,38} and naproxen³⁷ were found to be poorly degraded with UV. UV/H₂O₂ showed better removal of these compounds^{37,38}. A couple studies found that clofibric acid was poorly removed by ozonation even at higher doses^{10,33}.

Although oxidation processes will degrade most organic compounds, it is important to recognize that the products are almost certainly not fully mineralized to H₂O and CO₂. The objective of an oxidation processes is to change the compound so that it is no longer biologically active³⁴. While an oxidation process may destroy the parent compound, it may produce degradation products with unknown biological activity³⁴. AOPs have shown that they can completely degrade organic compounds, but more research into potential oxidation by-products is warranted.

Although oxidation processes are not likely to completely mineralize organic compounds in water, research has shown that partial oxidation of many recalcitrant compounds will substantially increase their biodegradability⁴⁸. This principle is increasingly used in water and wastewater treatment plants where an oxidation step immediately precedes a biological process to facilitate removal of resistant compounds. A good example is the drinking water treatment plant recently completed by the Albuquerque Bernalillo County Water Utility Authority. This plant provides ozonation immediately prior to biological filters that contain granular activated carbon. Pre-ozonation achieves partial oxidation of refractory compounds that allows rapid biodegradation by organisms attached to the GAC surface. The combination of advanced oxidation followed by biological active filtration might be a particularly effective method of eliminating PPCPs and EDCs, and more research into this process combination is warranted.

As mentioned in the section on reverse osmosis, some RO membranes should not be exposed to certain oxidants. For example the polyamide membrane will rapidly deteriorate if exposed to free chlorine¹⁴. Degradation of membranes must be considered if oxidation and membrane processes are included as sequential processes in treatment facilities.

Summary and Conclusions

The emerging problem of microconstituents in the nation's water supply is one that will likely shape the direction of water treatment for years to come. As water supplies get tighter and the demands for cleaner water increase, the ability of water treatment facilities to consistently produce reliable and clean potable water is essential. The ability to detect these compounds is continually improving and is part of the cause of the increased attention. Current methods can detect compounds at nanograms per liter.

This report evaluated research for water and wastewater treatment processes that have the potential of removing microconstituents from water. The processes reviewed are being used, or are similar to those being used, in the new, state-of-the-art water treatment facility in Cloudcroft, NM. These processes include membrane bioreactors, reverse osmosis, activated carbon, oxidation, and advanced oxidation.

Membrane bioreactors offer some advantages over conventional activated sludge processes including higher MLSS and smaller plant footprints. This is attributed to the membrane in the MBR, which completely retains suspended solids. The MBR delivers a high quality effluent that is largely disinfected and meets or exceeds regulations for traditional parameters in wastewater treatment such as BOD, COD, TSS, ammonia. The MBR process is comparable to conventional activated sludge for removing some targeted microconstituents and more efficient for removing other compounds. The MBR process cannot remove all targeted compounds to below the MRL and some compounds, such as carbamazepine, are not removed at all. The MBR can give adequate pretreatment for a reverse osmosis system.

The reverse osmosis process was found to be very effective at removing most of the targeted compounds studied. This process includes the use of both nanofiltration and reverse osmosis membranes. Some neutral hydrophobic compounds were not well removed by the RO process.

The activated carbon process was also found to be highly effective in removing most targeted compounds to a high degree. Both powder and granular activated carbon were found to be efficient and removal efficiencies are thought to be similar for the two. Time to breakthrough for hydrophobic compounds is much longer than for hydrophilic. NOM can greatly reduce removal efficiencies due to competition for adsorption sites. For PAC, increased removal efficiency for many compounds is dependent on both the PAC dose and the contact time. The most important parameter for GAC is the regular regeneration or replacement of the activated carbon.

Conventional oxidation processes such as chlorine have been widely used for many years as a disinfectant. Most conventional oxidants are not very effective at degrading organic microconstituents. Advanced oxidation processes, which form highly reactive, non-selective hydroxyl radicals, have shown that they can completely oxidize many targeted microconstituents. Both conventional and advanced oxidation processes may produce byproducts. Contact times and doses can be higher for organic microconstituent degradation than for disinfection. The AOPs of ozone and UV/H₂O₂ have the benefit of being systems that are widely used, have a high level of technical development in industrial applications, and their effectiveness is well established.

Many researchers have cited the need for a multibarrier approach in treating microconstituents. The processes reviewed closely match the processes used at the facility in Cloudcroft, NM and should prove to be a reliable system in greatly reducing or eliminating many microconstituents. What is still missing, though, is a general understanding of not only the occurrence and fate of these compounds in the environment, but also an understanding of their effect on human health.

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