ENVIRONMENTAL MICROPOLLUTANTS – THE ROLE OF CONCENTRATION ON TREATABILITY, TECHNOLOGICAL TREATMENT OPTIONS, AND BUSINESS CONSIDERATIONS

By

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LIST OF KEY ACRONYMS

ASP	Activate Sludge Process
AC	Granular Activated Carbon
BAT	Best Available Technology
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CWA	Clean Water Act
θ_h	Hydraulic Resonance Time
K	d^{-1}
k_d	d^{-1}
K_m	mg/L
MAR	Managed Aquifer Recharge
MBR	Membrane Bioreactor
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goals
MGD	Million Gallons per Day
MSW	Municipal Solid Waste
NF	Nano-filtration
PAC	Powdered Activated Carbon
PCPPs	Pharmaceuticals and Personal Care Products
PPB	Parts per billion
Q	Volumetric Flow Rate
RO	Reverse Osmosis
RR	Removal Rate
SDWA	Safe Drinking Water Act
TiO_2	Titanium Dioxide Nano particles
TKN	Total Kjehldahl Nitrogen
TMDL	Total Maximum Daily Load
TSS	Total Suspended Solids
UF	Microfiltration
UV	Ultra-violet
VSS	Volatile Suspended Solids
WWTP	Waste Water Treatment Plant
Y	Bacterial Yield, $\frac{mg\ VSS}{mg\ Substrate}$

CHAPTER 1

INTRODUCTION

Environmental issues can be described as inherently complex and often involve the intersection of many different fields including Law, Science, Engineering, Medicine, Economics, and Philosophy. Science and Engineering hold the keys to technological development necessary to provide clean water and remove micropollutants from wastewater. Many times regulations drive the development of new technology and the application of current technology to ensure that water remains clean for future generations. Additionally, philosophy and economics provide impetus to further develop technology, and helps to determine whether technology gets implemented and provide impetus for new policy through the adoption of new doctrines and beliefs. Therefore, when, how, and if environmental issues become addressed becomes a function of feasibility, the will to solve the problem at hand, and the economics of the solution chosen.

For this thesis, the issue of micropollutants (such as pharmaceuticals and personal care products) will be examined through many of the lenses listed above. In subsections below the motivation for removing micropollutants will be examined, along with philosophical arguments for addressing these substances in water, and finally the current state of the art in terms of science and engineering will be explored with a comprehensive literature review.

1. Motivation

Numerous countries around the world have recognized that water is becoming scarcer and as a result have begun to explore conservation methods including water recycling. Water is recognized as a critical resource for the future, and it has dramatic health consequences when it is not properly cared for. In many regions around the world, drought has left 1.2 billion people without access to safe water and 2.6 billion without access to sanitation [1]. In many regions, climate change has shifted the usual rain patterns making water scarce, resulting in the necessity for new policies and technologies [2]. Recycling water is becoming more common as advanced technologies such as Reverse Osmosis have developed to the extent of widespread commercialization [3, 4]. As an example, in San Diego California, in 2006 they received

only 24% of their normal rainfall during the rainy season [5]. As a result, it is proposed to expand their two recycled water facilities to help meet population growth in the region [5]. Another prime example is in southeast Australia which has been experiencing a drought for the past 10 years, resulting in large curtailing of water usage and conservation programs generating great interest in desalination and water recycling [6, 7, 8]. With increased interest in utilizing recycled water around the world, there are still concerns about this from both the consumer and technological standpoint.

Keeping in mind water is a precious resource, it is necessary in many cases to recycle water for aquifer recharge, use in agriculture, or after proper treatment, as drinking water. In countries such as Australia and on the West Coast of the United States, this process has already begun. One primary concern is for the accumulation of low levels of pollutants, i.e., micropollutants in recycled waters. These micropollutants include pharmaceuticals, pesticides, and other commercial/industrial organic compounds. Numerous researchers including the United States Geological Survey, USGS, recognize that many micropollutants are persistent in the environment, and in addition, carry potential risks to human and ecological health [9, 10, 11]. Many of these compounds pass through current treatment facilities and their fate and transport in the environment is not well understood [12]. If these compounds possess low biodegradability then they may persist in the environment indefinitely. At the current time, the best method for purification is reverse osmosis, RO, but this is expensive and energy intensive [6]. While energy usage is outside the scope of this thesis, it does intricately link to exploring the fate and usage of other treatment process that compete with reverse osmosis to remove the micropollutants. Additionally, it is important to try to prevent pharmaceuticals from reaching the environment through the development of "green pharmaceuticals" and through more effective recycling and disposal programs [13].

It is crucial to understand whether chemical or biological processes are able to degrade some of these Personal Care Products and Pharmaceuticals, PCPPs, to prevent their accumulation within the environment and to allow for safe usage as drinking water augmentation, irrigation, or aquifer recharge. Even if the state of the art technology such as RO was utilized, there is still the problem of what to do with the waste products, i.e. the retentate [4, 6]. It is the treatment of this retentate via chemical adsorption, biological treatment or advanced processes, or application of biological, adsorption or advanced processes to WWTPs to prevent entry into the environment of PCPPs that is of great interest.

2. Precautionary principle

One ethical and legal framework that has been applied to unknown hazards such as global warming is the precautionary principle, or:

> "The precautionary principle advises that lack of scientific evidence for a claim should not be taken as a reason for exercising a lack of caution when the risk is high. When the risk is high, and we have some reason to think that immediate action is required to avoid catastrophe, the precautionary principle states we should take that action" [14].

This approach seeks to protect the environment and public from excess risk in the face of a lack of scientific consensus and places the burden of proof rest with the parties advocating inaction [15] [16]. In Europe, this principle has become the dominate driver of regulation and policy within the environmental arena, since many of the problems faced in the environmental arena are wrought with uncertainty or are low probability events with drastic consequences [15] [16]. This principle has changed how environmental policy has been developed and instead of waiting for catastrophes to occur, seeks to prevent them. While this principle is widely applied in international agreements and protocols, such as the Kyoto Protocol, the US has generally not changed its regulatory framework to utilize this principle.

As PCPPs and their effects in the environment continue to be studied and better understood, it is likely in the future that they will become regulated under existing statutes, or become the subject of new regulations, statutes, or guidance documents [15] [17] [18] [19]. The question becomes, whether the response to PCPPs in the environment and the resulting response will be governed by the precautionary principle or not. In the case of PCPPs, there are numerous environmental impacts that can result from releasing these compounds in to the environment. One such example is the increased incidence of fish downstream of wastewater treatment plants turning into females as a result of the estrogen at low concentrations in the water [20]. This finding is alarming, and, if as a society we wish to protect the environment, even if it is for our own selfish use in the future, then, we must attempt to rectify the situation, even in the absence of absolute proof [15] [16]. Additionally, as fresh water resources continued to be strained by climate change and population growth, the push for water recycling will be necessary to augment dwindling supplies [4]. Thus, with water recycling, there will be a potential for concentrating PCPPs, which would potentially present an increased health and environmental hazard. In the end, the US

may choose to utilize the precautionary principle to guide its regulatory framework to protect human and environmental health.

To understand how the precautionary principle might apply to regulating PCPPs, blood thinners such as aspirin, warfarin, and Plavix will be used a case study. Blood thinners, like most pharmaceuticals, carry side-effects and potential hazards and thus must be viewed with caution. For example, Warfarin was used as a rat poison, and while a very effective anticoagulant clinically, patients must be monitored closely to prevent excessive bleeding [21, 22]. In the case of water recycling, there is the potential for the concentration of these particular substances thereby increasing the risk associated with these water sources. If we apply the precautionary principle to recycled water and regulate blood thinners, then while there may not be ample scientific evidence available when the regulations are written, the regulations should be written with the intent to prevent harm from occurring to end-users. This may result in a more strict regulation, but by the precautionary principle, it is better than waiting for scientific evidence to emerge before acting to regulate these substances.

While utilizing the precautionary principle does potentially cost more than waiting for scientific consensus to form, it is unlikely (based on history) that the United States will change its model. One of the most famous environmental disasters was Love Canal, and this site arguably helped to start the modern environmental movement [23, 24]. There were three different entities that dumped waste into the canal: first, Hooker Chemical disposed of approximately 21,800 tons of chemical waste in the trench between 1942-1953, second, the US Army used the landfill to dispose of parts of the Manhattan project and potentially some chemical warfare compounds, and third, the city of Niagara Falls also used it for municipal waste [23, 24]. The landfill was closed in 1953, and sold to Niagara Falls Board of Education, who opened an elementary school in 1955 to accommodate the growing population [23]. Housing development began at the same time and continued into the mid-1970s despite that in the late 1950s, "residents began to complain about children being burnt, nauseous odors, and black sludge" [24]. Heavy rainfall in 1975-1976 caused ground water contamination and ponding of hazardous chemicals [23]. As a result of the chemicals at the site and heavy rainfall, birth defects, miscarriages, and chromosome damage was observed in residents [23, 24]. Evacuations began in 1978 and continued through 1980 until President Carter on 10/1/1980 ordered an evacuation of all residents of love Canal because of the emotional

disturbance [24]. Love Canal was not an application of the precautionary principle, while the evidence was still coming in, it would have been precautionary if action had been taken in the 50s. On the whole, most superfund sites were cleaned up after hazards were already identified or after harm was observed. In general, it is rare that sites were cleaned up before negative attributes were observed. This will likely continue to be the method by which the United States operates and little or no action will occur prior to harm being scientifically observed. Another prime example of the United States not implementing the precautionary principle is Climate Change. Behind climate change now is a huge body of scientific literature with a consensus that global climate change is occurring [25, 26, 27]. Many International bodies agree that it needs to be addressed and the precautionary principle is often applied as a justification for action [25, 26, 27]. Despite this scientific evidence and international consensus, the US is not acting, along with the rest of the world, as quickly as may be required [25, 26, 27]. The potential consequences from CO_2-induced climate change are massive, and while there is high uncertainty of the effects and in the modeled projections, the precautionary principle would argue that action must be taken to avert potential disasters. Europe has embraced this theory, but the US to a large extent still considers inaction to be viable due to increased competition from developing nations like China.

Both Love Canal and Climate Change were examples in which the United States has not utilized a precautionary principle framework for regulating, and it is not likely that PCPPs will be an exception to this behavior. It is more likely that as new technologies develop, explored in Chapter 4 (page 83), PCPPs will be regulated only as hazards become identified rather than promulgated prior to the implementation of a viable technology.

3. Technological pragmatism

Many different ethical frameworks have been proposed to address environmental problems, but these frameworks mostly fail to account for the technological capabilities that constrain how a society can solve a current problem. Technological pragmatism is a descendent of environmental pragmatism and environmental ethics [28]. It seeks to blend the constraints of Science and Engineering with moral philosophy. When large issues such as sustainable water practices and sources of climate change seek to be addressed by traditional environmental ethics, all too often there are two schools of thought,

anthropocentric or human centered and non-anthropocentric or environmentally centered [19]. The problem with diametrically opposed frameworks is that there is little room for compromise and progress in terms of policy. Therefore, ethicists seek to apply a pragmatic approach to solving the dilemmas presented in environmental issues. The environmental pragmatist approach (compared to the non-anthropocentric ideal) addresses strong versus weak anthropocentrism (human felt preference versus human considered preferences) [18, 19]. It is the application of considered preferences where the moral argument for developing protection of the environment originates, even if it is an extension of ensuring continued use of the environment for future generations [18, 19, 29]. As a result, our degree of considered preferences, determines how we value of the environment and how much we will seek to protect it. From this forms the basis of technological pragmatism which incorporates scientific progress and technological considerations into policy decisions, or "the purpose of blending science with moral philosophy is that one cannot make educated policy decisions without considering both" [28]. Technological pragmatism goes on to argue that there is a moral obligation for the development and application of technology [28]. While this ethical framework was originally proposed to address climate change and an ethical framework for preventing it, it can be applied to any problem that requires a balancing of ethics and science. The regulation of micropollutants in the environment certainly qualifies within this framework.

Once establishing that there is a desire to remove these micropollutants from water and wastewater to prevent environmental damage or to ensure safety for drinking water, it becomes necessary to consider how to approach removing PCPPs through the lens of technological pragmatism. Currently, the removal of micropollutants is technologically limited and cost prohibitive due to their low concentration [30]. On the one hand people want their water to be pristine, accepting little to no contamination, but there is a technological limitation to getting water that clean in an economical fashion. In order to remove micropollutants, the implementation of a new technology is likely required to accomplish this goal. Technological pragmatism dictates that if a new technology was to be applied, like RO, to remove PCPPs, then the impact on the environment in terms of the complete lifecycle must be considered and not just the anthropocentric benefits associated with access to clean water. For example if RO was applied to wastewater effluents to remove carbamezipine, then there would need to be a consideration of whether the technology was sufficient to accomplish the job, what the general environmental benefits would be, and the

potential drawbacks of implementing the technology, as well as cost. In this case there are benefits for humanity and the environment in preventing the intake of Carbamazepine and preventing accumulation of this compound in the environment over time. On the other hand, implementation of RO necessitates a supply of more energy which is likely to come from fossil fuels, which would result in an increase in climate change impact. Climate change has many different negative environmental impacts that are beyond the scope of this work (see [2] and [27] for further reading), but these must be taken into account. In this case, technological pragmatism may argue that a current technology is not sufficient and rather would advocate for scientific development that would allow for the application of a cleaner technology. If on the other hand, there exists a cleaner technology that decreases environmental harm and provides humanity with clean water, then as a society we have a moral obligation to implement that technology. As to whether this technology exists yet from a scientific perspective, that question will be addressed within this work.

Overall, seeking to remove PCPPs for environmental and anthropocentric reasons is in line with environmental pragmatism, and by applying technological pragmatism, an optimal technology can and will be able to reach this goal. "Pragmatism embraces moral pluralism where there is no one correct practice or one set of practices to answer how we should proceed" [28, 29]. This is crucial, and while there are technologies currently available to remove these compounds, there is a limit to these technologies and hopefully within an open mind, scientists and engineers will continue to develop technology that will allow for these compounds to be successfully removed. Pragmatism can be an ethical framework in which to operate for policy, regulatory, and technology implementation. This viewpoint should be utilized as a framework to develop new regulations concerning PCPPs. In the next section, the regulatory framework, current and future, will be explored.

4. Relevant Laws Governing Water and Wastewater

Law and regulation has evolved over the past forty years to help protect the environment in the wake of numerous environmental disasters, such as Love Canal and the valley of drums. The modern environmental movement and the subsequent legislation were a response to these high profile events which had devastating impacts on communities. Some of these laws have sought to regulate water and the two

pieces of legislation most relevant are the Safe Drinking Water Act (SDWA) and Clean Water Act (CWA) [16]. The first law to effectively address water quality and regulate discharges was the CWA.

The CWA, was created to regulate discharges of pollutants and sets the standards that are applicable to Wastewater Treatment Plants, WWTPs. Prior to the CWA, the primary means of prosecuting water pollution causation was Tort law [16]. Under this subdivision of law, a particular pollutant must be connected to a particular source to result in liability, which became almost impossible after industrialization due to the number of sources discharging into surface waters [16]. As a result, the CWA regulates effluent discharges, which come out of a specific point source thereby allowing for liability to be created. The act, prohibits "all unpermitted discharges into navigable waters of the United States of pollutants from point sources, imposes effluent limitations on dischargers, and requires statewide planning for control of pollution from nonpoint sources" [16, p. 646]. There were three different types of pollutants that were regulated under the CWA: 1) conventional pollutants, which are pollutants amenable to biological treatment, 2) toxic pollutants, which "cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological malfunctions (including malfunctions in reproduction)" [31], and 3) Non-conventional non-priority pollutants, which includes everything else like ammonium and heat [16]. A subset of contaminants of interest were referred to as Priority Pollutants, for which EPA has established applicable technology-based standards and were the first individual substances to be regulated. Effluent limits also take into consideration: nutrients, pathogens, and sediment to maintain water quality in a given water body. To maintain the integrity of a water body, the EPA mandates certain technology be utilized for certain pollutants (specified in the individual NPDES permit).

The CWA was established as a technology forcing statute that required a specific technology to be utilized based of the type of contaminant being discharged. After 1989, the standards that were applicable to each of the three categories of pollutants were: Conventional pollutants required BCT under §301(b)(2)(E), Non-Conventional non-toxic pollutants required BAT, new sources of conventional and non-conventional non-toxic pollutants require BADT/NSPS under §306, and Toxic pollutants required BAT after the Flannery Decree, which was added to §301 from the original act (Guidelines for priority pollutant can be found in §304(m) , whereas everything else is governed under the impaired water lists and ICS under §304(l)) [16]. While technology was utilized as one means of protecting a water body,

sometimes technology was not enough to maintain the integrity of a given navigable water. When that occurred, the second mechanism of the act kicked in, which is known as Water Quality Standards. There are two components that are necessary to form a water quality standard: 1) a designated use and 2) a water quality criteria meant to preserve that designated use [16]. Water quality standards are continually devised by the state and reviewed by EPA [16].

Unlike the CWA which regulates the discharges into a water body, the SDWA was created to regulate the contents of water intended for distribution. The SDWA "regulates contaminants in drinking water supplied by public water systems, establishes a permit program regulating the underground injection of hazardous waste (to protect water supplies), and restricts activities that threaten sole-source aquifers" [16, p. 646]. Under this act, EPA set drinking water standards for public sources, but not private wells or bottled water [16]. There are two types of standards: 1) Maximum Contaminant Level Goals (MCLGs) which are non-enforceable and 2) Maximum Contaminant Levels (MCLs) which are enforceable [16]. MCLGs were set at a level of no known or anticipated adverse health effects with an additional safety margin and the MCL was set as close to MCLGs as possible with the feasible best treatment technology (cost is taken into account for large communities and was meant to be affordable) [16]. MCLs apply to any facility that supplies water for human consumption to at least 15 connections or approximately 25 people [16]. Currently there are more than 90 contaminants regulated, including disinfection byproducts, pathogens, and other chemicals [16]. The EPA has the ability under the act to consider adding contaminants to be regulated. As a result, the latest scientific and technological breakthroughs allow for the continued protection of health without excess risk.

It should be noted that no new environmental regulations have been passed through Congress in the past two decades and that most new applications or rulings issued by EPA have been accomplished through guidance. Considering this set of circumstances, it is highly unlikely that there will be new regulations that govern the discharge of micropollutants under the CWA or SDWA, in the future. With that said, it may become necessary to regulate these micropollutants via guidance issued by the EPA.

As a case study, estrogenic compounds will be examined with respect to how they might be regulated and how they could end up as being controlled under the CWA and SDWA. The CWA would govern discharges into the environment of estrogenic compounds whereas the SDWA would seek to protect

water destined for public water distribution. The mechanisms and requirement that would result in successfully regulating PCPPs would depend not only upon the availability of successful water treatment technologies, but also evidence of harm or hazard to human health or the environment. For the SDWA, there would likely be a recommended new technology applied to drinking water plants, and if water recycling were to become commonplace, then applicable MCLs and MCLGs for estrogenic compounds would be developed. This would definitely increase the cost of drinking water treatment, but might be necessary as health information becomes available for these compounds.

Many estrogenic compounds are recalcitrant and long-lived within the environment, making them likely to qualify under the CWA as a toxic pollutant [31]. Estrogenic compounds would likely qualify as a toxic pollutant, since numerous studies have shown that downstream of a WWTP, fish are largely female as a result of the increased estrogenic compounds in the water [20]. To regulate these compounds going into a specific body of water, first it must be known at what concentration fish begin to turn female. Once ascertaining this threshold concentration, water quality standards could be devised for a given water body (based on fish species response). After this, the relevant point sources discharging estrogenic compounds into the navigable water will need to be identified. Let's assume that there are two different dischargers, a WWTP and an industrial plant. Once determining the Total Maximum Daily Load, TMDL, for that water body, allowances in the NPDES permits for each discharger can be devised that will protect the water body for the designated use. This potential mechanism of regulation under the CWA would require the usage of "Best Available Technology," BAT, to control the discharges of the WWTP and the industrial plant. The allocations given to each of these would be dependent upon when each facility was built, how much each facility produces, and economic considerations such as the ability to pay for the required scale of treatment [16]. Regardless of which of the two dischargers will need to implement BAT and to what extent, the technology required to remove estrogenic compounds will likely be extremely costly and require advanced processes to prevent the compounds from reaching the water body.

Previous studies

1. Overview

Pharmaceuticals as they apply to agriculture, usage in agriculture, and potential health concerns have been a topic for many years, although methods of detection have been lagging. One such example was published by Morgan et al. in 1987, where agricultural and veterinary journals publish articles on livestock medicine issues [32]. Many organizations were already starting to think about how these products may adversely impact public health [32]. This was the beginning of PCPPs in the literature and it was not for over a decade that methods of detection improved to the extent that major studies were able to be conducted.

Previous authors have reported on the existence of PCPPs in the environment and the potential hazards associated with them. One of the first reviews written was by Daughton et al., which presents a large synthesis article on the presence of PCPPs and examines the associated risks with these compounds in the aquatic environment [33]. In the same year, the National Research Council published its review on hormonally active substances in the environment. This report demonstrated links with declining populations of some wildlife species, potential changes in structure and function relationships in wildlife, and a warning for observing human populations for signs of epidemiological changes and the incidence of "small penis size, abnormal testes in males, and abnormal ovaries in females" [20]. Hormonal compounds were not the only compounds of concern. Buser et al. examined ibuprofen in depth and its presence in surface waters and WWTP samples [34]. This paper was one of the first to demonstrate that Ibuprofen appears to be degraded by the treatment process unlike other PCPPs, such as diclofenac and clofibric acid [34]. Some of the earliest work published has been performed in Europe. Hirsch et al. focused on the presence of antibiotics in the environment and in wastewater effluents in Germany [35]. His group found that compounds from the antibiotic classes of acrolid antibiotics, sulfonamides, penicillins and tetracyclines were present in wastewater effluents and in streams, and did not appear to be easily degraded [35]. Also studying PCPPs in Germany, was Ternes in 1999, who's paper was one of the first to demonstrate the link between WWTP effluent as the source contributing to the presence of these compounds in the environment [36]. Additionally, his findings demonstrated that many of the compounds that were not removed

effectively during treatment were acidic in nature, including: "lipid regulators bezafibrate, gemfibrozil, the antiphlogistics diclofenac, ibuprofen, indometacine, naproxen, phenazone and the metabolites clofibric acid, fenofibric acid and salicylic acid as well as neutral or weak basic drugs such as: the betablockers metoprolol, propranolol and the antiepileptic drug carbamazepine" [36]. These PCPPs "were found to be ubiquitously present in the rivers and streams" [36]. Therefore, these authors helped to develop some of the first studies on PCPPs and to bring awareness of a potential developing environmental health problem.

One of the first comprehensive papers in the US that was written on the topic of PCPPs was by Koplin et al. and the USGS, which helped kicked off a major research efforts to characterize and address these compounds. The major paper was published in Environmental Science &Technology in 2002 by Koplin et al. [37]. This paper was the first nationwide study of 95 PCPPs from 139 streams over 30 states, and it found that 82 out of the 95 PCPPs, were present in detectable amounts [37]. The most frequently detected compounds were: "coprostanol, cholesterol, N,N-diethyltoluamide, caffeine, triclosan, tri(2-chloroetyl)phosphate, and 4-nonylphenol," but these compounds were not necessarily present in the highest concentrations [37]. Part of the reason that it took until 1999 to develop adequate analytical methods capable of detecting PCPPs at very low concentrations, was the technological limitations associated with instrumentation [37]. With that said, even today, the methods that are available are still cumbersome and time consuming to perform, but the methods are capable of quantifying the presence of these compounds in water samples.

The development of the methods that allowed for the detection of these compounds and continued evaluation of water samples have been spearheaded mainly by EPA and the USGS. The main analytical methods for measuring PCPPs include: EPA method 1694 [38], USGS adapted methods from Koplin et al. [10]. Other methods require more adaptation and further development, as with Batt et al. [39]. These methods primarily rely on liquid chromatography coupled to three MS units [39]. Additionally, these methods require large prep time and often require concentrating samples several orders of magnitude to improve the sensitivity of the equipment used for detection [38]. Therefore, the currently available methods are time consuming to produce results, but they do offer the ability for reasonable recovery of the substances of interest.

2. Methods

A comprehensive literature review was conducted and information was compiled into a series of tables. A review of 140 articles including review articles was conducted for literature values and compiled into four different tables. First, anytime an article mentioned a relevant WWTP influent, effluent, or environmental concentration it was added to Table 1. The minimum and maximum values were then found for each PCPP until the literature review was finished. Biodegradability, log Kow, and Solubility were taken from peer reviewed literature when available, and in its absence, were taken from EPA EPISUITES 4.11 [40]. Additionally, as removal efficiencies were found for various treatment methods, this data was compiled into three different tables: Table 2 (Biological treatment methods), Table 3 (Chemical processes), and Table 4 (Physical processes). The relevant concentrations that were utilized in these studies were also included for reference. These tables will be further discussed in the next subsection.

After compiling influent and effluent data in Table 1, a series of figures were constructed utilizing this data. First, a figure was constructed by utilizing the minimum and maximum influent concentrations for each species and plotting them in a semi-log fashion. The SDWA limit for phenol was used as a surrogate level for comparison with these compounds, since no limits currently exist for PCPPs. Second, a figure was constructed by utilizing the minimum and maximum effluent concentrations after having been concentrated by seven times (as would be the case for an RO process for each species), and plotting them in a semi-log fashion [41, 42]. The SDWA limit for phenol was used as a surrogate level for these compounds since no limits currently exist for PCPPs. Finally, six figures were created in total, one for the influent and one for the effluent, for a daily, monthly, and yearly sample mass flow of the PCPPs based on a total flow of 100 MGD as an example. These values were then plotted in a semi-log fashion.

After compilation of Log K_{ow} data in Table 1, a final series of figures were constructed. The data was grouped into three different groupings based on a hydrophobicity scheme by Rogers: log K_{ow} less than 2.5, log K_{ow} between 2.5 and 4, and log K_{ow} greater than 4 [43]. Plots were constructed of influent versus effluent for each set of compounds. A linear trend line was applied to the data and compared to a line with a 1:1 slope (representing no removal of the compounds). Compounds removed exhibit a ratio of effluent to influent concentrations less than 1.0.

3. Rationale for Tables and Figures from the literature

In order to compress a comprehensive literature review into a short amount of space, tables and figures were chosen to summarize the information. The 47 compounds that were explored in this study were chosen to provide a diversity of compound classes and were among some of the most prescribed drugs. While many more papers have been written on the removal of PCPPs from water and wastewater, enough papers were reviewed to gain a wide breadth of knowledge while avoiding redundancy. The information that was collected was then broken into four different tables. The first overviews the chemical characteristics of the compounds of interest along with their influent, effluent, and environmental concentrations presented in literature. The second, third, and fourth were organized into biological, chemical, and physical processes respectively. All of these tables provide an excellent medium to quickly and comprehensively review literature values in a way that has not previously been published.

Table 1: Concentration of PCPPs in the Environment (Note: all concentrations in µg/L unless stated otherwise)

Drug	WWTP influent concentration		WWTP effluent concentration		Environmental concentration		Bio-degradibility	Log Kow	Solubility	References
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum				
Acetaminophen	0.015	150	0.028	1.48	0.1	10	No, weeks[C]	0.461[a]	$1.4*10^4$ mg/L[a]	[10,44-47]
ASA	0.001	7	0.015	1.51	0.05	0.34	Yes, weeks[3]	1.191[a]	4600 mg/L[a]	[43, 44, 45, 48, 49]
Acebutolol	0.335	1.04	0.01	0.255	0.8	8	Yes, weeks[3]	1.71 [d]	$1.07*10^5$ mg/L[a]	[44, 50-52]
Amitriptyline	0.5	6.5	0.001	0.35						[44]
Atenolol	0.03	25	0.01	70	1.1415	14.2	No, weeks/months[c]	0.161[a]	$1.33*10^4$ mg/L[a]	[44, 47, 50, 52, 53]
Atrazine	0.032	0.87	0.049	0.87	2	2.01	No, months[c]	2.611[a]	34.7 mg/L[a]	[54, 55]
Bezafibrate	0.05	28	0.008	5	30	30	Yes, months[c]	4.25 [d]	7.927 mg/L[a]	[44, 50, 56]
Bisphenol A	0.088	11.8	0.006	4.09	0.0019	50	No, weeks/months[c]	3.32[a]	120 mg/L	[50, 57-59]
Caffeine	3.69	118	0.174	12	0.081	71.9	Yes, weeks[c]	-0.071[a]	$2.16*10^4$ mg/L[a]	[10, 43, 47, 50]
Carbamazepine	0.0819	22	0.042	2.44	0.11	2.3	No, weeks/months[c]	2.451[a]	112 mg/L[1]	[44, 47, 49, 50, 52, 60, 61]
Celiprolol	0.44	0.44	0.28	0.28	-	-	No, weeks/months[c]	1.92[a]	9401 mg/L[1]	[50]
Ciprofloxacin	0.09	15	0.007	5	0.02	0.03	No, months[c]	0.28[a]	$3*10^4$ mg/L[1]	[10, 44, 50, 52]
Codeine	0.1	45	0.025	8	0.012	0.019	No, weeks[c]	1.19[a]	9000 mg/L[1]	[43, 44]
Diclofenac	0.03	13	0.04	10.5	0.25	0.75	No, weeks/months[c]	4.51[a]	2.37 mg/L[1]	[44, 50, 62]
Doxycyclin	0.0025	2.48	0.023	1.09	ND	ND	No, months[c]	-0.02[a]	630 mg/L[a]	[10, 44, 50]
Venlafaxine (Effexor XR)	0.015	0.93	0.057	2.4	0.4	1.4	No, months[c]	3.28 [d]	1422 mg/L[b]	[63-65]
Erythromycin	0.1	10	0.008	6.5	0.01	12	No, recalcitrant[c]	3.06[a]	$1*10^6$ mg/L[b]	[10, 43, 44, 48, 50]

17α-estradiol	0.003	3.1	0.0002	0.055	0.03	0.074	Yes, weeks[c]	2.45[d]	558 mg/L[b]	[10, 44]
17β-estradiol	0.0001	0.01	0.0002	0.055	0.0001	0.16	Yes, weeks[c]	2.45[d]	558 mg/L[b]	[10, 44, 59, 66]
Estrone	0.0001	0.7	0.0002	0.01	0.0001	0.11	No, weeks/months[c]	3.131[a]	30 mg/L[a]	10, 44, 47, 55, 66, 67]
Fenofibric Acid	0.079	0.42	0.078	70	0.012	0.012	Yes, months[c]	5.19[d]	0.832 mg/L[b]	[10, 44, 50]
Gemfibrozil	0.03	18	0.003	5.5	0.048	0.79	No, weeks/months[c]	4.77[d]	8.42 mg/L[b]	[10, 44, 47, 50, 68]
Hydrochlorothiazide	0.6	10	1.7	12	0.00053	0.256				[44, 50, 69]
Ibuprofen	0.0143	300	0.03	45	0.05	3.87	Yes, weeks[c]	3.97[a]	21 mg/L[a]	[10, 43-45, 47, 50, 67]
Iopromide	0.01	9.205	0.01	9	0.011	0.91	No, months[c]	-2.05[a]	$3.35*10^5$ mg/L[b]	[44, 50, 70]
Iomeprol	6.05	6.05	1.606	1.606	0.01	0.89	No, months[c]	-2.79[a]	$1*10^6$ mg/L[b]	[50]
Iohexol	6.7	6.7	2.706	2.706	-	-	No, months[c]	-3.05[a]	$1*10^6$ mg/L[b]	[50, 70]
Iopamidol	2.3	2.3	1.9	1.9	0.17	2.8	No, months[c]	-2.42[a]	$1.04*10^5$ mg/L[b]	[50, 70]
Lipitor	0.025	0.55	0.01	0.575	0.324	0.448	No, months[c]	6.361[a]	0.013531 mg/L[b]	[54, 71, 72]
Meprobamate	0.0082	0.073	0.0057	0.0059	0.043	0.043	No, weeks/months[c]	0.701[a]	4700 mg/L[a]	[43, 48, 54, 63]
Metformin	18	105	1.3	26	0.11	0.15				[10, 73]
Metoprolol	0.01	2.29	0.018	4.9	0.145	0.145	Yes, weeks[c]	1.88[a]	$1.69*10^4$ mg/L[a]	[44, 50, 52, 74, 75]
Naproxen	0.04	70	0.001	2.62	0.0021	0.145	No, weeks[c]	3.181[a]	15.9 mg/L[a]	[43-45, 50, 58, 67]
Norfloxacin	0.018	0.96	0.007	0.33	0.12	0.12	No, months[c]	-1.03[a]	$4.02*10^4$ mg/L[b]	[10, 44, 50, 52]
Ofloxacin	0.007	35	0.007	1.75	0.0081	0.634	No, recalcitrant[c]	-0.39[a]	$6.87*10^3$ mg/L[b]	[10, 44, 50, 52]
Paraxanthin	26.732	26.732	0.836	0.836	-	-	Yes, weeks[c]	-0.39[a] (est)[2]	$2.2*10^5$ mg/L[b]	[50]

Progesterone	0.0022	0.00031	0.00058	0.00058	0.11	0.199	No, weeks/months[c]	3.87[a]	8.81 mg/L[a]	[10, 54]
Propranol	0.036	0.51	0.03	0.18	-	-	Yes, weeks[c]	3.48[a]	61.7 mg/L[a]	[50]
Roxithromycin	0.01	18	0.008	5	0.03	0.35	No, recalcitrant[c]	2.75[d]	$4.74*10^5$ mg/L[b]	[44, 50, 75]
Sotalol	0.37	3.28	0.13	1.12	-	-	No, weeks/months[c]	0.24[a]	$1.41*10^4$ mg/L[b]	[50, 52]
Sulfamethoxazole	0.003	10	0.003	5	0.066	2	No, weeks/months[c]	0.891[a]	610 mg/L[a]	[10, 43, 44, 47, 50, 60, 67]
Testosterone	0.0011	0.0012	-	-	0.116	0.214	No, weeks/months[c]	3.32[d]	23.4 mg/L[b]	[10, 54]
Triclosan	0.15	1.93	0.012	0.219	0.029	2.3	No, months[c]	4.76[a]	10 mg/L[a]	[10, 44, 50, 58]
Trimethoprim	0.005	10	0.04	1.34	0.15	0.71	No, days/weeks[c]	0.911[a]	400 mg/L[a]	[10, 44, 50]
Warfarin	-	-	-	-	ND	ND	No, weeks/months[c]	2.701[a]	17 mg/L[a]	[10, 76]
Zocor	0.004	0.004	0.002	0.002	-	-	No, weeks/months[c]	4.681[a]	0.03 mg/L[a]	[50]
Sertralie (Zoloft)	-	-	-	-	0.00029	0.00029	No, months[c]	1.67[d]	0.63763 mg/L[b]	[63]

a. Log Kow and solubility data was obtained from the EPA EPISUITE 4.11, downloaded in December 2012 to ensure accuracy and was up to date [40].
b. Estimated solubility data from EPA EPISUITE 4.11 [40].
c. Estimated Bio-degradability of compounds was obtained from the EPA EPISUITE 4.11 with BIOWIN model [40]
d. Estimated Log Kow data was obtained from the EPA EPISUITE 4.11, downloaded in December 2012 to ensure accuracy and was up to date [40].

Table 2: Summary of previous findings on removal efficiencies for selected PCPPs using biological based treatment.

PCPPs	Removal Rate ASP[e]	Removal Rate MBR[e]	Influent Concentration	Reference
Acetaminophen	98.4%-99.9%[d]	99.6%-99.9%[d]		[77]
		-66%[b]	.1505 µg/L	[78]
	100%[d]		37-130 µg/L	[79]
	100%[d]		1.571-23.2 µg/L	[80]
	>99%[d]		28.79-94.58 µg/L	[81]
	96%-100%[d]		1-26 µg/L	[82]
		99.82%-99.91%[d]	11.5 µg/L	[83]
	100%[d]		1.571-37.458 µg/L	[84]
ASA	95%-99%[d]		12.6-31.7 µg/L	[85]
	82%-99%[d]		1-7 µg/L	[82]
Acebutolol	38%-60%[d]		.04-1.040 µg/L	[52]
	58.2%[d]		0.355 µg/L	[50]
	-10%-95%[d]		0.810-9.867 µg/L	[86]
	54.9%-79.5%[d]		0.39-0.51 µg/L	[51]
Amitriptyline				
Atenolol	37%-77%[d]		0.350-1.71 µg/L	[52]
	56.7%[d]		0.03-1.197 µg/L	[50]
		5%[b]	0.2006 µg/L	[78]
	5%-95%[d]		0.99-8.384 µg/L	[86]
	31.5%-62.6%[d]		0.72-0.91 µg/L	[87]
	14.4%[d]		0.66-2.432 µg/L	[80]
	82%-93%[d]		0.916-2.44 µg/L	[88]
	20%-97%[d]		0.05-3 µg/L	[82]
	84%[d]		0.3-4.3 µg/L	[89]
	45%-92.2%[d]		0.51-0.8 µg/L	[51]
Atrazine				
Bezafibrate	60.8%[d]		0.05-4.9 µg/L	[50]
	9.1%[d]		0.048-0.361 µg/L	[80]
	23%-99%[d]		0.04-2 µg/L	[82]
	97%[d]		0.8-9 µg/L	[89]
	36.8%-99.5%[d]	77.3%-96.4%[d]	0.01-7.6 µg/L	[90]
Bisphenol A	60%-100%[b]		120-1600 µg/L	[57]
	75.8%-85%[d]	74.2%[b]	1.94-2.19 µg/L	[91]
	71%[d]		0.088-11.8 µg/L	[50]
	10.5%-98.7%[d]	92.7%-99.3%[d]	0.035-2.025 µg/L	[90]
Caffeine	96.9%[d]		3.69-118 µg/L	[50]
	100%[d]		54-120 µg/L	[79]
	94.9%[d]		5.01-65.625 µg/L	[80]
	0%-100%[d]		0.44-3.28 µg/L	[85]
	>99%[d]		29.09-53.32 µg/L	[81]
		98.83%-99%[d]	9.68 µg/L	[83]
Carbamazepine	-22% to -193%[d]		0.160-.820 µg/L	[52]
	-5.7%[d]		0.0819-1.68 µg/L	[50]
		-42%[b]	0.2013 µg/L	[78]
	-81.8%-10.8%[d]		0.66-1.0 µg/L	[87]
	-40%-18%[d]		0.130-0.40 µg/L	[79]
	9.5%[d]		0.106-0.173 µg/L	[80]
	0%-95%[d]		0.07-0.97 µg/L	[85]

	41%[d]		0.084-0.136 µg/L	[81]
	37.8%-64.9%[d]		0.064-0.099 µg/L	[88]
		0%-10%[b]	0.1-0.775 µg/L	[92]
	0%[d]		0.7-3.3 µg/L	[89]
		-9.5% to -4.55%[d]	0.042 µg/L	[83]
	0%[d]		0.18-2 µg/L	[93]
	-43.1%-13.8%[d]	-12.8%-12.5%[d]	0.01-1.85 µg/L	[90]
	-28.6%-34.5%[d]	-7.1%-30.9%[b]	0.7-2.25 µg/L	[94]
	-43.1% to -17.5%[d]		0.31-0.4 µg/L	[51]
Celiprolol	36.4%[d]		0.44 µg/L	[50]
	-60%-75%[d]		0.10-0.16 µg/L	[87]
	36%[d]		0.1-0.78 µg/L	[89]
Ciprofloxacin	79%-96%[d]		0-4.230 µg/L	[52]
	62.3%[d]		0.09-5.524 µg/L	[50]
	52%-90%[d]		0.43-1.10 µg/L	[79]
	57%[d]		0.16-13.625 µg/L	[80]
	37%-99%[d]		0.04-2 µg/L	[82]
	80%-95.5%[d]		0.42-0.65µg/L	[51]
Codeine	32.5%[d]		2.8605 µg/L	[50]
	79.2%-86.25%[d]		0.12-0.16 µg/L	[87]
	69.3%[d]		0.15-2.087 µg/L	[80]
	86.7%-91.8%[d]		0.055-0.338 µg/L	[88]
Diclofenac	34.6%[d]		0.16-3.1 µg/L	[50]
		5%[b]	0.1412 µg/L	[78]
	58%-78%[d]		0.14-0.28 µg/L	[79]
	5%[d]		0.232-0.561 µg/L	[80]
	0%-70%[d]		0.099-0.72 µg/L	[85]
	30%-100%[d]		0.25-0.9 µg/L	[82]
	33%[d]		0.5-3.5 µg/L	[89]
		-150% to -120%[d]	0.01 µg/L	[83]
	49.9%-88.4%[d]		0.901-1.036 µg/L	[95]
	33.3%[d]		0.85-2 µg/L	[93]
	7.1%-62.7%[d]	-6.6%-50.6%[d]	1.4-4.114 µg/L	[90]
	40%-59%[d]	55%-120%[b]	3.1-4.9 µg/L	[94]
Doxycyclin	35.4%[d]		0.067-2.48 µg/L	[50]
	50%[d]		0.181-1.295 µg/L	[81]
Venlafaxine (Effexor XR)				
Erythromycin	48.8%[d]		0.346-0.83 µg/L	[50]
	-38%-73%[d]		0.140-0.480 µg/L	[79]
	4.3%[d]		0.346-2.31 µg/L	[80]
	72%-89.8%[d]		0.032-0.08 µg/L	[88]
	41%-52.4%[b]	82.2%-98.6%[b]	0.354-1.514 µg/L	[96]
	25%[d]		0.56-1.1 µg/L	[89]
		4.55%-9.09%[d]	0.044 µg/L	[83]
	-128% to -33.3%[d]		0.071-0.141 µg/L	[95]
17α-estradiol	80%[d]		0.0008-.0103 µg/L	[86]
	0%-95%[d]		0.067-0.18 µg/L	[85]
17β-estradiol	60%-100%[d]		0.0035-0.0499 µg/L	[86]
	0%-95%[d]		0.145-0.19 µg/L	[85]
	83%-98%[b]		0.011-0.068 µg/L	[97]

	0%-99%[d]		0.01-0.162 µg/L	[98]
Estrone	30%-100%[d]		0.0058-0.012 µg/L	[86]
	-21%-68%[b]		0.021-0.068 µg/L	[97]
	33.3%-89%[d]		0.01-0.833 µg/L	[98]
	97.14%[d]		0.005-0.01 µg/L	[93]
Fenofibric Acid	-148.1%[d]		0.079 µg/L	[50]
	1.3%[d]		0.079-0.117 µg/L	[80]
Gemfibrozil	51.5%[d]		0.453-3.525 µg/L	[50]
	76%[d]		0.415-17.055 µg/L	[80]
	30%-99%[d]		0.05-3 µg/L	[82]
Hydrochlorothiazide	53.2%[d]		2.514 µg/L	[50]
	53.2%[d]		0.617-10.018 µg/L	[80]
Ibuprofen	0%[b,c]		0.4 µg/L	[57]
	52%-99.7%[d]	89%-99.8%[b]		[77]
	74.2%[d]		.0143-22.7 µg/L	[50]
	100%[d]		3.9-15 µg/L	[79]
	95%[d]		2.687-4.113 µg/L	[80]
	0%-98%[d]		12.9-50.6 µg/L	[85]
	65%-100%[d]		1-26 µg/L	[82]
	96%[d]		1.7-5.1 µg/L	[89]
		98.3%-99%[d]	5.32 µg/L	[83]
	-13.3%-53.3%[d]		7.741-33.764 µg/L	[95]
	62.5[d]		1.1-3.5 µg/L	[93]
	-4.2%-99.2%[d]	97.2%-99.2%[d]	0.01-2.448 µg/L	[90]
Iopromide	78.1%[d]		9.205 µg/L	[50]
	83%[d]		12-24 µg/L	[89]
	70%[d]		0.0001-7.5 µg/L	[93]
	-862% to -32%[d]		0.026-3.84 µg/L	[90]
Iomeprol	73.5%[d]		6.05 µg/L	[50]
	89%[d]		6-14 µg/L	[89]
Iohexol	59.6%[d]		6.7 µg/L	[50]
	89%[d]		7-11 µg/L	[89]
Iopamidol	17.4%[d]		2.3 µg/L	[50]
	17%[d]		0.7-3.9 µg/L	[89]
Lipitor (atorvastatin)	40%-80%[d]		0.04-2 µg/L	[82]
Meprobamate				
Metformin				
Metoprolol	2%-34%[d]		0.460-1.460 µg/L	[52]
	55.8%[d]		0.02-4.9 µg/L	[50]
	-35%-46.7%[d]		0.81-1.2 µg/L	[87]
	-50%-90%[d]		0.0046-0.473 µg/L	[86]
	6.5%[d]		0.02-0.052 µg/L	[80]
	64%-78.3%[d]		0.033-0.076 µg/L	[88]
	65%[d]		1.5-8.3 µg/L	[89]
	-1.9%-26.7%[d]		1.05-1.35 µg/L	[51]
Naproxen	81.6%[d]		0.206-23.21 µg/L	[50]
		80%[b]	0.1386 µg/L	[78]
	60.9%[d]		1.196-5.228 µg/L	[80]
	0%-95%[d]		2.54-4.09 µg/L	[85]
	60%-100%[d]		0.025-7 µg/L	[82]
		35.9%-41.22%[d]	0.262 µg/L	[83]

	73.08%[d]		0.6-2 µg/L	[93]
Norfloxacin	>90%[d]		0-0.96 µg/L	[52]
	54.3%[d]		0.066-0.25 µg/L	[50]
	30%-98%[d]		0.04-2 µg/L	[82]
	69.2%-86.7%[d]		0.078-0.18 µg/L	[51]
Ofloxacin	75%-88%[d]		0-.350 µg/L	[52]
	64.5%[d]		0.007-2.275 µg/L	[50]
	64.1%[d]		0.848-5.286 µg/L	[80]
	0%[d]		0.0021-1.14 µg/L	[88]
	20%-99%[d]		0.04-2 µg/L	[82]
	80%-92.3%[d]		0.01-0.13 µg/L	[51]
Paraxanthine	96.9%[d]		26.722 µg/L	[50]
	96.9%[d]		4.547-98.5 µg/L	[80]
Progesterone	0%[d]		0.01-0.02 µg/L	[98]
Propranol	48.5%[d]		0.036-0.51 µg/L	[50]
	-48%-45.2%[d]		0.04-0.073 µg/L	[87]
	-55%-80%[d]		0.0144-0.703 µg/L	[86]
	1%[d]		0.012-0.061 µg/L	[80]
	0%-60%[d]		0.2-0.39 µg/L	[85]
	59.2%-74.7%[d]		0.072-0.309 µg/L	[88]
	65%[d]		0.16-0.86 µg/L	[89]
	-590% to -235%[d]		0.06-0.119 µg/L	[95]
Roxithromycin	39.5%[d]		0.0272-1.5 µg/L	[50]
	54.4%-79.2%[b]	81.8%-97.2%[b]	0.279-1.39 µg/L	[96]
	33%[d]		0.39-1.23 µg/L	[89]
	8.7%[d]		0.012-0.05 µg/L	[93]
	-80%-43.8%[d]	34.4%-73.5%[d]	0.036-0.078 µg/L	[90]
Sotalol	54%-71%[d]		0.370-3.28 µg/L	[52]
	52.6%[d]		1.667 µg/L	[50]
	-60%-60%[d]		0.129-3.2 µg/L	[86]
	-31.5%-45.4%[d]		0.87-1.3 µg/L	[87]
	56.5%-83.2%[d]		0.04-0.222 µg/L	[88]
	48%[d]		1.2-3.8 µg/L	[89]
	59.4%-75%[d]		0.03-0.130 µg/L	[51]
Sulfamethoxazole	17.5%[d]		0.02-0.674 µg/L	[50]
		20%[b]	0.088 µg/L	[78]
		57%-71%[b]	0.2-0.85 µg/L	[92]
	43%-95%[d]		1.2-3.4 µg/L	[79]
	17.3%[d]		0.162-0.53 µg/L	[80]
	63%-68%[d]		0.984-2.148 µg/L	[81]
	62.7%-76.9%[d]		0.02-0.268 µg/L	[88]
	30%-92%[d]		0.04-2 µg/L	[82]
	9.1%-49.7%[b]	62.3%-76.9%[b]	0.206-0.391 µg/L	[96]
	24%[d]		0.59-1.05 µg/L	[89]
		63.9%-70.1%[d]	0.194 µg/L	[83]
	25%[d]		0.07-0.6 µg/L	[93]
	-279%-65.5%[d]	61.4%[d]	0.024-0.145 µg/L	[90]
Testosterone	50%-99%[d]		0.001-0.02 µg/L	[98]
		83.33%[d]	0.06 µg/L	[83]
Triclosan	65%-75%[b]			[57]
	76.8%[d]		0.3-1.93 µg/L	[50]

	92%-98%[d]		0.17-0.82 µg/L	[79]
	74.5%[d]		0.86-2.417 µg/L	[80]
		96.6%-97.3%[d]	0.74 µg/L	[83]
Trimethoprim	1.4%[d]		0.0535-1.3 µg/L	[50]
	-21%-92%[d]		0.39-0.77 µg/L	[79]
	5.1%[d]		0.078-0.197 µg/L	[80]
	39.2%-70.6%[b]	92%-100%[b]	0.0053-0.0597 µg/L	[96]
	69%[d]		0.84-1.36 µg/L	[89]
		-47.6 to -33.3%[d]	0.021 µg/L	[83]
	-94.4% to -35%[d]		0.213-0.3 µg/L	[95]

a. Lab conditions, single substrate
b. Multiple substrates, lab conditions
c. Higher than field-like concentrations, lab conditions
d. Field-like concentrations and species
e. ASP (Activated Sludge Process), MBR (Membrane Bioreactor)

Table 3: Summary of previous studies' findings on removal efficiencies for selected PCPPs using chemical processes.

PCPPs	RR[e] – Chemical Oxidation	RR[e] – Wet-air oxidation	RR[e] – Electro-chemical	RR[e] – Ozone or Ozone H_2O_2	Concentration in influent	Author
Acetaminophen			100%		7.8-3.74 µg/L	[42]
ASA						
Acebutolol				86%[d]	0.810-9.867 µg/L	[86]
Amitriptyline						
Atenolol				97%[d]	0.72-0.91 µg/L	[87]
				28.1%-97.4%[d]	0.911 µg/L	[84]
Atrazine			10%-98%		7.8-3.74 µg/L	[42]
Bezafibrate				37.4%-96.5%[d]	0.115 µg/L	[84]
Bisphenol A				68%-95%[d]	0.20-0.43 µg/L	[91]
				>99%[d]	0.242 µg/L	[99]
Caffeine			55%-100%		7.8-3.74 µg/L	[42]
				-33%-100%[d]	54-120 µg/L	[79]
Carbamazepine			23%-100%		7.8-3.74 µg/L	[42]
				88%-100%[d]	0.130-0.40 µg/L	[79]
				85.2%->98%[d]	0.106 µg/L	[84]
Celiprolol						
Ciprofloxacin				45%-100%[d]	0.43-1.10 µg/L	[79]
				36%->95%[d]	0.522 µg/L	[84]
Codeine				>98.7%[d]	0.378 µg/L	[84]
Diclofenac			90%-100%		7.8-3.74 µg/L	[42]
				>99.8%[d]	0.433 µg/L	[84]
Doxycyclin						
Venlafaxine (Effexor XR)			55%-100%		7.8-3.74 µg/L	[42]
				29.1%->96.6%[d]	0.179 µg/L	[84]
Erythromycin				45%-100%[d]	0.140-0.480 µg/L	[79]
				77.8%->86.1%[d]	0.072µg/L	[84]
17α-estradiol						
17β-estradiol						
Estrone						

Fenofibric Acid						
Gemfibrozil			70%-100%		7.8-3.74 µg/L	[42]
				84.9%-95.5%[d]	0.332 µg/L	[84]
Hydrochlorothiazide			30%-100%		7.8-3.74 µg/L	[42]
				34.8%->99.9%[d]	0.707 µg/L	[84]
Ibuprofen	0%[b,c]				0.4 µg/L	[57]
	52%-99.7%[d]	89%-99.8%[d]				[77]
			25%-75%		7.8-3.74 µg/L	[42]
	74.2%[d]				.0143-22.7 µg/L	[50]
Iopromide						
Iomeprol						
Iohexol						
Iopamidol						
Lipitor						
Meprobamate						
Metformin						
Metoprolol			60%-100%		7.8-3.74 µg/L	[42]
				97%[d]	0.0046-0.473 µg/L	[86]
		1.2%-25.8%[a]			0.10 µg/L	[100]
				37%->88.9%[d]	0.027 µg/L	[84]
Naproxen		1.7%-28.8%[a] 23.0%-86%[d]			0.10 µg/L	[100]
				>89%[d]	0.109 µg/L	[84]
Norfloxacin			85%-100%		7.8-3.74 µg/L	[42]
				-47%->78.9%[d]	0.038µg/L	[84]
Ofloxacin				92.3%-99.7%[d]	3.594 µg/L	[84]
Paraxanthin						
Progesterone						
Propranol				100%[d]	0.0144-0.703 µg/L	[86]
				78.1%->93.75%[d]	0.032 µg/L	[84]
Roxithromycin			40%-100%		7.8-3.74 µg/L	[42]
Sotalol				100%[d]	0.87-1.3 µg/L	[87]
Sulfamethoxazole				65%-92%[d]	1.2-3.4 µg/L	[79]
				58.9%->91.6%[d]	0.095 µg/L	[84]

Testosterone							
Triclosan					67.9%-78.5%[d]	0.246 µg/L	[84]
					78%-83%[d]	0.246-1.486 µg/L	[99]
Trimethoprim				83%-100%		7.8-3.74 µg/L	[42]
					100%[d]	0.39-0.77 µg/L	[79]
					90.4%->97.3%[d]	0.073 µg/L	[84]
Sertralie (Zoloft)							

a. Lab conditions, single substrate
b. Multiple substrates, lab conditions
c. Higher than field-like concentrations, lab conditions
d. Field-like concentrations and species
e. RR (Removal Rate)

Table 4: Summary of previous studies' findings on removal efficiencies for selected PCPPs using physical separation processes.

PCPPs	RR – NF or UF[e]	RR – MAR or WTLND[e]	RR – RO[e]	RR – UV[e]	TiO_2/UV	Adsorption – GAC[e]	Concentration	Author
Acetaminophen			97%-100%[D]				1.6-8 µg/L	[101]
	91%[B]						0.0908 µg/L	[78]
ASA	86%-90%[C]						25 µg/L	[102]
			100%[D]				10.25-38 µg/L	[101]
		95%-100%[B]					0.132-5.448 µg/L	[103]
Acebutolol	-4%[D]		62%-82%[D]	7%[D]			0.810-9.867 µg/L	[86]
Amitriptyline		70%-100%[B]					0.341-6.711 µg/L	[103]
Atenolol	85%[B]						0.2006 µg/L	[78]
	5%[D]		89%-99%[D]	30%[D]			0.72-0.91 µg/L	[87]
			>99%[D]				0.13-0.33 µg/L	[88]
		70%-95%[B]					3.09-33.106 µg/L	[103]
Atrazine								
Bezafibrate		95%-100%[D]						[104]
		50%-81%[B]					0.135-1.391 µg/L	[103]
Bisphenol A			95%-100%[D]			66%[C]	0.579 µg/L	[99]
							6.1-23 µg/L	[101]

Caffeine				-10%-80%[D]	54-120 µg/L	[79]
	82%-84%[C]				25 µg/L	[102]
				$\frac{155.6\ mg\ Diclofenac}{1\ g\ GAC}$	10000-15000 µg/L	[105]
				93%[C]	1.519 µg/L	[99]
Carbamazepine	93%[B]				0.2013 µg/L	[78]
				55%-90%[D]	0.130-0.40 µg/L	[79]
	24%-28%[C]				25 µg/L	[102]
			>99%[D]		0.029-0.052 µg/L	[88]
			95%-99%[D]		1.6-2.5 µg/L	[101]
				71%-93%[B]	0.65-0.9 µg/L	[92]
		-50%-60%[B]			0.104-3.11 µg/L	[103]
Celiprolol						
Ciprofloxacin				55%-100%[D]	0.43-1.10 µg/L	[79]
Codeine			>99%[D]		0.014-0.02 µg/L	[88]
Diclofenac	97%[B]				0.1412 µg/L	[78]
		60%-95%[D]				[104]
				75%-100%[D]	0.14-0.28 µg/L	[79]
	24%-44%[C]				25 µg/L	[102]
				$\frac{63.7\ mg\ Diclofenac}{1\ g\ GAC}$	10000 µg/L	[105]
			100%[D]		0.125-0.8 µg/L	[101]
		-48%-43%[B]			0.026-1.161 µg/L	[103]
			-141%-35.7%[D]		0.12-0.5 µg/L	[95]
Doxycyclin						
Venlafaxine (Effexor XR)						
Erythromycin				78%-90%[D]	0.140-0.480 µg/L	[79]
			>99%[D]		0.005-0.013 µg/L	[88]
		-100%-99%[B]			0.144-10.025 µg/L	[103]
	65.4%-79%[B]		98.6%-		0.135-0.368 µg/L	[96]

			100%[B]				
				6.3%-45.4%[D]		0.153-0.258 µg/L	[95]
17α-estradiol							
17β-estradiol							
Estrone							
Fenofibric Acid		70%[D]					[104]
Gemfibrozil			96%-100%[D]			0.425-4.1 µg/L	[101]
Hydrochlorothiazide							
Ibuprofen		80%-100%[D]					[104]
					75%-100%[D]	3.9-15 µg/L	[79]
		52%-72%[C]				25 µg/L	[102]
			97%-100%[D]			2.5-10.1 µg/L	[101]
		85%-98%[B]				0.968-6.328 µg/L	[103]
				51.7%-87.5%[D]		8.77-15.78 µg/L	[95]
Iopromide		65%-100%[D]					[104]
Iomeprol		80%[D]					[104]
Iohexol		80%[D]					[104]
Iopamidol		25%-80%[D]					[104]
Lipitor							
Meprobamate							
Metformin							
Metoprolol	10%[D]		95%-97%[D]	15%[D]		0.0046-0.473 µg/L	[86]
			>99%[D]			0.011-0.018 µg/L	[88]
		-5%-65%[B]				0.039-0.146 µg/L	[103]
Naproxen	78%[B]					0.1386 µg/L	[78]
		70%-95%[D]					[104]
	52%-93%[C]					25 µg/L	[102]
			99%-100%[D]			1.25-8 µg/L	[101]
		58%-90%[B]				0.4-3.504 µg/L	[103]

Norfloxacin							
Ofloxacin			>99%[D]			0.605 µg/L	[88]
Paraxanthine							
Progesterone							
Propranol	-28%[D]		96%[D]	-10%[D]		0.0144-0.703 µg/L	[86]
			>99%[D]			0.046-0.075 µg/L	[88]
		-20%-95%[B]				-20%-95% µg/L	[103]
				6.3%-45.4%[D]		0.357-0.414 µg/L	[95]
Roxithromycin		85%-98%[D]					[104]
	71.3%-91.5%[B]		99.2%-100%[B]			0.134-0.359 µg/L	[96]
Sotalol	-4%[D]		-4%-88%[D]	11%[D]		0.87-1.3 µg/L	[87]
			>99%[D]			0.0198-0.051 µg/L	[88]
Sulfamethoxazole	90%[B]					0.088 µg/L	[78]
		5%-98%[D]					[104]
			>99%[D]			0.024-0.038 µg/L	[88]
					77%-107%[B]	0.6-0.9 µg/L	[92]
		-20%-97%[B]				0.003-0.274 µg/L	[103]
	38.6%-82%[B]		95.2%-100%[B]			0.085-0.266 µg/L	[96]
Testosterone							
Triclosan					95%[C]	2.0232 µg/L	[99]
Trimethoprim		80%-90%[D]					[104]
		40%-80%[B]				0.46-6.79 µg/L	[103]
				D	90%-100%[D]	0.39-0.77 µg/L	[79]
				22.2%-46.3%[D]		0.388-0.414 µg/L	[95]
	45.9%-86.9%[B]		86.4%-100%[B]			0.015-0.02 µg/L	[96]

a. Lab conditions, single substrate
b. Multiple substrates, lab conditions
c. Higher than field-like concentrations, lab conditions
d. Field-like concentrations and species
e. RR (Removal Rate), NF (Nano-filtration), UF (Ultra-Filtration), MAR (Managed Aquifer Recharge), WTLND (Wetland), RO (Reverse Osmosis), GAC

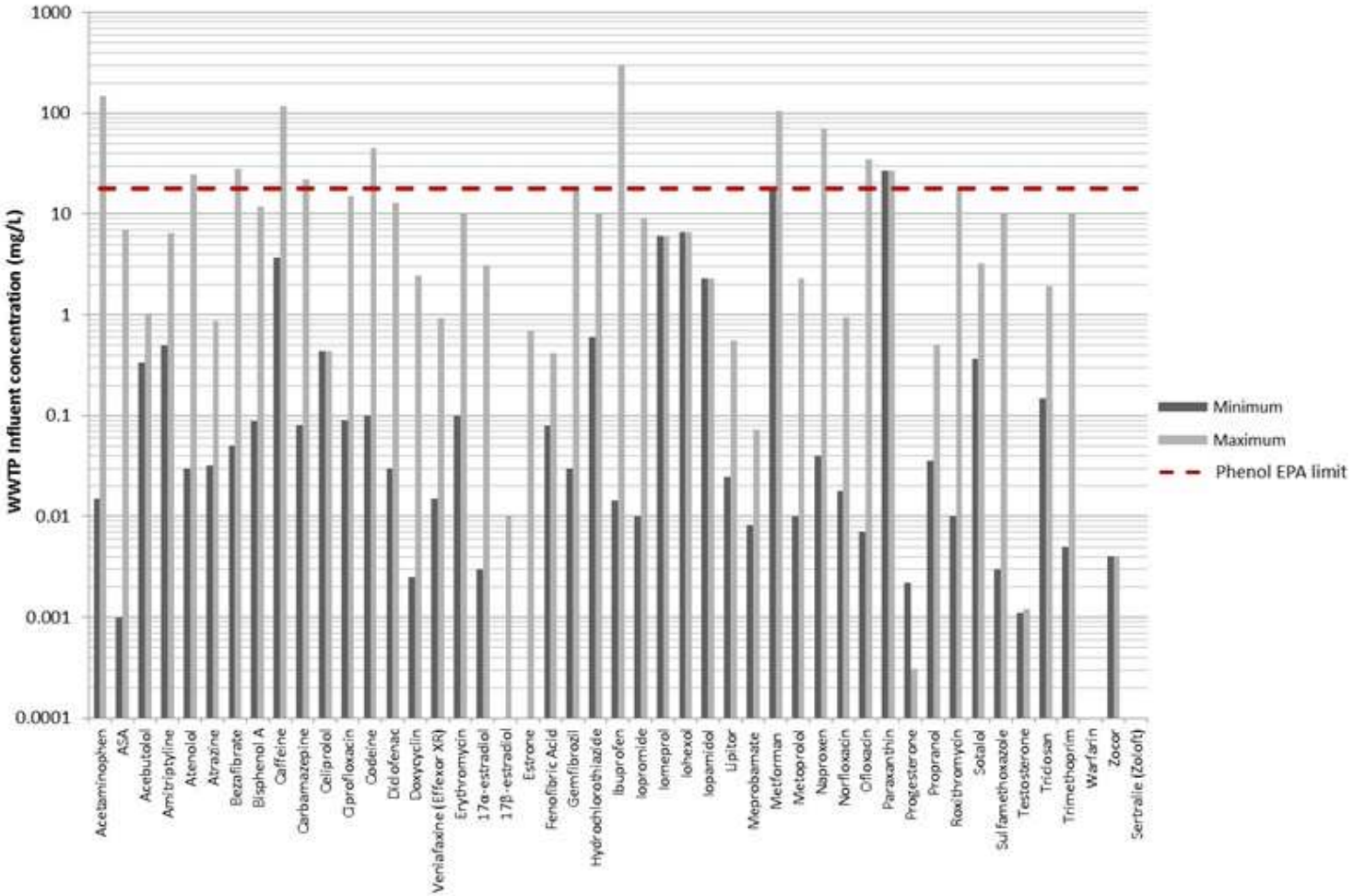


Figure 1: Comparison of WWTP influent concentrations for all micropollutants. Note, only 12 compounds exceed the 18ppb limit for phenol as a competitive substance.

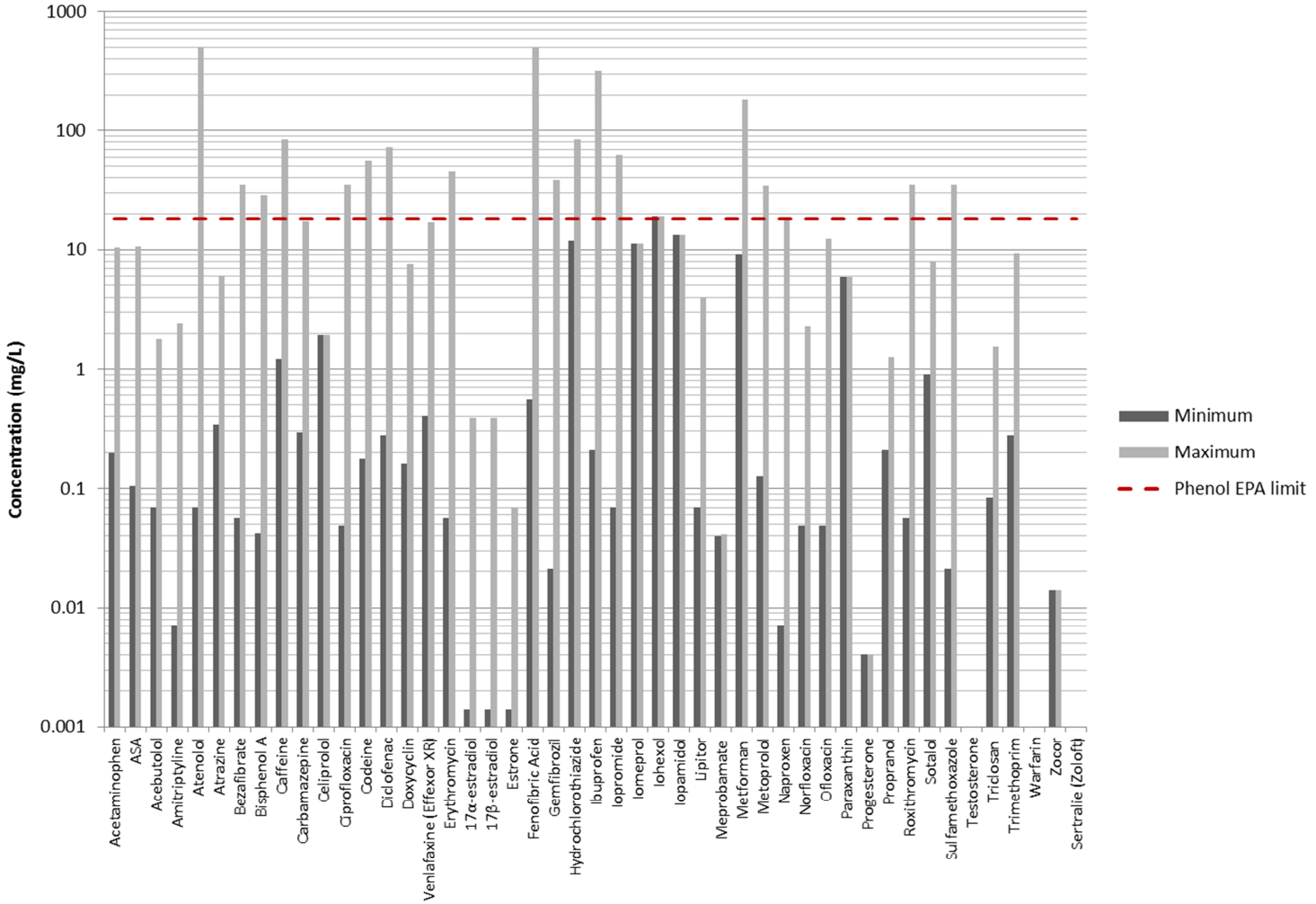


Figure 2: Comparison of RO retentate concentration after 7x concentration of wastewater effluent. Note, only 18 compounds exceed the 18ppb limit for phenol.

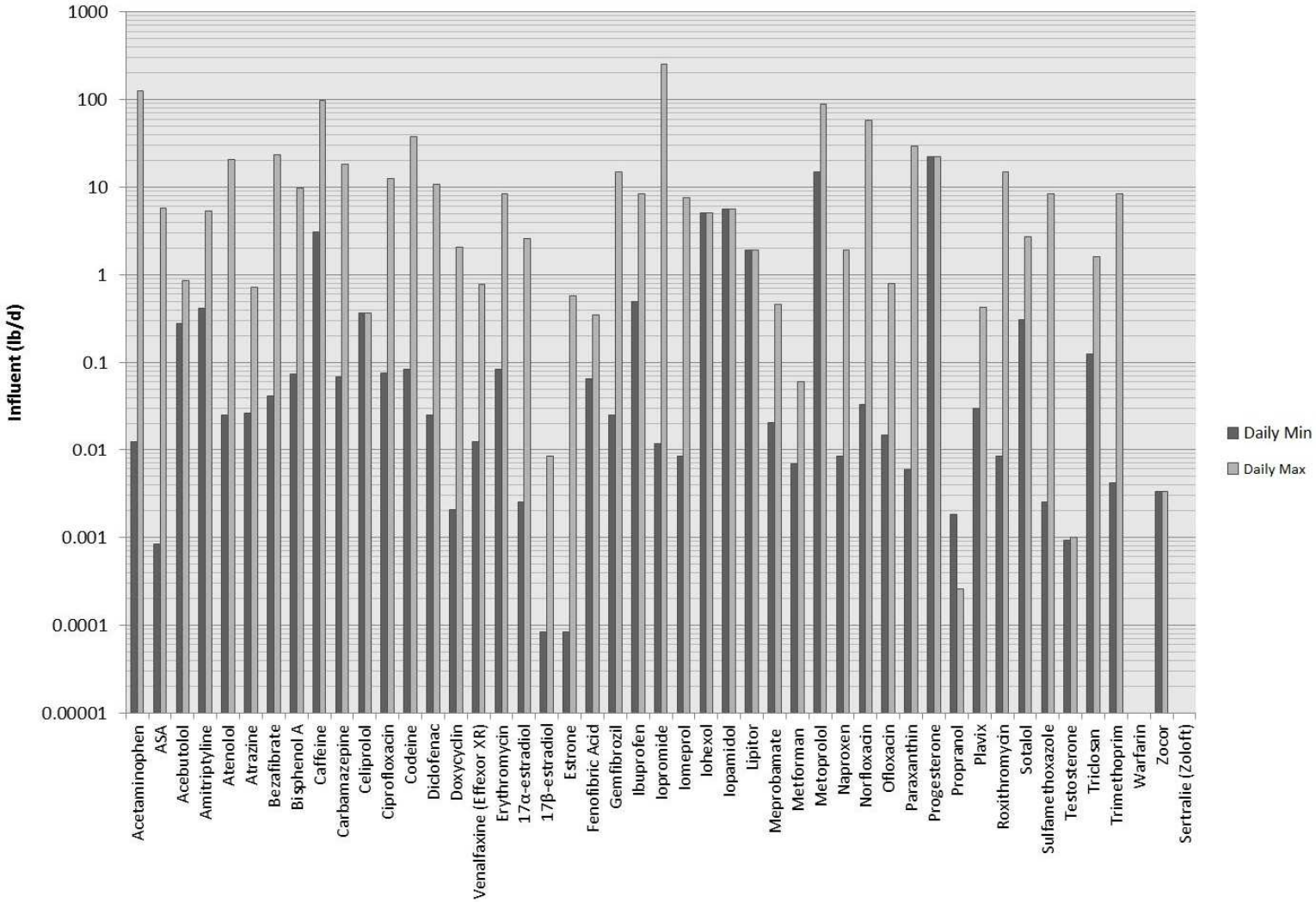


Figure 3: Daily influent flow of PCPPs entering a WWTP using 100 MGD Capacity as an example (Mass, lb/d=(Concentration, µg/L)*0.835).

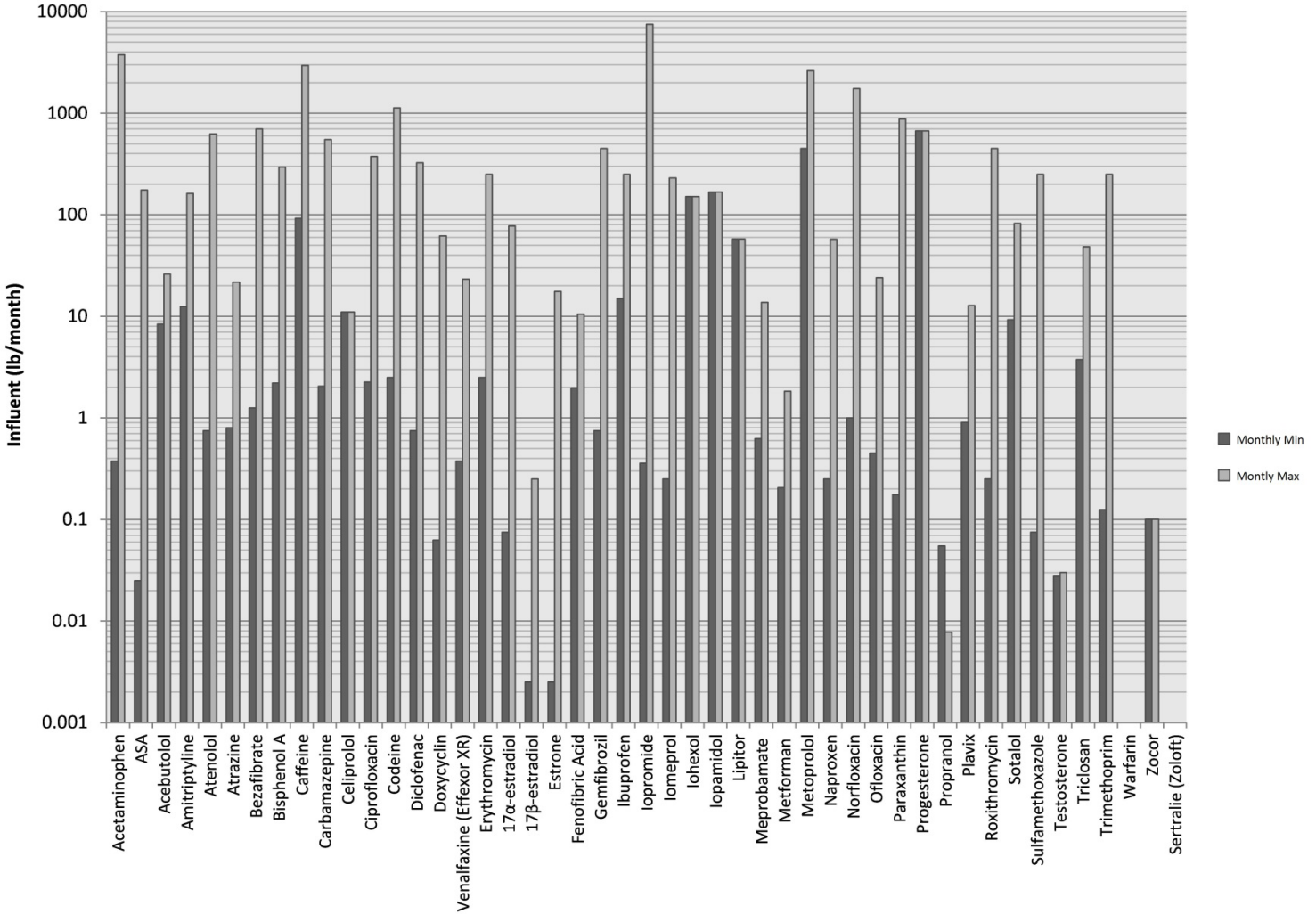


Figure 4: Monthly influent mass flow of PCPPs entering a WWTP using 100 MGD Capacity as an example (Mass, lb/month=(Concentration, µg/L)*28.05; assuming 30 days per month).

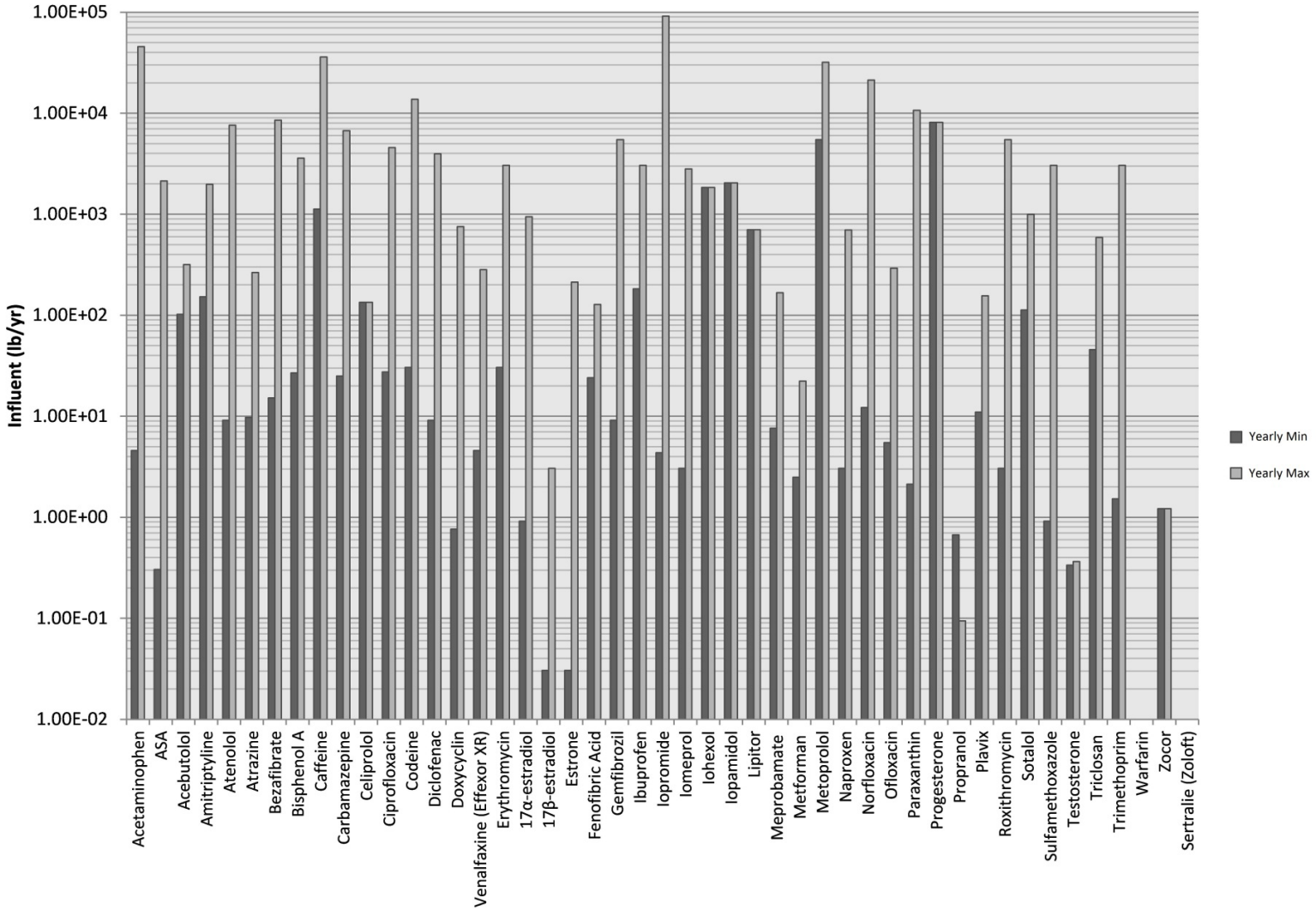


Figure 5: Yearly influent mass flow of PCPPs entering a WWTP using 100 MGD Capacity as an example (Mass, lb/year=(Concentration, µg/L)*304.8)

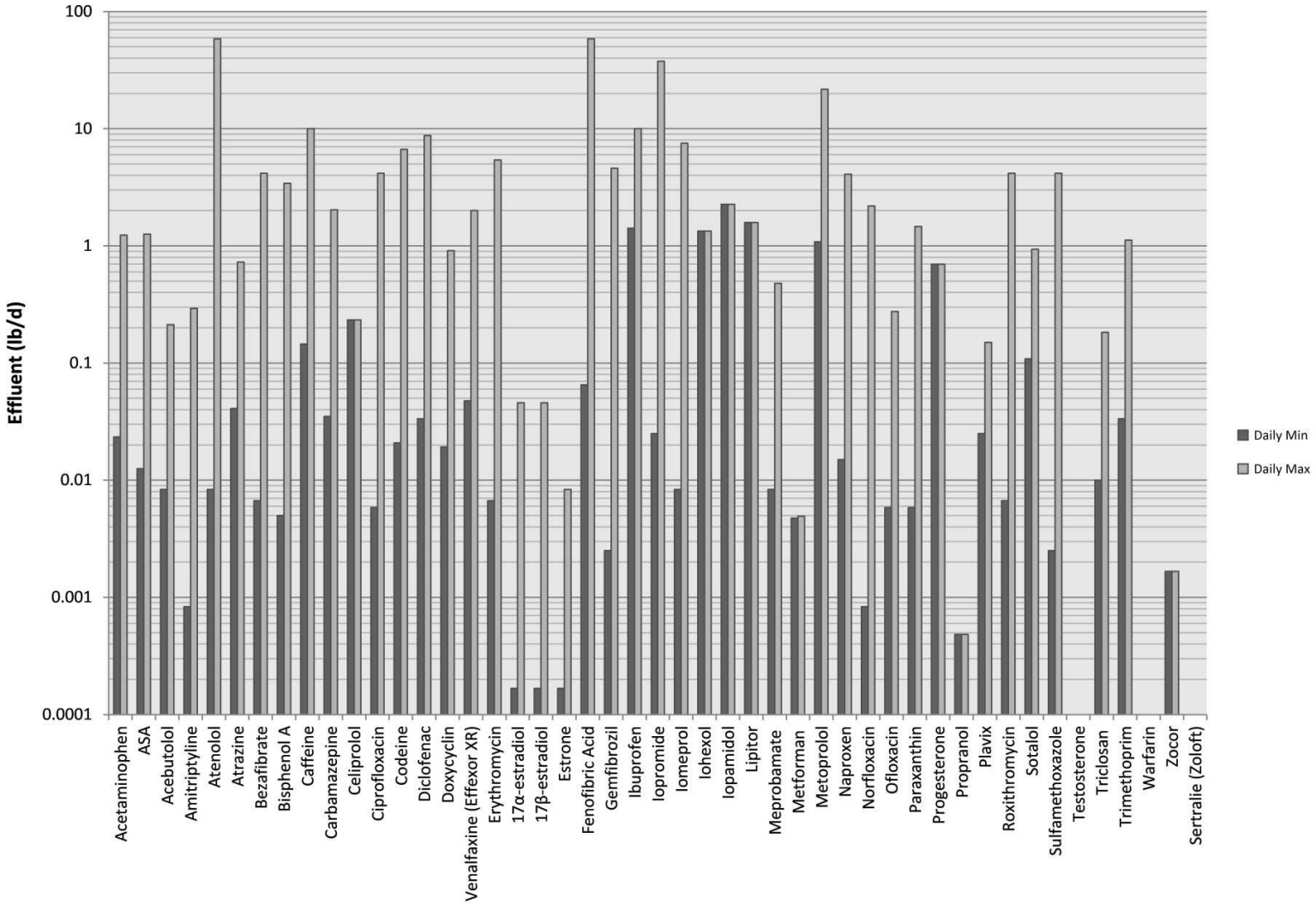


Figure 6: Daily effluent mass flow of PCPPs exiting a WWTP using a 100 MGD Capacity as an example (Mass, lb/d=(Concentration, µg/L)*0.835).

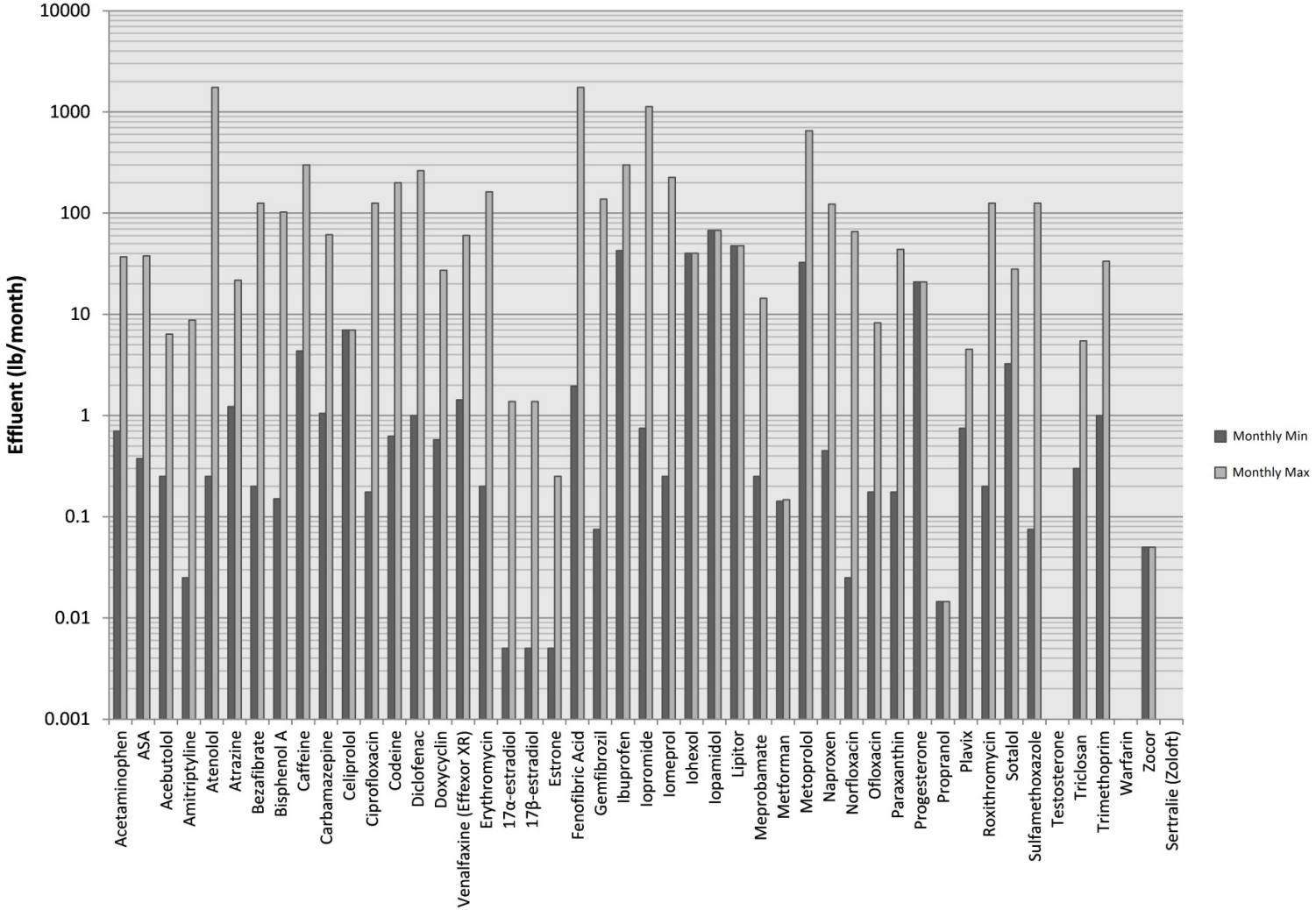


Figure 7: Monthly effluent mass flow of PCPPs exiting a WWTP using a 100 MGD Capacity as an example (Mass, lb/month=(Concentration, µg/L)*28.05).

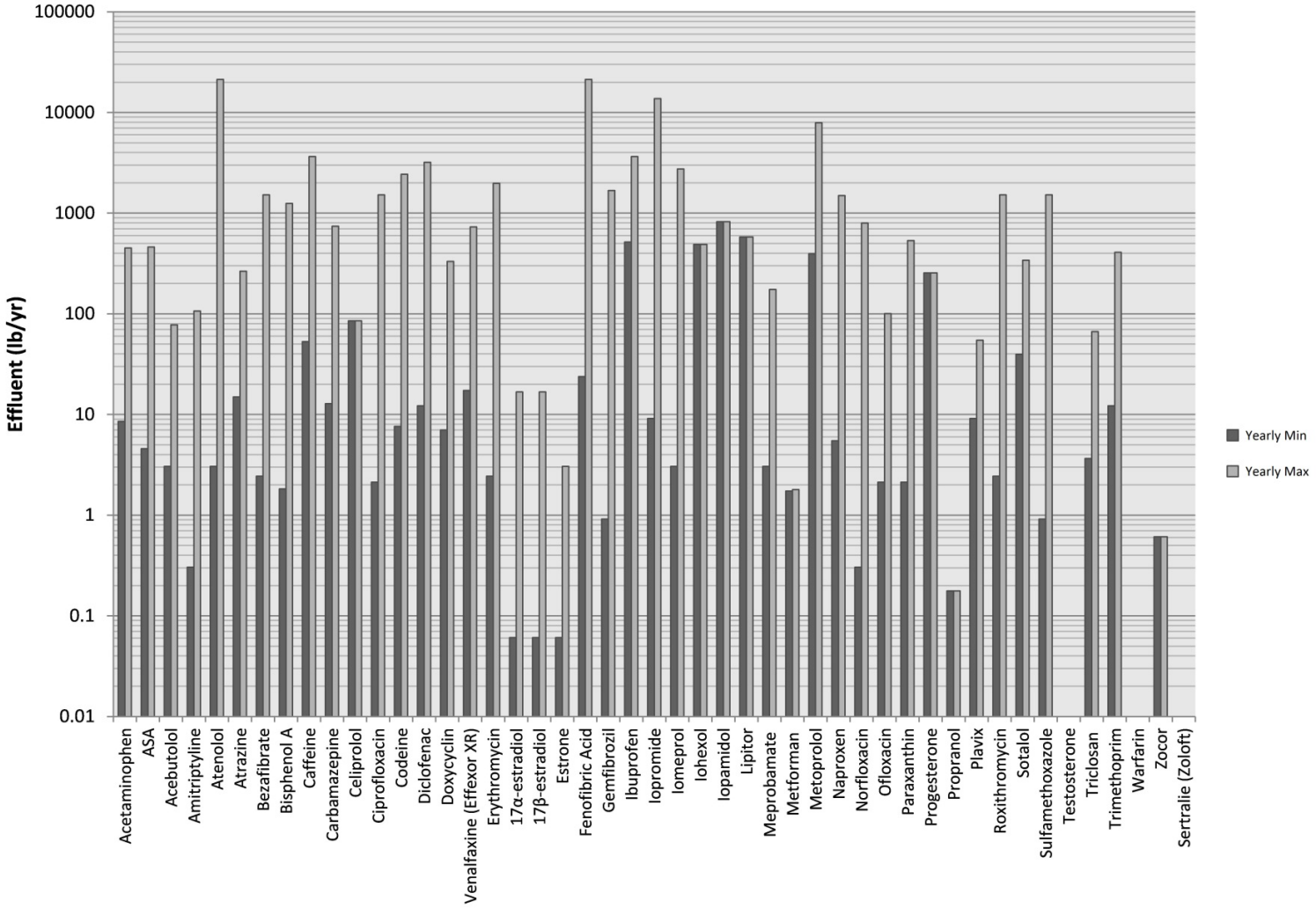


Figure 8: Yearly effluent mass flow of PCPPs exiting a WWTP using a 100 MGD Capacity as an example (Mass, lb/year=(Concentration, µg/L)*304.8).

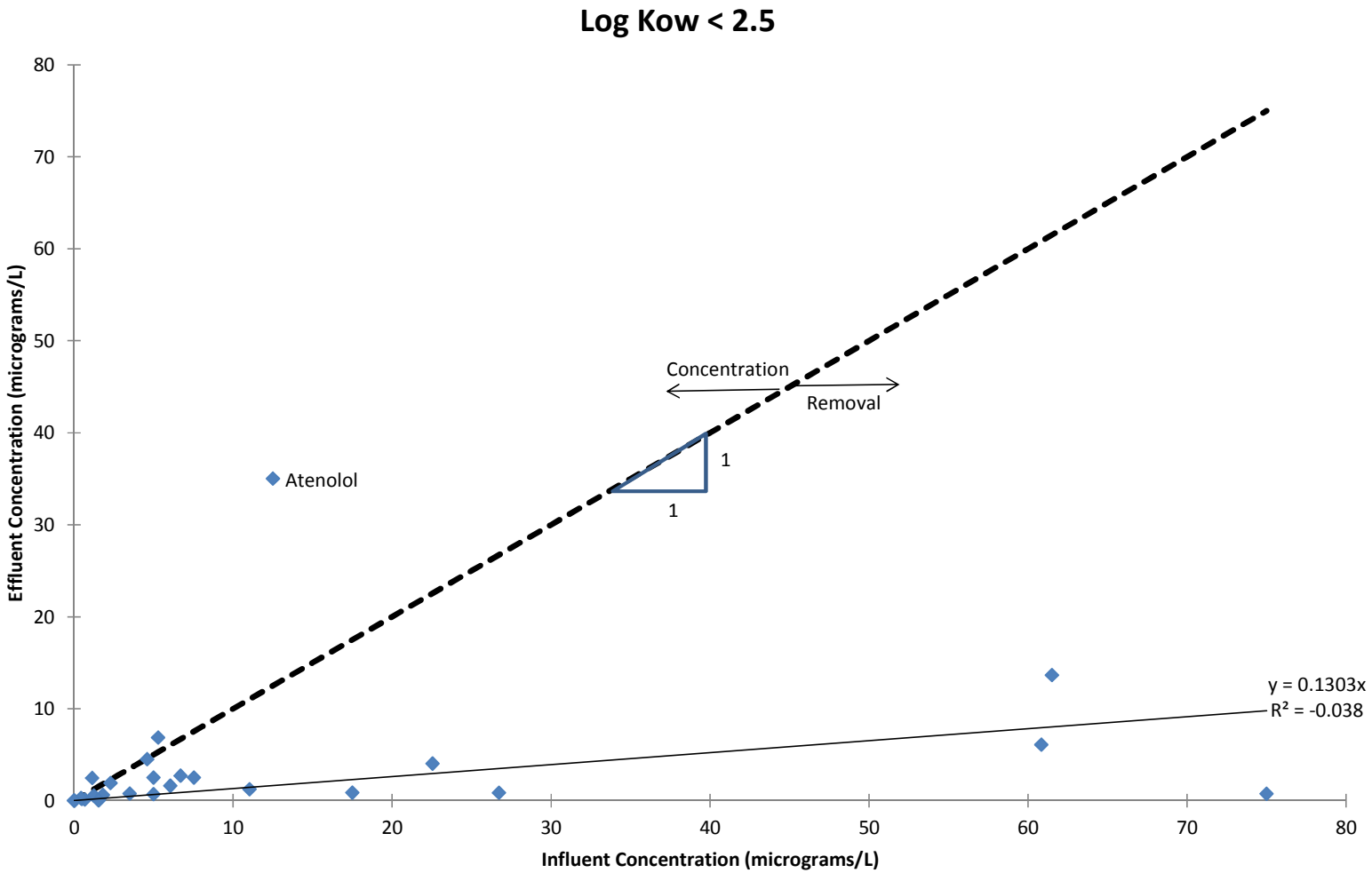


Figure 9: Influent versus Effluent concentration for Log Kow less than 2.5. The dashed line is a 1:1 relationship which would indicate that what flows into the plant is flowing out of the plant without treatment. Since the linear trend line demonstrates a slope of 0.1303, there is a clear removal of compounds by some process within the plant.

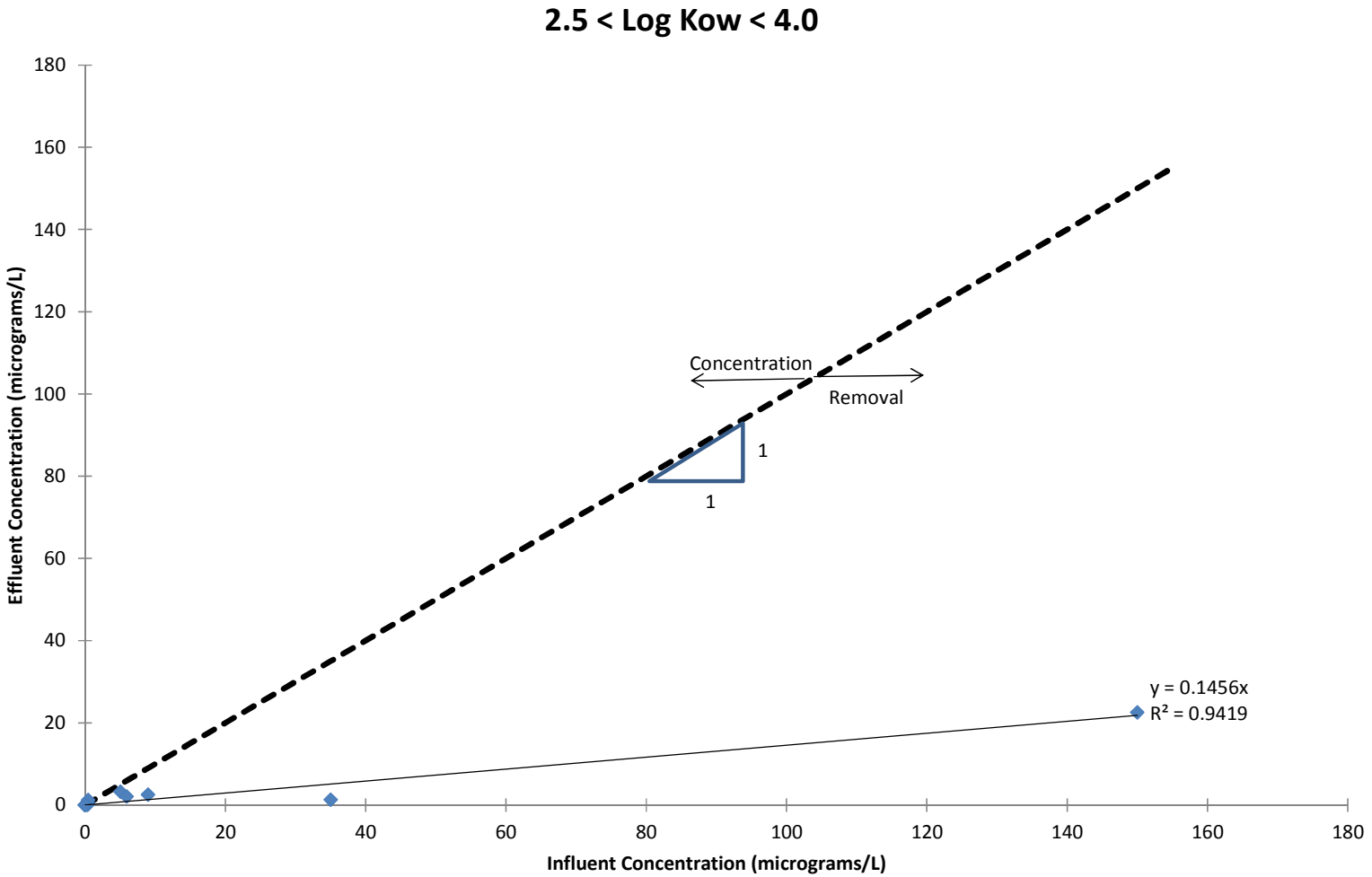


Figure 10: Influent versus Effluent concentration for Log Kow between 2.5 and 4. The dashed line is a 1:1 relationship which would indicate that what flows into the plant is flowing out of the plant without treatment. Since the linear trend line demonstrates a slope of 0.1456, there is a clear removal of compounds by some process within the plant.

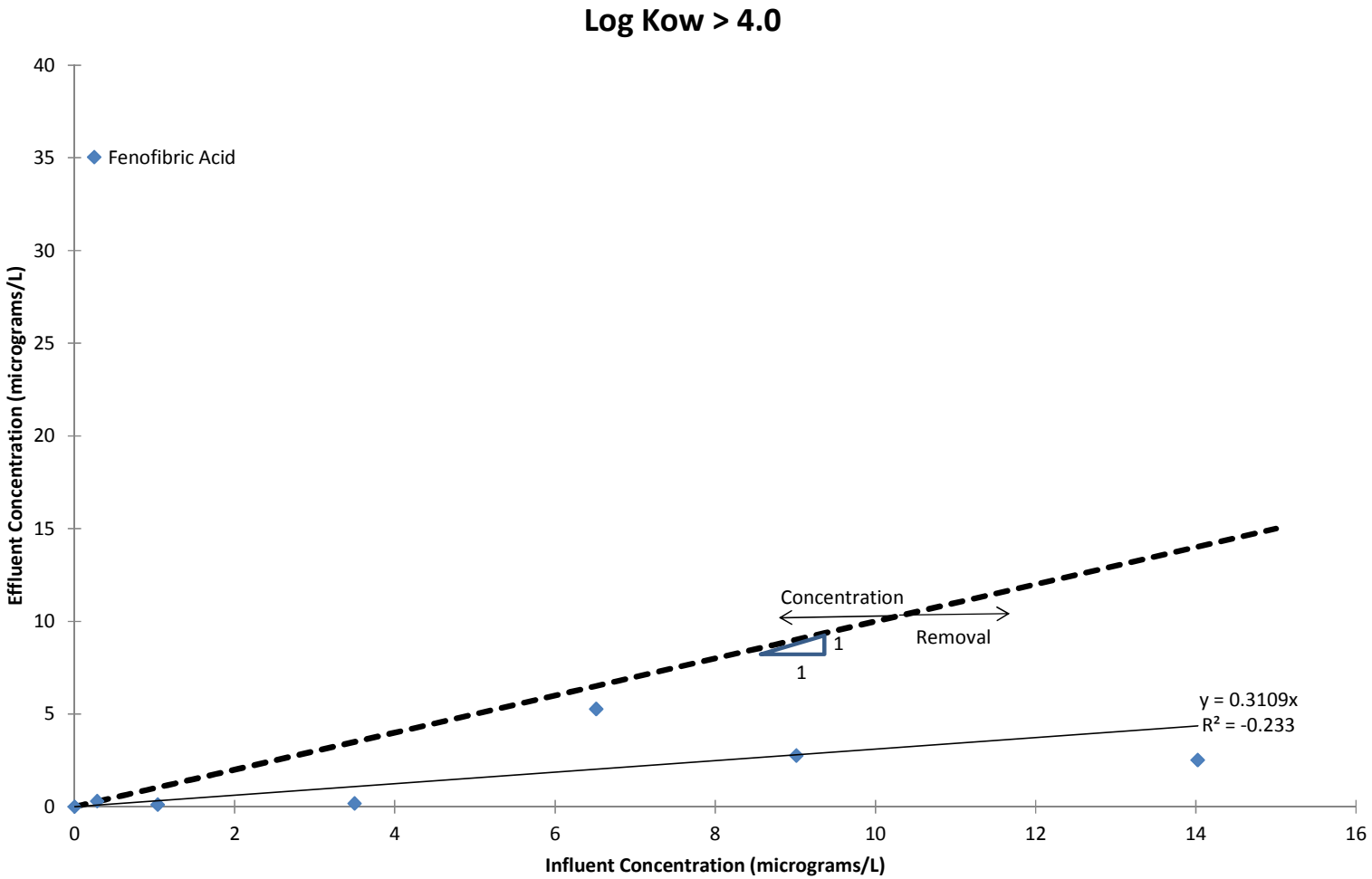


Figure 11: Influent versus Effluent concentration for Log Kow greater than 4. The dashed line is a 1:1 relationship which would indicate that what flows into the plant is flowing out of the plant without treatment. Since the linear trend line demonstrates a slope of 0.3109, which is less than one, there is a clear removal of compounds by some process within the plant.

Conclusions

1. Interpretation of previous study results

Previous studies concerning treatment methods for removing PCPPs and the concentrations found in conventional WWTPs and the environment revealed that many compounds were recalcitrant. Generally, 47 compounds were studied from various classes to gain general insights into the drugs that exist. First, it was examined what was going into the environment from wastewater effluents (see Table 1) and it was found that many of the 47 compounds going to the environment were not readily biodegradable. The average concentration in the effluent was around 1.8ppb, so in general the compounds were exiting the WWTP at extremely low concentrations. Many compounds like Atenolol, 17ß-Estradiol, Atrazine, Fenofibric Acid, Lipitor Carbamazepine were not very amenable to biological treatment. Knowing that these compounds were not extremely biodegradable, the treatment removal efficiencies of different treatment processes were examined. Many compounds like Atenolol, 17ß-Estradiol, Atrazine, Fenofibric Acid, Lipitor Carbamazepine, Ethromycin, Ibuprofen, Metoprolol, Ofloxacin, Propranol, roxithromycin, Sulfamethoxazole, and Trimethoprim have been observed to be recalcitrant (see Table 2). Generally, antibiotics, beta-blockers, and psychoactive compounds tend to be poorly removed with conventional biological treatment and in some instances further removal can be obtained via MBR processes. Many of the PCPP compounds were poorly removed by biological processes, but were removed with physical or chemical processes (see Table 3 and Table 4). Chemical processes in general were effective for removing PCPPs, with the exception of some antibiotics did not respond well to ozone oxidation, and metoprolol was not removed by Wet Air Oxidation. Finally, the physical separation processes appear to be dependent upon the concentration added and the properties of the molecules. For example, beta-blockers such as Metaprolol and Sotalol were poorly removed in any membrane process, adsorption, or UV process. This was likely due to the lack of favorable interactions between either the membrane surface or the activated carbon surface groups. Therefore, many of the compounds that were not very biodegradable can be treated with physical or chemical processes. While these methods appear to be effective, many of the studies were conducted under laboratory conditions with synthetic waste samples at higher concentrations than would normally be found in the effluent.

Many of the PCPPs that were present in the WWTP influent and effluent have concentrations in the ppt to ppb range, and therefore seem inconsequential in terms of a mass load. To better understand the mass of compounds that on average pass through a plant and the role that concentration can have on the potential removal of these compounds, Figures 1-8 were constructed. Using a readily biodegradable compound, phenol, as a comparison, it became apparent that many of these compounds will have a hard time competing with other compounds entering a WWTP. Of the 47 compounds studied, only 12 met or exceeded the NPDES or SDWA phenol limit prior to concentration, whereas 18 met or exceeded the phenol limit with concentration after RO (see Figure 1and Figure 2). Higher concentration of these compounds provides a higher probability that the compounds will undergo biological degradation. To provide context for the mass flows of compounds of interest, the daily, monthly, and yearly mass flows for each of the 47 compounds was shown in Figure 3, Figure 4, and Figure 5. The daily mass load ranged approximately from 0.0009 pounds per day for Estrone and 17β-Estradiol to 150 pounds per day for Iomeprol (based on 100 MGD plant flows). While the lower end of these values does not seem to constitute a substantial contribution, compounding these values yields startling results. The yearly mass load ranged approximately from 0.3285 pounds a year for Estrone and 17β-Estradiol to 54,000 pounds a year for Iomeprol. If compounds were not recalcitrant to biological treatment, then the mass flows to the environment should be lower than the influent mass flows. To provide context for the mass flows of compounds of interest, the daily, monthly, and yearly mass flows for each of the 47 compounds was shown in Figure 6, Figure 7, and Figure 8. The daily mass load ranged approximately from 0.0002 pounds per day for Estrone, 17α-Estradiol, and 17β-Estradiol to 60 pounds per day for Atenolol and Fenofibric acid. When these values were scaled to a year, significant contributions could be seen. The yearly mass load ranged approximately from 0.07 pounds per year for Estrone, 17α-Estradiol, and 17β-Estradiol to 22,000 pounds per year for Atenolol and Fenofibric acid. Comparing the mass flows on a given day to the effluent mass flows, it became evident that compounds are being removed during wastewater treatment. With all of this said, the concentrations that these compounds were entering and exiting the plant (see Table 1) were in the ppb to ppt range, but still constitute a sizeable mass flow due to the volumes encountered in WWTPs. As a result, even though the public and policymakers may perceive these compounds as being trace compounds, they must still be taken seriously. Finally, considering that the numbers presented apply to a single 100

MGD treatment plant, the mass load of these compounds when averaged across the country becomes substantial and helps to explain observed effects such as fish becoming all female downstream of a WWTP [20].

Table 5: Summary of Removal properties based of EI ratio

	Log Kow <2.5		Log Kow 2.5-4		Log Kow >4.0	
Number Concentrated	4	15.4%	1	10.0%	1	12.5%
Number Removed	20	76.9%	8	80.0%	5	62.5%
Neither removed or Concentrated	2	7.7%	1	10.0%	2	25.0%

Note: Concentration occurs when EI>1.2, Removal occurs when EI < 0.8, and neither removal or concentration occurs when $0.8 \leq EI \leq 1.2$

There is a fundamental relationship between Log K_{ow} and solubility, which plays a role in PCPPs in a WWTP. Generally, as the Log K_{ow} increases, the solubility of a compound decreases and it becomes more likely that the compound will partition to a solid or surface phase, for example sludge solids in a WWTP [106, 107]. Looking at Figure 9, Figure 10, Figure 11, in general PCPPs were removed by the conventional WWTP processes. Table 5 summarizes the removal or concentration of compounds as a function of Log K_{ow}. There were few exceptions to the removal of PCPPs during biological wastewater treatment and these exceptions include: Atenolol (Log K_{ow} = 0.161, Effluent:Influent ratio (EI) = 2.797), 17ß-Estradiol (Log K_{ow} = 2.45, EI = 5.465), Atrazine (Log K_{ow} = 2.611, EI = 1.019), Fenofibric Acid (Log K_{ow} = 5.19, EI = 104.44), and Lipitor (Log K_{ow} = 6.361, EI = 1.017). These compounds become more concentrated rather than being removed during biological treatment. The mechanism by which these compounds become more concentrated in the effluent than in the influent is not well understood, but adsorption processes associated with sludge and reversible desorption in a cyclic fashion could occur [108, 109]. Additionally, as the Log K_{ow} increased, there was a larger amount of chemicals coming out compared to lower Log K_{ow} values (Log K_{ow}<2.5: EI=0.1303, 2.5<Log K_{ow}<4: EI=0.1456, Log K_{ow}>4: EI=0.4634). Therefore, as the Log K_{ow} increases and the molecules become less soluble and more hydrophobic, there will generally be a higher concentration of the compound in the effluent and the fractional removal will be less. While the list of PCPPs in this thesis is not exhaustive, Log K_{ow} was predictive of the concentration in the effluent and thus, if the Log K_{ow} was known for any PCPP, it likely would follow the same general trend as shown in Figure 9, Figure 10, and Figure 11. As a result, the

larger the Log Kow was the higher likelihood the pollutant will be found in the effluent. Potential mechanisms underlying the removal of these compounds will be explored in subsequent chapters, although potential removal processes include: sludge adsorption (irreversible or reversible), biological degradation, and biological transformation.

2. Preview and Hypotheses

This thesis will seek to answer key questions related to biological treatment, adsorption processes, the viability of advance treatment processes, and business considerations to remove PCPPs from water. The hypotheses are: How does the concentration of these micropollutants affect their ability to be treated? How are carbon adsorption and biological treatment affected by competition of other substrates? To what extent will current technology allow for their safe removal from discharge sources?

The remainder of this work will explore methods of removal of PCPPs in depth. In chapter two, biological treatment will be analyzed with and without competitive effects to see if further biological treatment will be fruitful. In chapter three, chemical adsorption will be analyzed with a Freundlich isotherm model to determine how its application could aid in the removal of PCPPs. Finally, in chapter four, advanced processes with special consideration for cost will be analyzed to assess their feasibility for removal of PCPPs.

CHAPTER 2

THE ROLE OF CONCENTRATION ON BIODEGRADATION

Introduction

1. Overview

Wastewater treatment plants are typically biological based treatment processes. Wastewater treatment seeks to: "reduce BOD, reduce toxics or carcinogens, remove metals, N, and P, and remove pathogens" [110]. Biological treatment is a bacteria based processes where the bacteria utilize the compounds as substrates for catabolism [106]. In other words, the bacteria feed on organic chemicals that make up BOD and reduce it over time [111]. The biological activity occurs via an activated sludge process. ASP involves the oxidation of organic matter, which results in conversion to new cell mass and then gravity sedimentation of the bacterial flocks, which separates the biomass from the effluent [110]. In the context of a WWTP, ASP constitutes only a portion of the treatment process.

WWTPs operate in four definable phases: Screening, Primary treatment, Secondary treatment, and Tertiary/Advanced treatment. First, the screening step occurs at the intake to the plant and its purpose is to remove debris that would otherwise disrupt plant operation [106, 110]. Next, primary treatment occurs via gravity sedimentation, which removes solids (organic and inorganic) on the basis of size and density [110]. Afterward, secondary treatment via biological treatment usually consists of an ASP and nutrient removal [110]. Disinfection may occur by death of the infectious agents in the ASP and/or post disinfection (usually by chlorination [110]. Finally, Tertiary/Advanced (see chapter 4), includes chemical processes such as ozonation, advanced oxidation, etc. [110].

Within WWTP, authors have reported substantial variation in the removal efficiencies of PCPPs. The PCPPs in the influent of WWTPs include: analgesics, antibiotics, anticonvulsants, psychoactive drugs, cholesterol-lowering agents, imaging contrast media, and estrogenic compounds [110]. Many of the concentrations of these compounds in the influent can easily exceed 1 μg/L, thereby exceeding trace amounts, but not enough to make it a dominant species [110]. The removal is a function of secondary treatment, filtration, and disinfection, and solid retention time [111]. The effect of this variation on

removal efficiency results in many of the effluents containing recalcitrant compounds that are persistent in water supplies and potentially contaminate finished drinking water even after treatment [110]. Additionally, water bodies during dry spells can contain significant contributions of effluent (50-90%) and therefore become contaminated with PCPPs [110]. Therefore, the PCPPs enter into the environment, and if they are recalcitrant, will be immune to ASP and accumulate in the environment.

2. Literature review

Numerous authors have written about the existence of PCPPs in WWTP influent and effluents, along with the subsequent concentrations that are found in the environment see Table 1, page 15). The influent range of PCPPs was between 0.0001 and 70 µg/L, indicating that there is a substantial variation in the load of chemicals entering a WWTP. On the other hand, the WWTP effluents demonstrated a range between 0.0002 and 70 µg/L showing that removal was to some degree occurring, but this trend did not necessarily hold for every chemical studied. This effluent discharge results in a mass flow to the environment, which, then depending on the characteristics of the compounds, will have an excellent reflection in the concentrations found in the environment. The environmental concentrations observed in various studies exhibited a concentration range between 0.0001 to 71. 9 µg/L. Finally, the removal efficiencies for ASP WWTPs and MBR WWTPs are shown in Table 2 (see page 18). These tables demonstrate that many compounds are recalcitrant to conventional ASP WWTPs. On the other hand, many of the compounds that are biologically recalcitrant demonstrate potential for removal in MBR plants.

Methods

1. Literature Values and Previous studies

A comprehensive survey of the literature was conducted to ascertain the concentrations of PCPPs of interest and their treatability. 140 journal articles were compiled with values for influent, effluent, and environmental concentrations (see Table 1). Of these 140 journal articles, 10 were comprehensive review articles that formed the basis of producing the final list of PCPPs. Minimum and maximum values were compiled with measurements being taken within the United States being given preference and non-US data

being utilized when US data was not available. Additionally physical and chemical data concerning biodegradiblity, log K_{ow}, and solubility data was estimated in EPISUITES 4.1 [40].

Additionally, a literature search was also conducted to ascertain the effectiveness of different treatment methods currently employed in either lab-scale or in the field. 140 journal articles were compiled to determine the minimum and maximum values for each PCPP in a given process (see Table 2, Table 3, and Table 4). By assessing the current practices in the field, it became possible to estimate the removal efficiencies for each of the various treatment methods.

2. Probability Plots and Distribution Determination

Probability plots were constructed to determine the distributions of influent, effluent, and environmental concentrations; as well, averages of the literature values. All probability plots were constructed in Excel® under the same procedure. First, the concentrations of interest were rank ordered from smallest to largest. Then a probability was computed by using the formula: $p = \frac{rank}{\#\ of\ items\ to\ rank+1}$, and taking the normsinv(p) and loginv(p). The obtained values were then plotted with probability (as number of standard deviations from the mean) versus concentration (S with two standard deviations from the mean), on log normal and normal scales to determine the distribution for each parameter of interest (based on curvature and R^2 value).

3. Monte Carlo Simulation

In order to study the role of concentration on biodegradation, a Monte Carlo simulation was conducted for CSTR and Batch reactors with and without competitive effects due to other substrates. The Monte Carlo simulation was conducted in Microsoft Excel® 2010. The simulation utilized 1000 trials and all variables were subject to the appropriate distributions. In order to roll the dice for each trial, the random() function in Excel® was utilized to generate a probability between 0 and 1 for each of the variables. The dice roll was separate for each of the variables of interest, K_m, k_d, Y, k, and S_2. To generate values for each of these, the normsinv(p) and loginv(p) functions were used with the dice roll for each variable in the trial, with the relevant mean and standard deviation (shown in Table 6). For K_m, k_d, Y, and

k, the values for phenol were used as a surrogated for the compounds of interest due to the wide availability of data, and the fact that Phenol is the a relatively biodegradable compound that is frequently found in industry and medicine. Phenol is also well regulated within the current regulatory scheme and as such provides an excellent model. The means and standard deviations were compiled from Magbuana et al., which provided an excellent sampling of experimental data and literature values [112].

Table 6: Constants used in Monte Carlo Simulation for Biodegradation [113] [106] [112]

Constants	mg VSS/ mg Phenol	k_d, d^{-1}	k, d^{-1}	K_M, mg/L	S_2 mg/L
Mean	**0.85**	**0.03**	**4.86**	**0.63**	**0.001889***
Standard Deviation	**0.20**	**0.01**	**1.94**	**0.86**	**0.015625***
Distribution	**Normal**	**Normal**	**Log**	**Log**	**Log**
***Values obtained by averaging and standard deviation of all the influent concentrations found in Table 1. The 45 pharmaceuticals of interest, therefore form a distribution with a mean and standard deviation. This distribution was log-normal.					

After extracting the parameters for each of the trials, the competitive and non-competitive trials were completed. The dice were re-rolled for 1000 trials for each of the cases (CSTR and Batch with and without competitive effects). Utilizing the values from the pertinent distributions, values for each of the scenarios were found. First, equation 3k was solved for batch with a non-competitive single substrate (phenol). Then a CSTR was solved with a non-competitive single substrate with θ_c of 1, 2, 5, 8, 10, 12, 14, 16, 18, and 20 days. After completing the calculations for the non-competitive cases, the calculations were redone to account for competitive effects by solving equations 7j and 8i. For each of the four scenarios, averages and standard deviations were obtained across the 1000 runs, and the average was plotted with two standard deviations indicated.

4. Results Analysis

The final results were plotted as a percent of the compound that was removed by biological degradation. It was assumed that the influent, effluent, and environment inputs contained 45, 44, and 38 compounds respectively.

Biodegradation: Minimum Achievable Substrate Concentration

1. Introduction

When organic compounds biodegrade, a portion of the compound is used for energy to drive metabolism of the bacteria; while the other portion is used for growth as a carbon source [113] [106]. That is exhibited schematically in Figure 12.

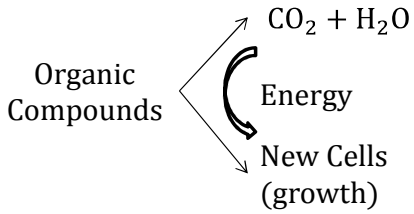


Figure 12: utilization of organic compounds.

Then, any model of biodegradation must include both substrate utilization and microbial growth. Simple first-order biodegradation models without considering active microorganisms is incomplete and will yield erroneous results, especially when low substrate concentrations are considered [113]. With respect to low concentrations of substrates , a minimum achievable substrate concentration, S_{min}, is reached when the microorganisms can no longer grow faster than they die off, or the growth rate = the death rate (endogenous decay) [113]. The values of S_{min} will depend on the reaction conditions (flow regime) and therefore differ between batch or plug flow conditions and continuously stirred conditions (CSTRs). The equations for S_{min}, can be constructed for each case and are considered in the subsequent sub-sections.

2. Batch Reactor

Beginning with the Monod Model of microbial metabolism and separate rate equations for substrate utilization and net microbial growth [113]:

Substrate utilization:

$$\frac{dS}{dt} = -\frac{kXS}{K_m + S} \tag{1}$$

Net Microbial Growth:

$$\frac{dX}{dt} = Y\left(-\frac{dS}{dt}\right) - k_d X = Y\frac{kXS}{K_m + S} - k_d X \tag{2}$$

Growth Death

Where, X is microbial biomass, Y is the microbial yield coefficient, S is the substrate concentration, k is the specific substrate uptake rate, k_d is the endogenous decay coefficient, and K_m is the half saturation constant. In order for microorganisms to grow or at least maintain a level of subsistence, $Growth \geq Death$, or

$$\frac{YkXS}{K_m + S} \geq k_d X \tag{3a}$$

And, dividing by X (microbial biomass):

$$\frac{YkS}{K_m + S} \geq k_d \tag{3b}$$

Now we can solve for the concentration of substrate needed to support microbial growth, S_{min} or:

$$\frac{YkS_{min}}{K_m + S_{min}} = k_d \tag{3c}$$

Then, rearranging and finally solving for S_{min}:

$$S_{\min}\ (Yk - k_d) = k_d K_m \tag{3d}$$

$$\boldsymbol{S_{min} = \frac{k_d K_m}{Yk - k_d}} \tag{3e}$$

Also, the batch reactor situation is assumed to be representive of a plug-flow continuous reactor.

3. CSTR with Recycle

For ASPs, the system can be broken down into the aeration basin and clarifation (used to segregated/concentrate and recycle biomass). This leads to several separate considerations in solving for the constituents in completely mixed processes. This is indicated in Figure 13 as the three distinct mass balance envelopes that can be considered:

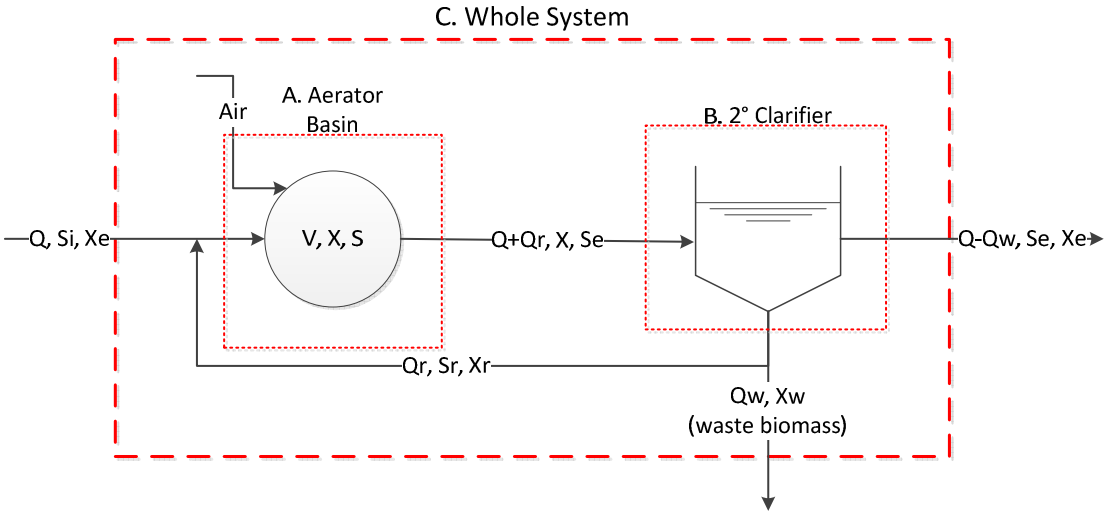


Figure 13: CSTR with Recycle. Three envelopes for mass balance analysis: A) around the aeration basin, B) around the secondary clarifier, and C) around the entire system. Q is flow rate, X is microorganism concentration, S is substrate concentration. Subscripts i indicate influent, r indicates the recycle loop, w is the waste biomass and e is effluent.

Starting with the Aerator (Envelope A),

$$V\frac{dX}{dt} = QX_{in} - QX + QRX_R + V\frac{YkXS}{K_m + S} - Vk_dX \tag{4a}$$

Then assuming X_{in}=0 and dividing by V yields:

$$\frac{dX}{dt} = -\frac{Q}{V}X + \frac{Q}{V}RX_R + \frac{YkXS}{K_m + S} - k_dX \tag{4b}$$

Assuming steady state conditions ($\frac{dX}{dt} = 0$), the equation becomes:

$$0 = -\frac{Q}{V}X + \frac{Q}{V}RX_R + \frac{YkXS}{K_m + S} - k_dX \tag{4c}$$

Then, around the entire system (Envelope C), the equation becomes:

$$V\frac{dX}{dt} = QX_i - QX_e - Q_wX_w + V\frac{YkXS}{K_m + S} - Vk_dX \tag{4d}$$

Assuming that X_i and X_e are equal to zero, the equation becomes:

$$V\frac{dX}{dt} = -Q_wX_w + V\frac{YkXS}{K_m + S} - Vk_dX \tag{4e}$$

Dividing through by VX and assuming steady state ($\frac{dx}{dt} = 0$) yields the equation:

$$0 = -\frac{Q_wX_w}{VX} + \frac{YkS}{K_m + S} - k_d \tag{4f}$$

Where $\frac{VX}{Q_w X_w} = \theta_c$, which is the biomass residence time (amount of time a bacterial cell (the biomass) resides in the system, on average) and substituting, then:

$$0 = \frac{-1}{\theta_c} + \frac{YkS}{K_m + S} - k_d \tag{4g}$$

Rearranging the equation and solving for S_{min} yields:

$$\frac{1}{\theta_c} + k_d = \frac{YkS_{min}}{K_m + S_{min}} \tag{4h}$$

$$\left(\frac{1}{\theta_c} + k_d\right)(K_m + S_{min}) = YkS_{min} \tag{4i}$$

$$YkS_{min} = K_m\left(\frac{1}{\theta_c} + k_d\right) + S_{min}\left(\frac{1}{\theta_c} + k_d\right) \tag{4j}$$

$$YkS_{min} - S_{min}\left(\frac{1}{\theta_c} + k_d\right) = K_m\left(\frac{1}{\theta_c} + k_d\right) \tag{4k}$$

$$S_{min}\left(Yk - \left(\frac{1}{\theta_c} + k_d\right)\right) = K_m\left(\frac{1}{\theta_c} + k_d\right) \tag{4l}$$

And, finally solving for S_{min},

$$\boldsymbol{S_{min} = \frac{K_m\left(\frac{1}{\theta_c} + k_d\right)}{\left(Yk - \left(\frac{1}{\theta_c} + k_d\right)\right)}} \tag{4n}$$

Note, for systems without recycle, such as maybe assumed for a lake, $\theta_c = \theta_h$ (hydraulic residence time).

4. Multiple Substrate competition

Some bacteria utilize more than one substrate in a competitive fashion in order to grow. The result of this is that the previous set of equations must be modified to incorporate the effects of multiple substrates in solution [113]. For two substrates, the substrate rate equation may be modified as follows:

$$\frac{dS_1}{dt} = \frac{-kXS_1}{K_{m,1} + S_1 + K_{m,1}K_{m,2}S_2} \tag{5a}$$

This may be written as a summation for n-substrates [113] (look for additional reference):

$$\frac{dS_1}{dt} = \frac{-kXS_1}{K_{m,1} + S_1 + K_{m,1} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} \tag{5b}$$

Then, the biomass growth equation may be rewritten, or :

$$\frac{dX_1}{dt} = -Y * \frac{dS}{dt} \tag{5c}$$

$$\frac{dX_1}{dt} = \frac{YkXS_1}{K_{m,1} + S_1 + K_{m,1} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} \tag{5d}$$

This equation is then substituted into the equations for batch reactors and CSTRs to derive a multiple substrate competitive Monod model. The S_{min} values for multiple substrates can be found in a similar manner to a single substrate. This was done using equation 5d by considering S_1 as our primary substrate.

5. Multiple Substrate Competition Batch Reactor

In order for microorganisms to grow or at least maintain a level of subsistence, $Growth \geq death$:

$$\frac{YkXS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} \geq k_d X \tag{6a}$$

And dividing by X (microbial biomass),

$$\frac{YkS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} \geq k_d \tag{6b}$$

Now we can solve for S_{min}, or:

$$\frac{YkS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} = k_d \tag{6c}$$

Collect S_1 on each side:

$$YkS_{1,min} - k_d S_{1,min} = k_d K_{m,1} + k_d * K_{m,1} * \Sigma_{i=2}^{n}\left(K_{m,i}S_i\right) \tag{6d}$$

Finally, rearranging and solving for $S_{1,min}$:

$$\boldsymbol{S_{1,min} = \frac{K_{m,1} + K_{m,1} * \Sigma_{i=2}^{n}\left(K_{m,i}S_i\right)}{\frac{Yk}{k_d} - 1}} \tag{6e}$$

6. Multiple Substrate Competition CSTR with recycle

Beginning with the same configuration in Figure 13, the analysis begins with the aeration basin (A),

$$V\frac{dX}{dt} = QX_{in} - QX + QRX_R + V\frac{YkXS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} - Vk_dX \quad (7a)$$

Then assuming X_{in}=0 and dividing by V yields:

$$\frac{dX}{dt} = -\frac{Q}{V}X + \frac{Q}{V}RX_R + \frac{YkXS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} - k_DX \quad (7b)$$

Assuming steady state conditions ($\frac{dx}{dt} = 0$), the equation becomes:

$$0 = -\frac{Q}{V}X + \frac{Q}{V}RX_R + \frac{YkXS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} - k_DX \quad (7c)$$

Then, around the entire system (C), the equation becomes:

$$V\frac{dX}{dt} = QX_i - QX_e - Q_wX_w + V\frac{YkXS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} - Vk_dX \quad (7d)$$

Assuming that X_i and X_e are equal to zero, the equation becomes:

$$V\frac{dX}{dt} = -Q_wX_w + V\frac{YkXS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} - Vk_dX \quad (7e)$$

Dividing through by VX and assuming steady state ($\frac{dx}{dt} = 0$) yields the equation:

$$0 = -\frac{Q_wX_w}{VX} + \frac{YkS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} - k_d \quad (7f)$$

Where $\frac{VX}{Q_wX_w} = \theta_c$, which is the mean cell residence time (amount of time a bacteria resides in the system, on average) and substituting, then:

$$0 = \frac{-1}{\theta_c} + \frac{YkS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} - k_d \quad (7g)$$

Rearranging the equation and solving for $S_{1,min}$ yields:

$$\frac{1}{\theta_c} + k_d = \frac{YkS_1}{K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)} \quad (7h)$$

$$YkS_1 = \left(\frac{1}{\theta_c} + k_d\right) * \left(K_{m,1} + S_1 + K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)\right) \quad (7i)$$

$$YkS_1 = \left(\frac{1}{\theta_c} + k_d\right) * K_{m,1} + \left(\frac{1}{\theta_c} + k_d\right) * S_1 + \left(\frac{1}{\theta_c} + k_d\right) * \left(K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)\right) \quad (7j)$$

$$YkS_1 - \left(\frac{1}{\theta_c} + k_d\right) * S_1 = \left(\frac{1}{\theta_c} + k_d\right) * K_{m,1} + \left(\frac{1}{\theta_c} + k_d\right) * \left(K_{(m,1)} * \Sigma_{i=2}^{n}(K_{m,i}S_i)\right) \quad (7k)$$

$$S_1 * \left(Yk - \frac{1}{\theta_c} - k_d\right) = \left(\frac{1}{\theta_c} + k_d\right) * K_{m,1} + \left(\frac{1}{\theta_c} + k_d\right) * \left(K_{(m,1)} * \Sigma_{i=2}^{n}\left(K_{m,i}S_i\right)\right) \quad (7l)$$

$$S_{1,\min} = \frac{\left(\frac{1}{\theta_c} + k_d\right) * K_{m,1} + \left(\frac{1}{\theta_c} + k_d\right) * \left(K_{(m,1)} * \Sigma_{i=2}^{n}\left(K_{m,i}S_i\right)\right)}{Yk - \frac{1}{\theta_c} - k_d} \quad (7m)$$

$$\boldsymbol{S_{1,\min}} = \frac{\boldsymbol{K_{m,1} * \left(\frac{1}{\theta_c} + k_d\right) * \left(1 + \Sigma_{i=2}^{n}\left(K_{m,i}S_i\right)\right)}}{\boldsymbol{Yk - \frac{1}{\theta_c} - k_d}} \quad (7n)$$

Note, for systems without recycle, such as maybe assumed for a lake, $\theta_c = \theta_h$ (hydraulic residence time). A summary of the equations derived for the minimum substrate concentrations is presented in Table 7.

Table 7: Summary of derived minimum substrate equations for various reactor types

Type of Reactor	S_{min} w/o competition	S_{min} with competitive effects
Batch	$S_{minimum} = \frac{K_m}{\frac{Yk}{k_d} - 1}$ (eq. 3e)	$S_{1,min} = \frac{K_{m,1} + K_{m_1} * \Sigma_{i=2}^{n}\left(K_{m,i}S_i\right)}{\frac{Yk}{k_d} - 1}$ (eq. 6e)
CSTR with recycle	$S_{minimum} = \frac{K_m\left(\frac{1}{\theta_c} + k_d\right)}{Yk - \left(\frac{1}{\theta_c} + k_d\right)}$ (eq. 4n)	$S_{1,\min} = \frac{K_{m,1} * \left(\frac{1}{\theta_c} + k_d\right) * \left(1 + \Sigma_{i=2}^{n}\left(K_{m,i}S_i\right)\right)}{Yk - \frac{1}{\theta_c} - k_d}$ (eq. 7n)
CSTR without recycle	Eq. 4n; $\theta_h = \theta_c$	Eq. 7n; $\theta_h = \theta_c$

Results

Utilizing Monod kinetics and accounting for competitive effects during Monte Carlo simulation, the results are presented in the sections which follow. The first set of results obtained examined the distribution of results obtained in batch, CSTR, and literature review data to determine the underlying distributions of values. These values were crucial to the modeling exercise, since utilizing competitive effects creates a dependence on the concentration of the other substrates in solution. Therefore, this concentration and distribution must be determined in order to proceed.

Probability Plots

Utilizing data that was compiled from the literature search, probability plots for the influent, effluent, environmental, and average concentrations of PCPPs were compiled (see Figure 14, Figure 15,

Figure 16, and Figure 17 respectively). The average and the minimum and maximum concentration for the compounds examined demonstrated that log-normal distributions were reasonable fits for influent, effluent, and environmental concentrations with R^2 values of 0.8884, 0.9655, and 0.917 respectively. As a result, the influent case (Figure 14), was utilized as the basis of the competitive average and standard deviation values, and was assumed to be log normal.

Once the Monte Carlo simulation results were obtained, probability plots of the S_{min} for both batch and CSTR (see Figure 18, Figure 19), with and without competition, revealed log-normal distributions were a reasonable fit (visual linearity and $R^2 > 0.9$). This was expected, since most of the inputs were log-normally distributed.

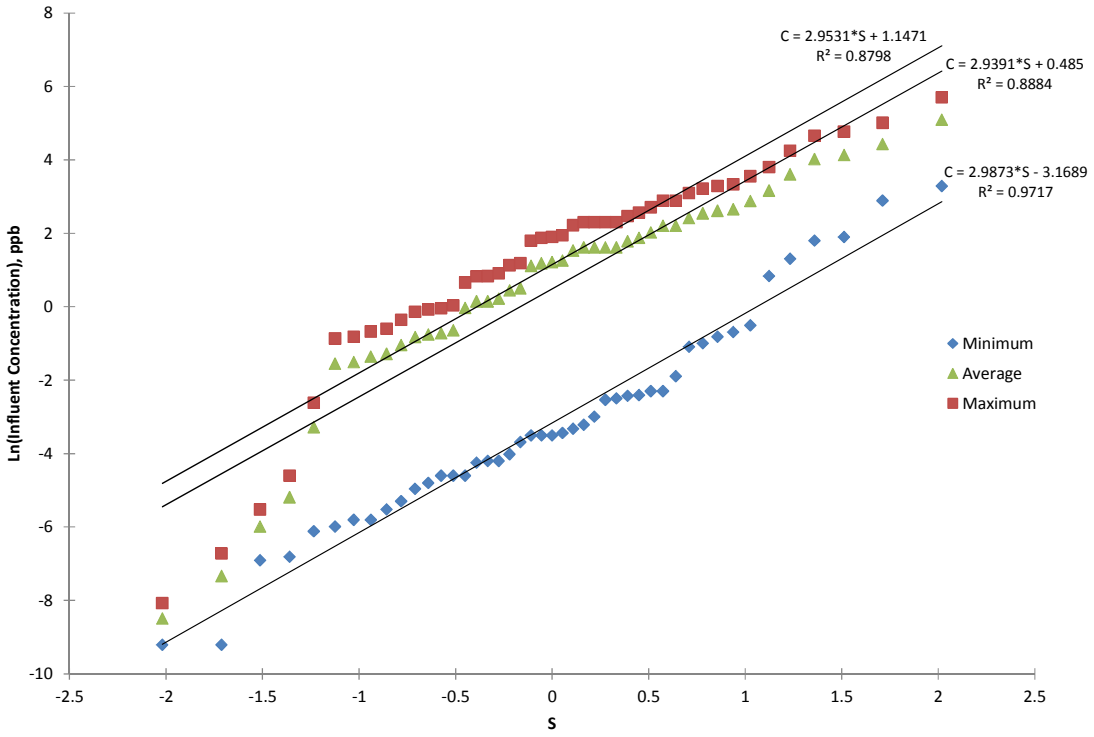


Figure 14: Influent probability plot demonstrates generally a log-normal distribution for all three sets of data, i.e. minimum, average, and maximum concentrations detected (data from a variety of sources, see Table 1).

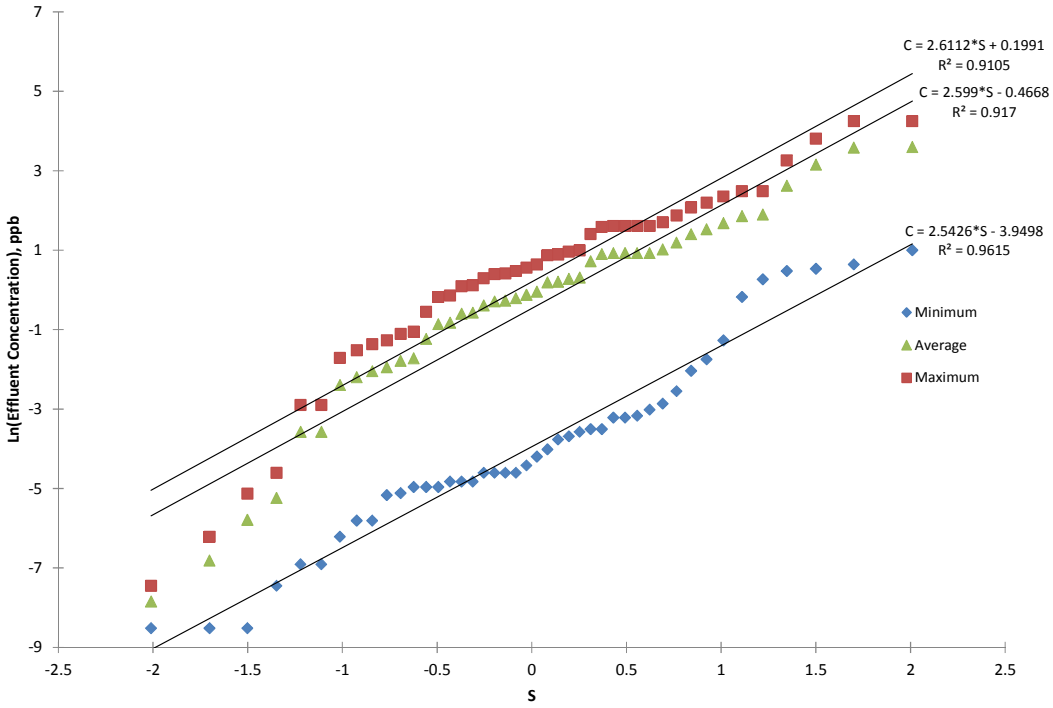


Figure 15: Effluent probability plot demonstrates generally a log-normal distribution for all three sets of data, i.e. minimum, average, and maximum concentrations detected (data from a variety of sources, see Table 1).

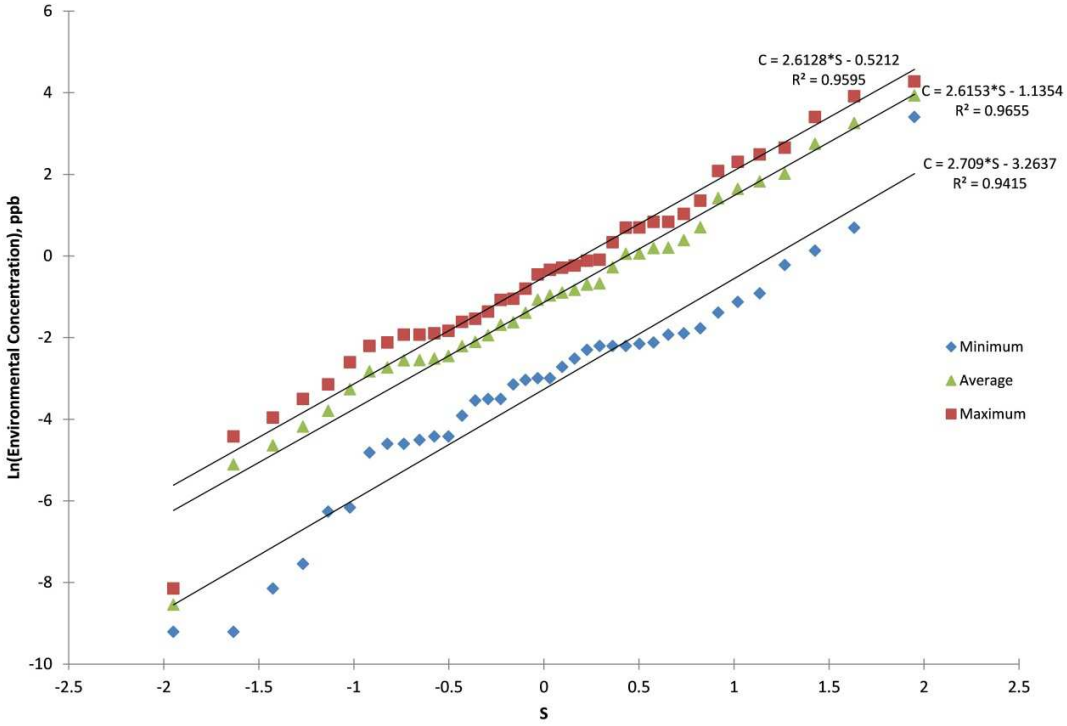


Figure 16: Environmental concentration probability plot demonstrates generally a log-normal distribution for all three sets of data, i.e. minimum, average, and maximum concentrations detected (data from a variety of sources, see Table 1).

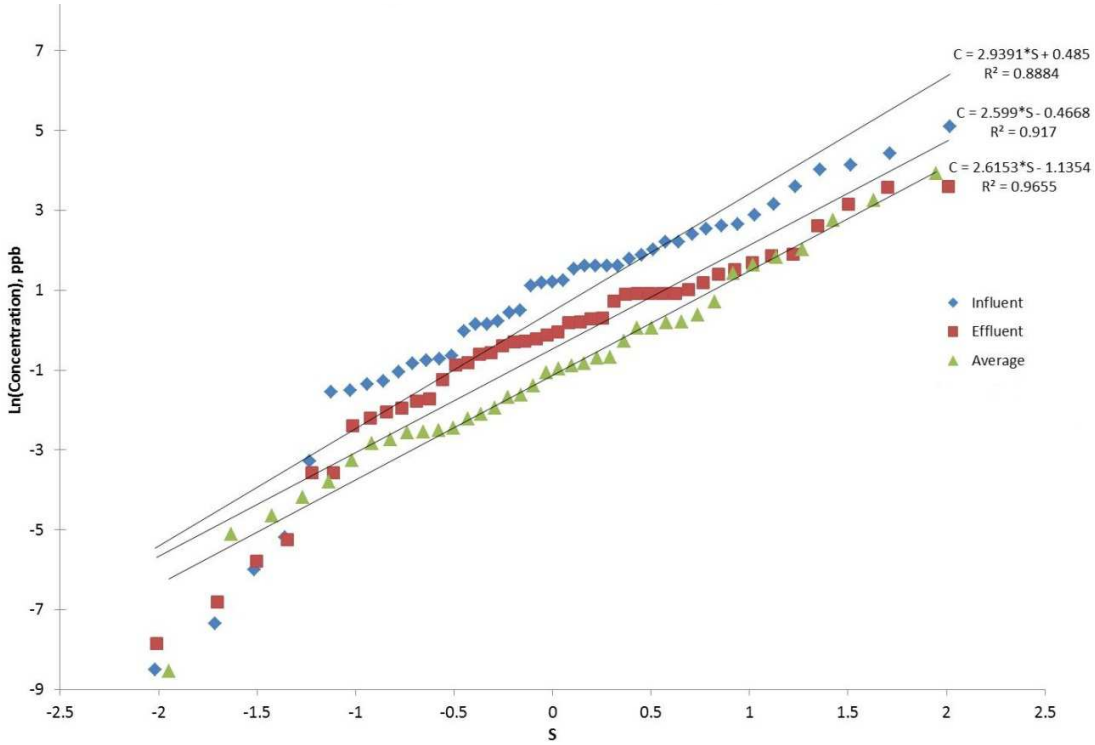


Figure 17: Average probability plot demonstrates log-normal distributions for the averaged values for the influent, effluent, and environmental concentrations compiled from a literature search.

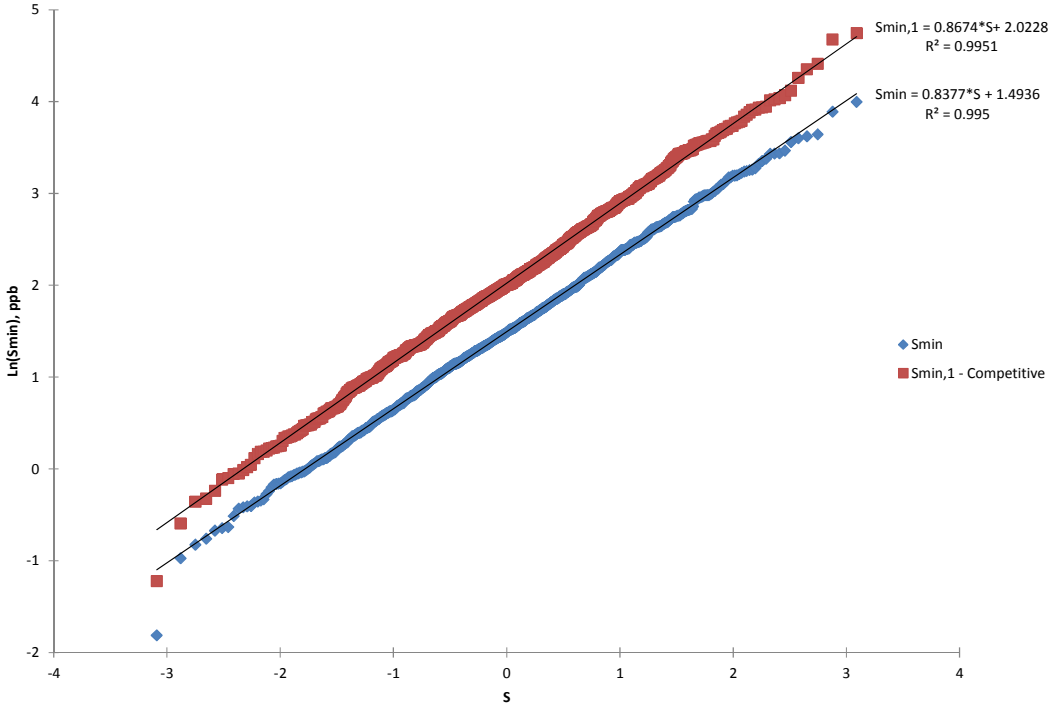


Figure 18: S_{min} batch reactor probability plot demonstrates log-normal distributions for the values obtained by 1000 trials for both competitive and non-competitive cases.

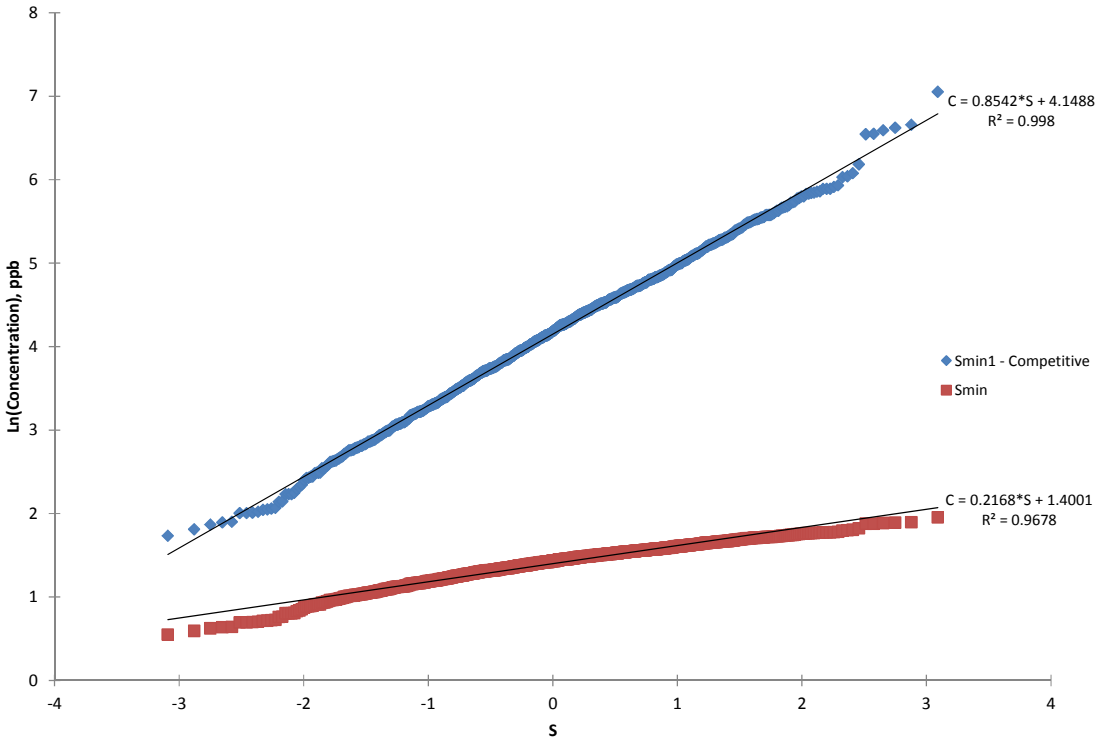


Figure 19: S_{min} CSTR reactor with a $\boldsymbol{\theta_C}$ of 5 days probability plot demonstrates log-normal distributions for the values obtained by 1000 trials for both competitive and non-competitive cases.

Non-Competitive Kinetics

When competitive effects are disregarded, an idealized case is modeled where a single substrate is being consumed by a bacterial species without regard to the other organic and inorganic compounds that would be present in the influent of a WWTP. The results displayed in Figure 20, represent the most optimal case for determining the substrate concentration necessary for the rate of bacterial growth to equal the bacterial death rate. If this concentration is not exceeded, then the bacterial counts will dwindle and further utilization of the substrate will cease.

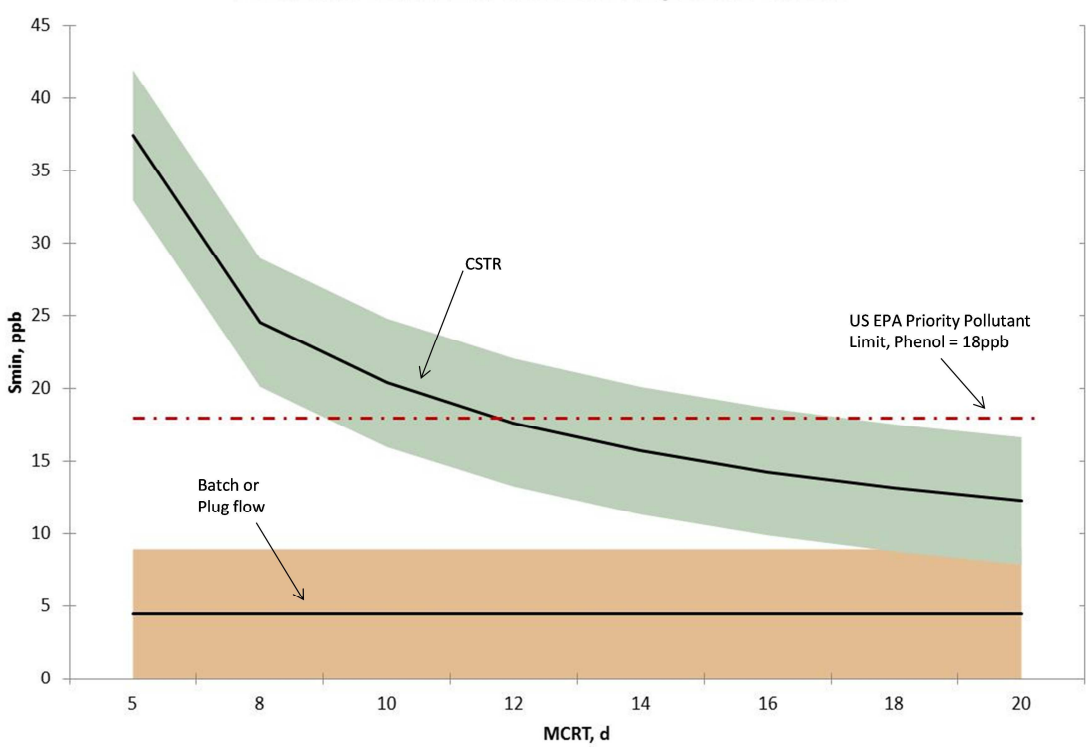


Figure 20: Minimum substrate concentrations S_{min}, for batch and CSTR reactors without competition. Non-competitive phenol degradation demonstrates a substantially lower minimum concentration for plug flow reactors than CSTR reactors. The range of operating parameters in a WWTP shows that the minimum necessary concentration for a substrate decreases with increasing MCRT (based on Monte Carlo simulation of equations 3e and 4n, using phenol as a surrogate substrate, and parameters listed in Table 6). Note: the shaded region of this figure is one standard deviation from the average.

In terms of a typical WWTP, MCRT is one of the dominant variables that can be controlled by the operators of the plant. This parameter has a drastic effect on the minimum substrate concentration necessary to sustain bacterial growth. Utilizing the range of MCRTs that are typical for WWTP operations (5 to 20 days), demonstrates that the minimum concentration necessary to maintain bacterial counts varies between 37 ppb to 13 ppb for MCRTs of five and twenty days respectively. This means that in order for a PCPP to be potentially biodegraded, it must exceed this level in the influent. On the other hand, the plug flow reactor demonstrates a small range of S_{min} with an average of 4.47 ppb with a standard deviation of 2.23 ppb. One might also note that the batch or plug-flow results appear to be the limit for the CSTR (CSTR$\rightarrow$PF as $\Theta_c \rightarrow \infty$). There is no dependence on the MCRT in the plug flow case, but it is interesting to note that the S_{min} is substantially lower than in the CSTR case. The significance of this is that a few more compounds than in the CSTR case maybe biodegraded due to the lower minimum concentrations. Very few of the compounds included in this study have influent concentrations that exceed the S_{min} values

predicted in Figure 20. As a result, within most WWTPs, biological degradation is not expected to a large extent. If these compounds were concentrated to sufficient levels to maintain bacterial growth, they could then be potentially biodegraded and would become an attractive substrate for the bacteria. Additionally, the US EPA priority pollutant limit intersects the average CSTR minimum concentration with a mean cell residence time of 13 days for CSTR and the minimum for the batch reactors are always lower than the limit for phenol. The implications of this is that the effluent that is leaving most facilities regulated by NPDES permits will not exceed the median MCRT for CSTRs and as a result, will most likely not undergo any further biological degradation. Also, any species in the influent that are below S_{min} will tend to be outcompeted by the higher concentration substrates. This helps to explain the phenomena of some PCPPs that are in the ppt range that simply pass through the plant.

Unfortunately, real world conditions do not involve a single substrate with a single bacterial species. Waste streams entering a typical WWTP are complex mixtures of compounds and bacteria, necessitating that competition will occur and the highest concentration substrates will be preferentially degraded.

Competitive Kinetics

When competitive effects are taken into account, a more realistic case is modeled where multiple substrates are competing to be consumed a bacterial species. This competition would occur due to the complex nature of the organic compounds that are present in the influent of a WWTP. Therefore, the results obtained in Figure 21, represent a more realistic case for determining the bacterial concentration necessary for the degradation of a single substrate of minimal concentration to occur. If this minimum concentration is not met, then the bacterial counts will dwindle and biodegradation will cease.

In terms of a typical WWTP, the MCRT is one of the dominant variables that can be controlled by the operators of the plant. This parameter has a drastic effect on the minimum concentration necessary to sustain bacterial growth. Utilizing the range of MCRTs that are typical for WWTP operation, modeling demonstrates that the minimum concentration necessary to maintain bacterial counts varies between 65 ppb to 13 ppb for MCRTs of five and twenty days respectively. Additionally, the US EPA priority pollutant limit never intersects the CSTR range. On the other hand, the plug flow reactor demonstrates a small range

of S_{min} with an average of 7.58 ppb with a standard deviation of 2.36 ppb. There is no dependence on the MCRT in the plug flow case, but it is interesting to note that the S_{min} is substantially lower than in the CSTR case. The implications of this is that the effluent that is leaving most facilities regulated by NPDES permits will not exceed the median MCRT for CSTRs and as a result, will most likely not undergo any further biological degradation. Also, any species in the influent that are below S_{min} to begin with will tend to be outcompeted by the higher concentration species. This helps to explain the phenomena of some PCPPs that are in the ppt range that simply pass through the plant.

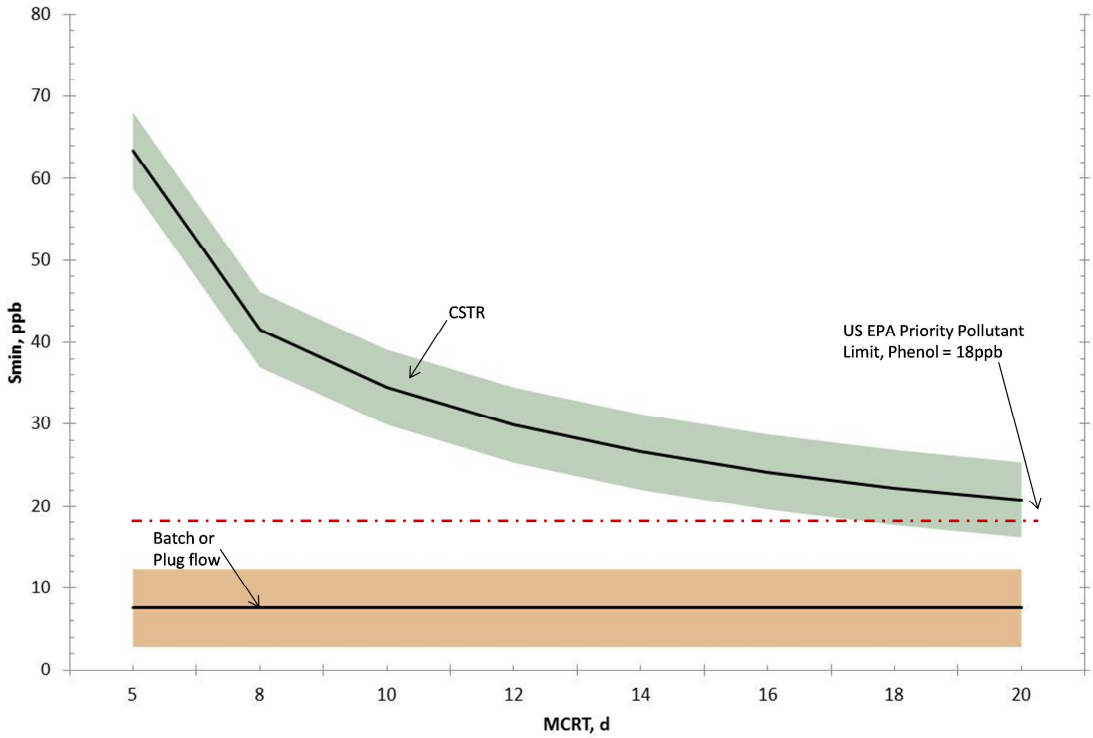


Figure 21: Minimum substrate concentrations, S_{min}, for batch and CSTR reactions with competitive substrate effects. Competitive degradation demonstrates a substantially lower minimum concentration for plug flow reactors than batch reactors. The range of operating parameters in a WWTP shows that the minimum necessary concentration for a substrate decreases with increasing MCRT (based on Monte Carlo simulation of equations 6e and 7n, using phenol as a surrogate substrate, and parameters listed in Table 6).

Discussion

Biological degradation of any organic molecule is a function not only of the type and amount of bacteria present within the culture, but also, the concentration and number of chemical substrates that are present within the wastewater. Within WWTP influents, there are thousands of compounds that will eventually be competing for different bacteria that will specifically digest them. While a single bacteria

species will not digest all of these compounds, there will be multiple compounds that are most likely competing to be the substrate of choice for that particular bacterial species. As a result, the modeling exercise demonstrates that adding just one more competitive substrate means that the minimum concentration necessary for degradation must increase and almost double (equal concentrations or equally competing substances). This means that only compounds that are present in the highest concentrations will be effectively degraded biologically. Therefore, in order for a PCPP to be potentially biodegraded, it must be present in the influent at a sufficient level to be preferentially degraded.

Accounting for competitive effects amongst species increased the necessary minimum concentration substantially by adding one competitive substrate into the reactor. It is important to note that these concentrations with two substrates competing results in approximately a 75% increase in the minimum concentration of that substrate for a CSTR and a 70% approximate increase for batch/plug flow reactors. This indicates that as more substrates are considered to be competing for the same bacterial species (a more realistic scenario); there will be a further increase in the minimum concentration of the compounds to allow bacterial colonies to be maintained. In the context of WWTP influent, there will be scenarios where there are more than two substrates competing for a bacterial species, which would produce an underestimation of the minimum concentration by the model. Additionally, different kinetic parameters (K_m, k, and k_d) for each substrate will affect the relative contribution of that substrate to raising competitively the overall minimum concentration for another substrate. This will become crucial as not all substrates will have to meet the same minimum concentration, and will instead be based upon what other substrates are present and competing for that bacterial species.

If the 45 compounds that were considered for this study are considered at their influent concentrations, less than 10% of those compounds would be even potentially biologically degraded (see Figure 22). This assumes that the maximum concentration of that compound is present and that the minimum substrate concentration is utilized to produce the most optimal result. This will not necessarily be the case for a WWTP where more than two substrates maybe competing for the same bacterial species. The general result shows that as more species are added, the minimum concentration necessary for biological degradation increases. As a result, due to the complex nature of the waste stream entering a WWTP, there will rarely be an optimistic case where a single substrate is interacting with a single bacterial

species. Even if the most optimistic case is assumed, a compound would need to be present within the influent waste stream above the S_{min} (13-37 ppb depending on MCRT). Very few of the compounds in this study fit within those parameters (less than 20%). Then, either the biokinetic parameters are more favorable than those used as a surrogate, i.e., $k > k_{phenol}$ or $K_m < K_{m,phenol}$, or for many PCPPs there must be other processes occurring within the treatment plant that remove these compounds.

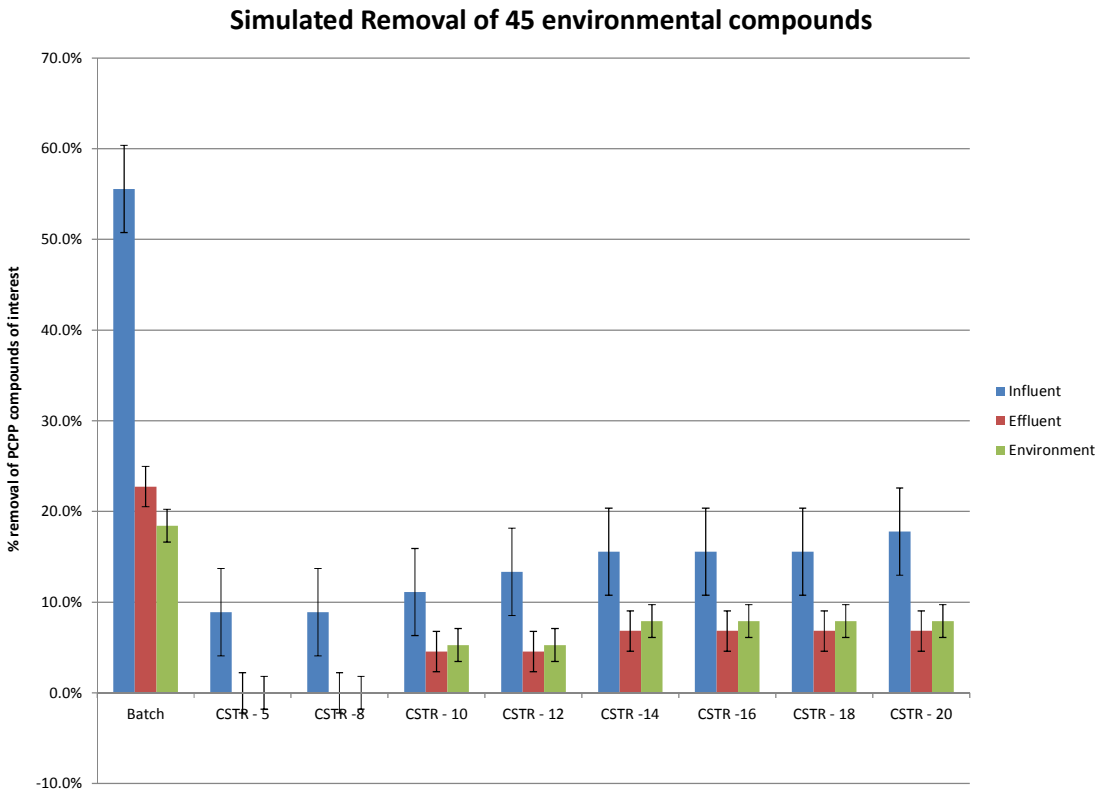


Figure 22: Utilizing the best case scenario of non-competitive kinetics; most WWTPs behaves as a CSTR and very few of the compounds of interest are present in the influent at a sufficient concentration to undergo further biodegradation. Removal of the 45 selected compounds of analysis demonstrates that in terms of a CSTR less than 18% of the 45 will be removed, while in the batch case fewer than 55% will be removed. This finding is crucial, since it demonstrates that removal of any species is very dependent upon the concentration of that species present in the inflow. As a result, at best less than 18% of the PCPPs would be removed if only two species were in competition with one another.

Membrane Biological Reactor, MBRs

It should be noted that MBRs are a special class of bioreactors, operated as a CSTR with a membrane to restrict the flow of solids (biomass) in the final effluent. This implies that MBRs can operate at higher MCRTs, and then, the results for MBRs would be more similar to batch reactors (MCRT > 20

days). Data from the literature (see Table 2, page) entirely supports this view, showing lower effluent concentrations of PCPPs than CSTRs for many substrates of interest.

Conclusions

Biological degradation can only account for a small portion of the removal that is witnessed within a WWTP. Potential removal mechanisms for substrates that are substantially lower than the minimum substrate concentrations modeled are sludge adsorption (either reversible or irreversible) [114], chemical transformation as a result of the employed treatment process, hydrolysis, or photolysis [115]. While there may be other processes occurring within the WWTP, further studies must be conducted to ascertain the exact fate and transformation of these PCPPs. However under normal circumstances, it is unlikely that the fate can be readily understood and quantified due to the difficulty and expense of measuring these compounds and their reaction byproducts within the plant.

CHAPTER 3

THE ROLE OF CONCENTRATION ON ADSOPRTION PROCESSES

Introduction

1. Adsorption Overview

There are two different types of sorption processes that can occur, either as as reversible or irreversible reactions. First, absorption is defined by, the substance being drawn in, and is integrated into the absorbent [106, 116, 117]. Conceptually, this process can be demonstrated with a sponge that is compressed and then immersed in water, and when the sponge is released, the water becomes a part of the sponge. The second process is adsorption and occurs when the sorbate binds to the surface of the absorbent [106, 116, 117]. Conceptually, any chemical that could bind to the surface of the sponge and not enter the matrix space would be considered to be adsorbed (e.g. grease). For the purposes of this study, adsorption is of interest and is the driving force governing the potential removal of pollutants. There are two different types of processes that govern adsorption process: 1) physisorption which occurs as a result of Van der Walls forces or other weak attractive forces between the adsorbent and the sorbate and 2) chemisorption which occurs as a result of chemical bonding or reaction between the adsorbent and the sorbate [106, 116, 117]. Physisorption, or physical adsorption, is reversible whereas, chemisorption is the irreversible transformation of solute catalyzed by the surface of the adsorbent [106, 116, 117].

Reversible processes are characterized by “adsorption isotherms” and numerous models have been developed to describe the behavior of the adsorbent and adsorbate. Isotherms are a graph of the amount of adsorbate that has adsorbed onto the adsorbent as a function of the gas pressure or concentration of the adsorbate at a constant temperature [106, 116, 117]. The shape of the isotherm led to the development of different models to describe the empirical data. The primary isotherm models are linear, Langmuir (BET is a generalization of this model), and Freundlich [106, 116, 117]. The shapes of each of these models vary: the linear model does not reach a maximum whereas the Langmuir model eventually reaches a maximum value (noting that this is rarely observed in the lab unless high concentrations are utilized [106, 116, 117].

The Freundlich model's shape is depended on the sorbate concentration to some power, n, where: if it is equal to one produces a linear graph, if it is less than one resembles an inverse exponential curve shape, and if n is greater than one, resembles an exponential curve shape [106, 116, 117]. Selection of a model is dependent upon inherent assumptions for each model, but for PCPPs and micropollutants, the most common model applied is the Freundlich.

There are numerous types of adsorbents each with different applications and properties with the most common being activated carbon. Good adsorbents have a large exposed surface area and the more surface area exposed, the better the adsorbent [118]. Commonly encountered adsorbents are shown in Table 8 below.

Table 8: Common Adsorbents Utilized in Industrial, Chemical, Commercial, and WWTP Processes

Natural	
Peat	Adsorbs more than lignite…compaction in the earth from Peat->Lignite->Coal decreases surface area, thereby decreasing the adsorption capacity
Lignite	Formed by decaying of biological material via biochemical and geochemical processes
Fuller's Earth	Sedimentary clay or clay like material
Bentonite	Impure clay composed mainly of montmorillonite. Many different types, but named after predominate element (K, Na, Ca, or Al)
Synthetic and Chemically Modified	
Activated Carbon	Carbon chemically processed to increase surface area
Bone Char	Produced by charring bone, have lower surface area than AC
Activated Alumina	Manufactured from aluminum hydroxide
Silica Gel	Granular and porous form of SO2 made from silicate
Bauxite	Aluminum ore that can be chemically modified into an adsorbent
Molecular Sieves	Zeolite metal aluminosilicates - Composed of porous aluminosilicate frameworks of SiO4 and AlO4
Chitosan	Made by chemically treating shrimp and other crustacean shells
Ion Exchange Resins	Synthetic organic polymer substrates that are formed into a bead matrix. Four different functional groups: 1) strongly acid, 2) strongly basic, 3) weakly acidic, and 4) weakly basic

Source: [118]

One of the most utilized adsorbents in industrial and chemical processes is activated carbon. It is composed of a graphite lattice and can be produced relatively inexpensively [118, 119]. Activated carbon can come from any carbon containing substances, but it commonly is derived from: coal, peat, wood, or coconut shells [118, 119]. Also during the production process, the surface of the adsorbent can readily be modified in many instances to allow for adsorption in the desired application. Finally, activated carbon has been shown to effectively adsorb organic substances and non-polar substances making it suitable as a potential treatment technology for micropollutants [118, 119].

2. Derivation of Freundlich Model

The Freundlich Isotherm model was first proposed in 1909 as an empirical equation that fits a curve of adsorption density (sorbate/sorbent) to the concentration of solute in the liquid or gas pressure at equilibrium. Traditionally, the equation has been treated as an empirical equation, but Weber demonstrates that the Freundlich model is a special case of Gibbs Surface Energy [117, 120, 121]. Beginning with Γ_a, Gibbs surface excess,

$$\Gamma_a = q_e = -\frac{C_e}{RT}\frac{d\sigma^\circ}{dC_e} \tag{2a}$$

or,

$$q_e = \frac{C_e}{RT}\frac{\sigma_0^\circ - \sigma_s}{Q_a^\circ}\frac{dq_e}{dC_e} \tag{2b}$$

Where: q_e is amount of sorbate absorbed to the adsorbent surface, C_e is the solution equilibrium concentration, σ_0° is the initial surface tension of the pure solvent, and σ° is the surface free energy. The surface free energy is given by:

$$\sigma^\circ = \sigma_0^\circ\left(1 - \phi_m^\circ\right) + \sigma_S^\circ\phi_m^\circ \tag{2c}$$

Where is ϕ_m° the fractional surface coverage. Integrating the previous equations yields:

$$\ln(q_e) = \frac{RTQ_a^\circ}{\sigma_0^\circ - \sigma_s}\ln(C_e) + \ln K \tag{2d}$$

Which reduces to the Freundlich equation if, $n = \frac{RTQ_a^{\circ}}{\sigma_0^{\circ} - \sigma_s}$, or:

$$\boldsymbol{q_e = K_f C_e^{\frac{1}{n}}} \tag{2e}$$

or,
$$\boldsymbol{q_e = K_f C_e^{n}} \tag{2f}$$

One limitation of the derivation shown above is that the surface excess being equal to the q_e, is only valid when there are "high surface concentrations and low residual concentrations of solute in solution" [117, 120, 121]. Equation 2e can be further modified by substituting $qe = \frac{C_0 - C}{D_0}$ and taking the log of both sides yielding:

$$\boldsymbol{\log\left(\frac{C_0 - C}{D_0}\right) = \log(K_f) + \frac{1}{n}\log(C_e)} \tag{2f}$$

3. Derivation of Competitive Freundlich Model

The Freundlich isotherm, derived in the previous section, was a useful tool when a single component was of interest, but this was rarely the case in situations outside of the laboratory setting. Therefore, a multicomponent isotherm model was required to understand the effects of competitive substances in solution and how they affect one each other's ability to adsorb. A multicomponent isotherm was proposed by Sheindorf and Rebhun in 1981 and has become known as the SRS equation [122]. In order to derive a multicomponent isotherm, each component must be assumed to follow the Freundlich isotherm. The SRS equation can be derived by starting with an exponential distribution of adsorption energies,

$$N_i(Q) = \alpha_i e^{-\frac{n_i Q}{RT}} \tag{3a}$$

$$i = 1, \dots, k \tag{3b}$$

Where, $N_i(Q)$ is the number of sites having adsorption energy Q. To be able to arrive at a Freundlich model, a competitive Langmuir model can be utilized as a starting point. Then, the surface coverage at every energy level can be described by,

$$\theta_i = \frac{b_i C_{e,i}}{1 + \Sigma_{j=1}^{k} b_j C_{e,j}} \tag{3c}$$

$$b_i = b_{i0} e^{\frac{Q}{RT}} \tag{3d}$$

Where, b_i is the adsorption coefficient, which varies with the adsorption energy for that particular component. From here, if there is an incremental increase dQ in Q, then it becomes possible to find fraction of the total sites that have that range of adsorption energy, or:

$$d\Theta_{Ti}(Q) = \Theta_i(Q) N_i(Q) dQ \tag{3e}$$

Integrating equation 3e from negative infinity to positive infinity, allows for the total coverage by sorbate i to be found:

$$\Theta_{Ti} = \int_{-\infty}^{\infty} \frac{b_{0i} e^{\frac{Q}{RT}} C_{e,i}}{1 + \Sigma_{j=1}^{k} b_{0j} e^{\frac{Q}{RT}} C_{e,j}} * \alpha_i e^{-\frac{n_i Q}{RT}} dq \tag{3f}$$

$$\Theta_{Ti} = \frac{\alpha_i RT b_{0i}}{n_i} \; C_f \left(\Sigma_{j=1}^{k} b_{0j} C_j \right)^{n_i - 1} \tag{3g}$$

Simplifying where, $K_{F,i} = \alpha_i RT b_{0i}^{n_i}$ and $\alpha_{ij} = \frac{b_{0j}}{b_{0i}}$, which is the competition coefficient. The final form of the multicomponent isotherm is given by,

$$\boldsymbol{q_i = K_{F,i} C_i \left(\Sigma_{j=1}^{k} (\alpha_{ij} C_j) \right)^{n_i - 1}} \tag{3h}$$

And solving for one of the components in a bi-solute solution yields,

$$\boldsymbol{q_1 = K_{F,1} C_1 (C_1 + \alpha_{12} C_2)^{n_1 - 1}} \tag{3i}$$

This model does collapse down to the original Freundlich monocomponent isotherm equation if, C_2=0,

$$q_1 = K_{F,1} C_1 * (C_1 + \alpha_{12} * 0)^{n_1 - 1} \tag{3j}$$

$$q_1 = K_{F,1} C_1^{1 + n_1 - 1} = \boldsymbol{K_{F,1} C_1^n} \tag{3k}$$

The multicomponent isotherm was useful for describing the behavior of numerous sorbates in solution but does presuppose that the competition coefficient can be found for each species interacting with one another. When competition occurs under isothermal conditions, the competition coefficient approaches unity and if

they compete equally with one another, then $\alpha_{1,2} = 1$. In this study, it will be assumed that any mixed sorbates will be equally competitive.

4. Literature Review

Generally, adsorption of organic substances like PCPPs, has been previously reviewed and has demonstrated good removal of many of these compounds. Removal efficiencies were compiled during a comprehensive literature review conducted in the first chapter of this work (See Table 4, page 25). The papers reviewed were restricted to GAC, however, the type of GAC differed in most cases. These authors demonstrated a wide variation in removal efficiencies of compounds with a few general trends observed. First, when higher than field like conditions (ppb concentrations) were utilized, substantially better removal was observed than when field like conditions were utilized, removal in many cases was dependent upon what else was in the samples and whether or not the compound was readily removed. For example, many studies utilized field-like conditions and showed excellent removal, but conducted their experiments in distilled water instead of wastewater or synthetic wastewater. As a result, the competition effects that would be present in synthetic wastewater and wastewater were not evaluated. Second, the papers demonstrate a potential for removal of certain PCPPs while a substance like caffeine, exhibited a wide range of removal from -10% to 80% [99]. Adsorption processes appear to be mediated by the presence or lack of hydrophobic interactions with the surface of the adsorbent [123]. While this explains a portion of the behavior, the surface groups of activated carbons may also undergo electrostatic interactions to adsorb the sorbate [123]. While both of these explanations are common in literature, the exact mechanism of adsorption of PCPPs is still not well understood and will require further research to explain the phenomena described in peer-reviewed literature.

Adsorption has been well addressed by various authors but studies tend to be restricted to one to a few compounds in solution. Some of the most important PCPPs to be removed due to their potential are estrogenic compounds. Novel materials have been utilized for the adsorption of Bisphenol A and 17α-Ethinyl Estradiol with single-walled carbon nanotubes (SWCNT), which demonstrated a high adsorption capacity and hysteresis for both compounds [124]. Another estrogen derivative, 17-ß Estradiol, was tritium labeled (able to detect down to 1.36 ng/L) and demonstrated removal efficiencies of 95% from pure water

and raw water samples [125]. While some estrogenic compounds are absorbable, another estrogenic compound nonylphenol was poorly adsorbed due to high log K_{ow} [126]. Like estrogenic compounds, Naproxen and carbamazepine removal appears to be a function of hydrophobicity and as log K_{ow} increased, the compounds became less and less adsorbed [126]. Additionally, caffeine was adsorbed in a dose dependent fashion, whereas diclofenac was not efficiently adsorbed [105]. Therefore, at least for estrogenic and other pharmaceutically active compounds, one predictor of adsorption density of a particular compound is log K_{ow}. Another set of compounds of interest are antibiotics. Unlike estrogenic and other pharmaceutically active compounds, one of the most important factors in the removal of antibiotics is pH. For trimethoprim, the Toth isotherm describes the adsorption behavior better than the Freundlich isotherm and adsorption capacity appears to increase with decreasing pH [127]. Sorption is dependent upon pH, and at acidic pHs the surface charge of the sorbents and ionization of sorbate help to drive the adsorption process [128]. While activated carbon is a useful adsorbent, adsorption of nalidixic acid onto resin is vastly superior. This is due to the fact that the aromatic ring forms key bonds with neutral and anion-exchange polymers to allow adsorption to occur [129]. Additionally, below the pKa of the nalidixic acid, neutral aromatic polymer matrices are better suited to removing the compound [129]. Therefore, for antibiotics, pH appears to be the dominant variable controlling absorption.

While numerous authors have published papers on the adsorption of phenolic compounds, there is not a wide body of literature available with constants for modeling and predicting the behavior of PCPPs. As a result, the adsorption of phenolic compounds were used as a surrogate for PCPPs. Phenolic compounds are among the most well characterized compounds in the literature. Additionally, there is a large body of literature available that allow for the collection of a broad range of constants with a high degree of certainty that their values are accurate. The values from various studies are shown in Appendix I (see page 117). Numerous types of adsorbents have been examined, but activated carbons are the most common, along with bentonite. Phenolic compounds are well studied and the parameters for Freundlich isotherms can have large variations: Phenol (K_f: 0.008-89.43, n: 0.037-3.84615) [130, 131, 132, 133, 134, 135, 136, 137, 138, 139], 2-Chlorophenol (K_f: 0.566-169.2, n: 0.286-28.57143) [132, 140, 141, 137], 4-Chlorophenol (K_f: 0.03458-101.504, n: 1.873-3.737) [132, 142, 137], Dichlorophenol (K_f: 1.75-220.9557, n: 0.144-3.925) [132, 136, 137], Trichlorophenol (K_f: 2.965-588.7, n: 0.1512-6.821) [132, 143, 136, 137],

Pentachlorophenol (K_f: 14.12-31.33, n: 2.132-3.236) [132], and P-Nitrophenol (K_f: 0.0302-166.5, n: 0.1494-4.235) [141, 142, 136]. This wide degree of variation demonstrates that a single set of values cannot be utilized.

Methods

1. Literature Values and Previous Studies

A comprehensive survey of the literature was conducted to ascertain the concentrations of PCPPs of interest and their treatability. 140 journal articles were compiled with values for influent, effluent, and environmental concentrations (see Table 1). Of these 140 journal articles, 10 were comprehensive review articles that formed the basis of producing the final list of PCPPs. Minimum and maximum values were compiled with measurements being taken within the United States being given preference and non-US data being utilized when US data was not available. Additionally physical and chemical data concerning biodegradiblity, log K_{ow}, and solubility data was calculated in EPISUITES 4.1 when citations were not available in EPISUITES 4.1 [40]. From this data, probability plots were constructed to determine standard deviations for use as parameters for modeling.

Additionally, a second literature search was conducted with respect to Freundlich models for the removal of Phenol by Activated Carbon adsorption. This literature search revealed 45 articles and these values were compiled. All of these papers were selected to have GAC as their adsorbent, although there was some variation on the type of GAC across these papers. In order to compare the values obtained from these papers, the units of K_f were converted to a single set of unified units (see Appendix I, page 115). Finally, Phenol was chosen as a surrogate for the removal of PCPPs, since it is the most studied environmental contaminant, has similar properties to the PCPPs of interest, and represents a compound that readily participates in the adsorption process.

2. Probability Plots, Statistical Analysis, and Distribution Analysis

All distribution fitting was conducted with EasyFitXL Professional 5.5, produced by Mathwave Data Analysis and Simulations (http://www.mathwave.com/en/home.html). This program is able to test the

fit of 55 different probability distributions (see Appendix II, page 120) and provides recommendations on the best fit to utilize the data provided. In order to recommend the best distributions that fit the inputted data, EasyFitXL utilizes three goodness of fit models (Komogorov Smirnov, Anderson Darling, and Chi-Squared). With each distribution, and goodness of fit test, the program determines whether the distribution fits given a significance value (α) of 0.2, 0.1, 0.05, 0.02, and 0.01. In the event that the best distribution fit does not have significance at any of the values, the top distribution is still assumed to be acceptable if it is a visual fit. Finally, all statistical analysis such as mean, standard deviations, and p-values were found with the built in functions specific to the distribution selected. The final output for choosing distributions for each set of data can be found in Appendix III (see page 121).

3. Modeling Exercise

In order to accomplish the modeling portion of the exercise, Matlab R2012a was utilized to construct an algorithm based on Freundlich adsorption (eqn. 2f). The program was created to solve equation 2f, where: C is the equilibrium concentration, C_0 is the initial concentration, D_0 is the carbon dose, 1/n and K_f are constants from the adsorption isotherm graph [116, 117]. The final program is shown in Appendix IV (see page 151). It should be noted that the initial version of this program decoupled n and K_f and generated separate distributions for these variables, but this was not statistically valid. The program was run for the 10%, 50%, and 90 percentiles for the influent concentration to the adsorption process. For each one of these concentrations, 45 different runs were performed corresponding to each paired set of n and K_f values from the literature. These values were also run at one specific carbon dosage and the process was repeated for carbon doses of 0.01, 0.1, 0.2, 0.5, 1, 2, 4, 6, 8, 10 g/L. To plot each data point, the distribution for a certain carbon dose at a specific influent percentile was evaluated in EasyFitXL with the same procedure as described in the previous section. After each distribution was found, the mean and standard deviation for that specific set of runs (n=45), allowed for one data point to be plotted. This

process was then repeated for the next carbon dose at a specific influent concentration. After modeling was completed, these points were then connected to create a relationship between carbon dose and the influent concentration. It should be noted that the original model decoupled K_f and n values and created random distributions for each that were not statistically appropriate. To have any significant results, K_f and n must be coupled together. Finally, probability plots were all constructed with Matlab's built in statistical tool box with the distributions found for each set of points.

4. Competitive Freundlich Isotherm

In order to study the role of competitive effects on adsorption density, a Monte Carlo simulation was conducted for a multicomponent isotherm. The Monte Carlo simulation was conducted in Microsoft Excel® 2010. The simulation utilized 1000 trials and only K_F was varied according to the distribution of literature values. In order to roll the dice for each trial, the random() function in Excel® was utilized to generate a probability between 0 and 1 for the variables of interest. To generate a K_f value, the loginv(p) function was used with the dice roll for each variable in the trial, with the mean and standard deviation for K_f (μ=1.4561, σ=2.673). After the inverse, the closest of the paired n and K_f values were utilized for that particular dice role. For K_f and n, the values for phenol were used as a surrogated for the compounds of interest due to the wide availability of data, and the fact that it is a fairly absorbable compound that is frequently found in industry and medicine. Phenol is also well regulated within the current regulatory scheme and as such provides an excellent model. The means and standard deviations were compiled from a comprehensive literature review for Freundlich constants (see Appendix I, pg.115). Each trial was completed for a different set of competitive phenol concentrations, Ce_{phenol} of 0, 1, 2, 5, 8, 11, 14, and 18 ppb. Equation 3i was solved for each trial for a given Ce_{phenol}, and equilibrium concentrations of PCPPs of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, and 10 ppb. At each relevant concentration of PCPPs, the 1000 trials were averaged to obtain a single adsorption density value for a given equilibrium concentration of Ce_{phenol} and Ce_{PCPP}. The final results were plotted as Adsorption density versus the equilibrium concentration of PCPPs.

5. Results Analysis

The final results were plotted as a percent of the compound that was removed by adsorption. It was assumed that the influent, effluent, and environment inputs contained 45, 44, and 38 compounds respectively. The plotting of results in this fashion allows for trends to be extracted.

Results

Utilizing Freundlich isotherms and accounting for multicomponent systems during Monte Carlo simulation, the results are presented in the sections which follow. The first set of results obtained examined the effect of carbon dose and the underlying distributions behind the n and K_F literature values. These values were crucial to the modeling exercise, since utilizing competitive effects depends on the concentration of the other substrate in solution. For the final set of modeling results, a competitive isotherm was utilized to examine the role of competition on the removal of PCPPs. Therefore, for the competitive isotherms to be calculated, it was necessary to first find the distributions associated with various constants.

Table 9: An example ranking of probability distributions for the individual Freundlich Parameters.

Rank	n	Kf
1	Cauchy	Weibull
2	Log-Logistic	Log-Pearson 3
3	Dagum	Burr
4	Dagum (4p)	Log-Logistic (3p)
5	Kumaraswamy	Dagum
6	Exponential (2p)	Weibull (3p)
7	Weibull	**Lognormal (3p)**
8	Frechet (3p)	Gen. Gamma (4p)
9	Exponential	Lognormal
10	Log-Pearson 3	Pearson 6
11	Fatigue Life (3p)	Burr (4p)
12	Weibull (3p)	Fatigue Life (3P)
13	Gen. Gamma (4p)	Log-Logistic
14	Burr	Frechet(3p)
15	Inv. Gaussian (3p)	Dagum (4p)
16	Burr (4p)	Pareto 2
17	Gen. Extreme Value	Pearson 6 (4p)
18	Pearson 6	Gen. Gamma
19	**Lognromal (3P)**	Gen. Gamma (3p)

1. Distribution Analysis

Freundlich isotherm constants, n and K_F were first determined by distribution fitting in order to successfully be applied to Monte Carlo modeling. The

end result was that a log normal distribution was selected as the best visual fit for each of these (see Table 9). Although this was not the best fit, a log normal was selected to keep the values coupled, so that each followed the same distribution. An Anderson-Darling test for n revealed that at α=0.01 and 0.02 a log normal distribution could not be rejected, while at all α values in the Kolmogorov-Smirnov test, the distribution was rejected. Ultimately for n, a visual inspection of a log normal fit, demonstrated a reasonable fit and in combination with the Anderson-Darling test, allowed for the lognormal distribution to be selected. As for K_f, an Anderson-Darling and Kolmogorov-Smirnov test was performed and revealed that at all significance levels (α=0.01,0.02, 0.05, 0.1, and 0.2) the log normal distribution could not be rejected. Furthermore, the distribution provided a good visual fit to the data. Therefore, the reasonable visual fit and the results of the Anderson-Darling and Kolmogorov-Smirnov tests allowed for a log normal distribution to be selected. The mean and standard deviation of the lognormal distribution for K_f and n were: K_f (μ=1.4561, σ=2.673) and n (μ=0.37267, σ=1.2159).

The average influent concentration was utilized for PCPPs to arrive at a range of values for modeling. The previous results on a distribution analysis were presented in Shown in Figure 14 (page 55). This figure demonstrates that the data follows a log normal distribution reasonably well with a fitted trend line of R^2 = 0.8884. Additionally, Kolmogorov-Smirnov, Anderson-Darling, and Chi-Squared tests were performed to ascertain whether a log-normal distribution was a reasonable fit. For the Anderson-Darling and Kolmogorov-Smirnov tests, revealed that at all significance levels (α=0.01,0.02, 0.05, 0.1, and 0.2) the log normal distribution could not be rejected while for the Chi-Squared test all significance levels except for α=0.2 stated that the log normal distribution could not be rejected. Therefore, while EasyFit XL ranked the lognormal distribution as 17th, the results of the Chi-Squared, Anderson-Darling, and Kolmogorov-Smirnov tests, along with visual fitting allow for the lognormal distribution to be confirmed for the average influent values.

2. Non-Competitive Adsorption

When competitive effects are disregarded, an idealized case is modeled where a single substrate is being adsorbed onto the activated carbon surface without regard to other organic and non-organic compounds that would be present in a WWTP. The results are displayed in Figure 23 and represent the most optimal case for adsorption of PCPPs. Carbon dose will play a crucial role in how much removal occurs of a given single substrate.

Table 10: Summary of Non-Competitive Adsorption results as a function of Carbon Dose

Carbon Dose (g/L)	Initial Concentration (ppb)	Projected PCPP final concentration (ppb)	% Removal
0.1	0.0859	0.0235	72.6%
	1.6242	0.5218	67.9%
	30.6950	13.1954	57.0%
0.2	0.0859	0.0231	73.2%
	1.6242	0.4804	70.4%
	30.6950	11.2601	63.3%
0.5	0.0859	0.0228	73.4%
	1.6242	0.4440	72.7%
	30.6950	9.6441	68.6%
1	0.0859	0.0228	73.5%
	1.6242	0.4312	73.5%
	30.6950	8.8925	71.0%
2	0.0859	0.0227	73.5%
	1.6242	0.4175	74.3%
	30.6950	8.2321	73.2%
4	0.0859	0.0227	73.6%
	1.6242	0.4239	73.9%
	30.6950	7.6527	75.1%
6	0.0859	0.0226	73.7%
	1.6242	0.4133	74.6%
	30.6950	7.4245	75.8%
8	0.0859	0.0226	73.8%
	1.6242	0.4101	74.7%
	30.6950	7.3034	76.2%
10	0.0859	0.0225	73.8%
	1.6242	0.4075	74.9%
	30.6950	7.2219	76.5%

In terms of an activated carbon process, carbon dose is one of the dominant variables that can be controlled by plant operators. This parameter has a large effect at lower doses on removing PCPPs, but eventually the benefit of adding more activated carbon does not have a substantial effect. This asymptote occurs around 2 g/L of activated carbon for the 33rd and 50th percentiles, and at around 4 g/L for the 67th percentiles (see Table 10). The largest response seems to occur between 0.001 to 0.5 g/L of carbon. For removal efficiencies, at 2 g/L PCPPs were 77.6%, 78%, and 78.4% removed for the 33rd, 50th, and 67th percentiles respectively. There was little additional response going to 10 g/L, which resulted in 83.2%, 84.2%, and 85.4% removal for the 33rd, 50th, and 67th percentiles respectively percentiles (see Table 10). While there is a difference between a carbon dosage of 10 g/L and 2 g/L in terms of raw percentages, it should be noted that other factors such as cost may drive operator decisions as to how large of a dose to add. It should also be noted that there is more of a dose response to those PCPPs that were present at concentrations above the average value and it would be expected that as the

equilibrium concentration continues to increase toward the far extreme of the distribution, that the dose response will become more extreme.

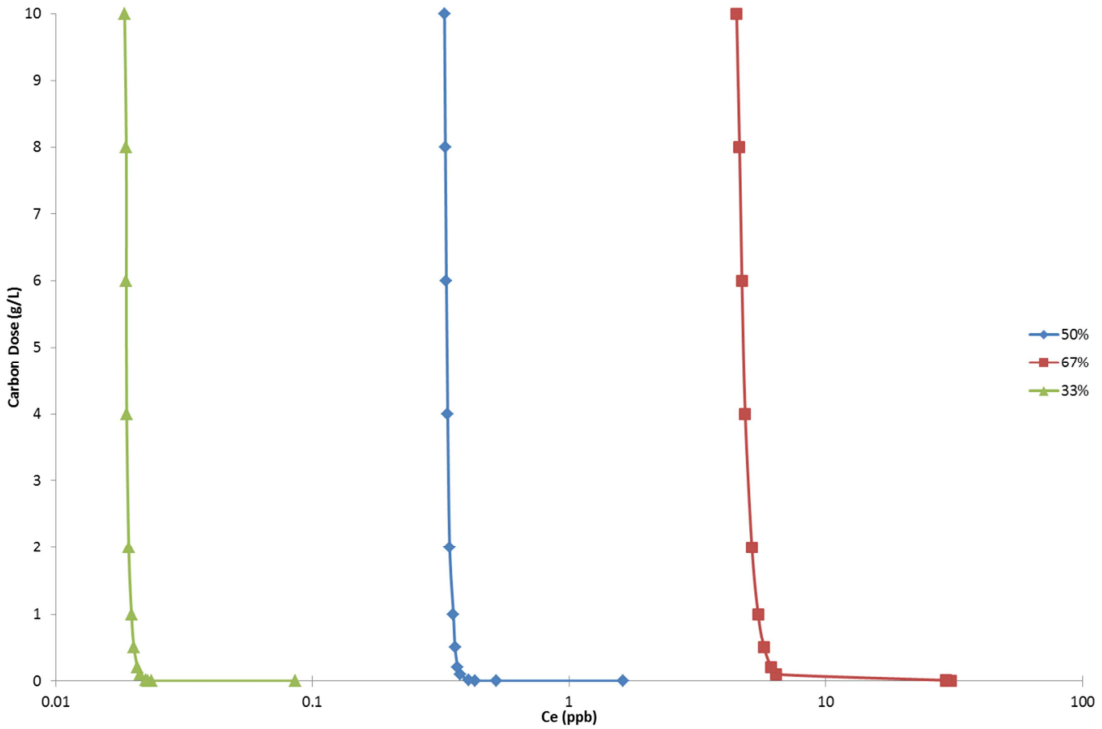


Figure 23: Removal of PCPPs at influent concentrations of the 33rd, 50th, and 66th percentiles (mean ±standard deviation) demonstrates a carbon dose dependent removal, with a high degree of response even at low dosages. Note: the last data point is the initial concentration of an average PCPP, which were 0.086 ppb, 1.624ppb, and 30.695ppb for the 33rd, 50th, and 66th percentiles respectively.

Unfortunately, real world conditions do not involve a single substrate being adsorbed onto activated carbon. Waste streams within a WWTP are complex mixtures of organic, inorganic, and biological materials, necessitating that competition will occur and that this competition will have an inhibitory effect on the lower concentration substances.

3. Competitive Adsorption

When competitive effects are taken into account, a more realistic case is modeled where multiple substrates are being adsorbed onto a single activated carbon surface. This competition would occur due to the other organic and non-organic compounds that would be present in a WWTP. Therefore, the results

that are displayed in Figure 24, represent a more realistic case for determining the adsorption density of PCPPs in the presence of a competitor.

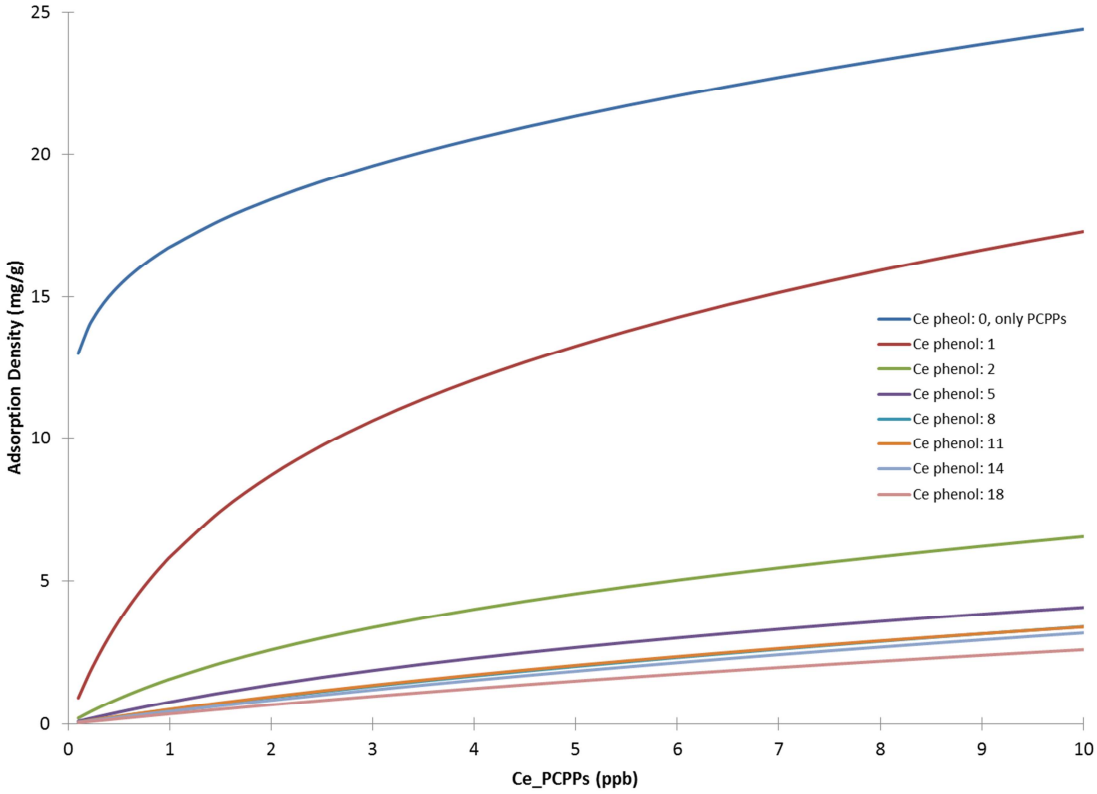


Figure 24: Two component competitive degradation of PCPPs is modeled and demonstrates that as the concentration of the competitive species increases, the adsorption density decreases. The range of PCPPs was 0.1 to 10 ppb and was modeled with equation 3i, using phenol parameters for K_f and n, and phenol as the dominant competitive species.

In terms of an activated carbon process, carbon dose and competitive species concentration are some of the dominant factors that will affect the adsorption density. As competitive species are added to form a multicomponent adsorption process, the species with the highest concentration with dominate the adsorption density if they are adsorbed equally. As the equilibrium concentration of phenol increased from zero, to one, to two, to eighteen ppb, the resulting adsorption density being approximately 18.8, 7.8, 2.4, and 0.75 ppb respectively for PCPPs. It was important to note that the addition of one competitor at one ppb at the average PCPP concentration of 1.6ppb, the decrease in adsorption density was over 50% indicating that isothermal equally competitive sorbates will have a significant impact on how much of a single substrate will be adsorbed. Therefore, this helps to explain some of the literature values where lower concentrations of compounds tend to not undergo adsorption and remain untreated.

Discussion and Conclusions

Adsorption onto activated carbon is not only a function of the carbon dose, but also the concentration and number of chemical substrates that are present within wastewater. Within the WWTP influent, there are thousands of compounds that will be in competition with one another for the sites on the activated carbon surface. As a result, the compounds that are present in the highest concentrations, as long as they allow for favorable surface interactions, will be preferentially adsorbed and will decrease the adsorption density of the lower concentration sorbates, i.e., PCPPs. This implies that the concentration of compounds like PCPPs need to be much higher than currently present in order to become competitive with the dominant species. Therefore, in order for any one given PCPP to be adsorbed, it must either increase in concentration relative to the dominant species, or must have more favorable surface interactions with the activated carbon surface groups to become more competitive. Additionally, the amount of carbon that is added will have an effect on the amount of removal that occurs. While only a monocomponent system was analyzed in this work, it is likely that there would also be a dose response in a competitive situation. As the amount of carbon added to the system increased, there would be more surface area available for adsorption. The result of this would be that there would still be preferential adsorption of the highest concentration compounds, until their concentrations became competitive with the other species. Then there would be increased competition for the remaining spots.

Competitive species in water and wastewater treatment plants will have an effect on whether or not a given species will adsorb onto the activated carbon. With only one competitive species under isothermal conditions, the adsorption density of PCPPs decreased by more than half. This effect of decreasing adsorption density will be compounded by the complex nature of water and wastewater. The net result will be a drastic decrease in adsorption density for lower concentration PCPP compounds, which are not in a position to outcompete other compounds. Typical domestic wastewater influent concentrations are characterized as shown [106]:

COD-430 mg/L,
Alkalinity-200 mg/L,
BOD-190 mg/L,
TSS-210 mg/L,
VSS-160 mg/L,
TKN-40 mg/L,
NH_4-N-25 mg/L,
Phosphorous-7 mg/L.

Given that the average PCPP compound is present in the influent at 0.0016 mg/L, these other compounds that can be adsorbed are present at much higher concentrations in the influent and will most likely be preferentially adsorbed. The only other means of overcoming the difference in concentration would be that the competition coefficients would be substantially more favorable for the PCPPs than for the other major constituents of the wastewater effluent. To accomplish this, the competition coefficient can partially compensate for a large concentration coefficient, but there is a practical limit on how large this coefficient can become. The competition coefficients reported by Sheintuch, state that a coefficient of 10 is usually expected as a maximum [122, 134]. Therefore, it is highly unlikely that PCPPs will be preferentially adsorbed before the other major constituents of wastewater. In the context of WWTP effluent, there will be scenarios where there are more than two substrates competing for the same adsorption site, and depending on the competition coefficients and Freundlich constants that may change over time, the model may underestimate the impact of additional species being present in the water. Therefore, the competition coefficients amongst the sorbates will play a key role in determining how much of a given substance will be adsorbed successfully and if another substance is more preferentially adsorbed, then that will have an impact on the ultimate amount adsorbed of the lower concentration substance.

While activated carbon adsorption has been the focus of this chapter, sludge sorption (adsorption onto the biomass grown on wastewater constituents) has been posited as a removal mechanism for some PCPPs. Sorption can occur via either adsorption or absorption [123]. Adsorption occurs by "hydrophobic interaction of the aliphatic and aromatic groups of a compound with the lipophilic cell membrane of the microorganisms and the fat fractions of the sludge" and absorption occurs by "electrostatic interactions of positively charged groups with the negatively charged surfaces of the microorganisms" [123]. With that said, these sorption processes appear to only apply to PCPPs that are not highly polarized, which for these highly polarized substance sorption onto sludge is essentially negligible [123]. On the other hand, specific interactions have been reported for flurochinolones and tetracyclines [123]. Some authors have observed

sorption for 17-α Estradiol between 10-30% and that the variability can be explain by "sorbent-specific characteristics such as organic carbon content, particle size, pH, salinity, and ion content that varies from plant to plant" [144]. Therefore, some adsorption of certain PCPPs may occur onto the biomass. This helps to explain the removal efficiencies observed in Table 4 (see page 25) and further research must be conducted to determine the extent to which sorption processes occur under wastewater influent conditions with extreme competition for the removal of PCPPs.

Therefore, adsorption by activated carbon may be a useful process for the removal of PCPPs as a tertiary treatment in a WWTP as long as there is a lack of high concentration competitors to impede the process. Future research must address: 1) the isotherm constants for competitive adsorption for PCPPs, 2) the mechanism of removal for activated carbon adsorption of PCPPs in the presence of higher concentration adsorbents, 3) further materials research for novel adsorbents that will be more selective for PCPPs, 4) development of better models to predict the behavior of new pharmaceuticals in adsorption processes, and 5) decreased cost for regeneration of activated carbon to allow for more wide usage. It should be noted however that under normal circumstances, the determination of constants and concentrations is extremely difficult due to the difficulty and expense in measuring these compounds. Therefore, improved instrumentation will become necessary to allow for proper quantification of many of the research goals enumerated above.

CHAPTER 4

ALTERNATIVE TREATMENT METHODOLOGY, COST ANALYSIS, AND CONCLUSIONS

Introduction

1. Reverse Osmosis

Reverse Osmosis (RO) is a commonly applied process for the removal of undesired solutes and has been applied for the production of fresh water from seawater. Like microfiltration, ultrafiltration, and nanofiltration, RO is characterized by the pore size that dictates its rejection of solutes [41, 145]. As the pore size decreases, the membrane becomes increasingly more selective and allows fewer and fewer solutes to pass through the membrane. The primary function of this technology has been its application of water desalting [41, 145]. The driving force for the RO process is pressure, and there is resistance due to the buildup of ionic compounds in the rejection stream [41, 145]. As a result, osmosis is partially a passive process, and equilibrium occurs when the osmotic pressure prevents the passage of a solvent across the membrane [41, 145]. Therefore, if more solute is to be driven across the membrane, then a pressure gradient will be needed. Osmosis, by definition, is the diffusion of a solvent from one side of a semi-permeable membrane to a more concentrated solute side in order to equalize the concentration of the two sides [41, 145]. There are three different osmotic pressure situations that can exist. The first circumstance is a hypotonic situation, which donates water across a membrane to dilute the hypertonic side, causing the concentration of hypotonic side to increase [41, 145]. On the other hand, the hypertonic side causes water to move across a membrane to dilute the hypertonic side (higher concentration of solute) [41, 145]. Finally, if there are equal concentrations on both sides, the sides are balanced and are referred to as isotonic [41, 145]. These traditional definitions are for osmosis processes, and RO operates in reverse. The reject stream contains all of the concentration, while what crosses the membrane to the other side is pure water [41, 145]. Therefore, to drive the water from the concentrated to the diluted side a pressure gradient must be utilized to drive water against its natural gradient.

Depending on the application of RO, different materials are better suited to certain conditions. The first category of membranes are seawater membranes, which operate with water that contains salt on a 3-5% by weight basis and requires a pressure differential of 800-1000 psi to operate [41, 145]. These membranes tend to be utilized for desalinization of seawater for generation of freshwater. The second category of membranes are brackish water membranes, which operate with water that contains salt concentrations of 2000 to 10,000 ppm and requires less pressure at 200-400 psi [41, 145]. The drop in operating pressure as compared to seawater, is due to the drop in osmotic pressure that must be overcome in order to drive clean water across the membrane. Finally, low-pressure nanofiltration operates at 100-150 psi at salt concentrations of 200-500 ppm [41, 145]. Therefore, as the amount of ionic substances decrease in concentration, the osmotic pressure decreases, and the necessary pressure to create clean water decreases, thereby decreasing overall energy requirements. Membranes can be composed of different materials, and these materials have different efficiencies associated with them. In order of development and efficiency, the common materials are: 1) Cellulose Acetate, 2) Polymers, and 3) Composites [41, 145]. Therefore, a choice of membrane is usually a tradeoff between flux and rejection, so as the flux increases, the pore size decreases and as does the rejection of solutes.

RO treatment has numerous pros and cons associated with its usage that must be considered to determine whether or not to apply the technology. RO advantages include: generation of high quality water output; effective removal of organic compounds, salts, natural minerals, and micropollutants; removal of 95-99% of TDS; removal of chemicals such as asbestos, arsenic, some pesticides, fluoride, lead, mercury, and radium; low installation cost; and commercially available membrane modules with low installation time [41, 145, 116, 146, 147, 148, 149]. RO disadvantages include: increased membrane fouling and operating costs, high quality inflow requirements (lots of a pretreatment), high maintenance costs and membranes costs, dangerous molecules are still able to snake through the membrane, since rejection is not 100%, removes healthy minerals in water that have to be added back in (trace elements key in biology), and limited treatment per square foot of membrane compared to alternatives and slow process [41, 145, 116, 146, 148, 149]. Therefore, depending on the application and value of the water being produced, the advantages can outweigh the disadvantages, allowing for RO to be effectively utilized.

A comprehensive literature review demonstrates that RO generally removes many biologically recalcitrant PCPPs. RO literature review can be found in Table 4 on page 25.

2. Filtration

Filtration has many different applications and is principally characterized by pore size and operating pressures needed for filtration to occur. Ultrafiltration, microfiltration, and nanofiltration are not fundamentally different and are differentiated by the size of the molecule that is rejected [116, 150]. Microfiltration (MF) has pore sizes between 0.03-15µm; nanofiltration (NF) has pore sizes between 0.0005-0.02µm; and ultrafiltration (UF) has pore sizes between 0.002-10µm [116, 150]. These membranes work by discriminating on the basis of molecule size, shape, and flexibility, and the filtration process is powered by pressure (except microfiltration does not necessarily have to be) [116, 150]. Unlike RO, which requires high pressures to overcome the osmotic pressure, UF, NF, and MF are not affected by osmotic pressure, and these membranes operate at low-pressure differences, 5-100 psi [116, 150]. Typical operating parameters, which allow these membranes to be operated economically, are a pressure difference of 10-50 psi and a water flux of 20-50 $\frac{gal}{ft^2 day}$ [116, 150]. Overall, UF, NF, and MF are currently used commonly due to their lower cost compared to an RO system, but they do not remove nearly as many compounds as a RO system due to larger pore sizes.

Membrane filtration treatment has numerous pros and cons associated with its usage that must be considered to determine whether or not to apply the technology. The advantages of utilizing filtration over other technologies are its proven track record in industrial, chemical, and biomedical applications, and it is cost effective when the value of the recovered product is greater than the process cost [41, 116, 145]. On the other hand, filtration has disadvantages associated with

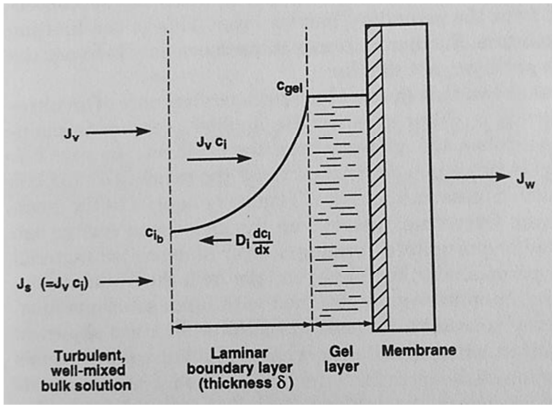


Figure 25: A gel layer is formed where rejected solutes need to back diffuse to the main stream. Reproduced from: [41].

it including: become increasingly energy intensive as pore size decreases (i.e. microfiltration->ultrafitlration-> nanofiltration), high incidence of membrane fowling and gel layer formation like RO, prohibitive cost, and decreased membrane fluxes with decreasing pore size, thereby decreasing the potential volume that can be treated at one given time [41, 116, 145]. The formation of a gel layer formation is a natural part of the membrane operation process and is depicted in Figure 25. As the membrane runs and pressure is applied to the membrane, a gel layer will form thereby decreasing performance [41, 116, 145]. This gel layer will become consolidated with an increasing applied pressure gradient, thereby creating an inverse relationship between pressure and the formation of a gel layer [41, 116, 145]. The gel layer is where rejected solute collect and must back diffuse into the mainstream. As a result, resistance will form to a purified solution crossing the membrane [41, 116, 145]. At high-enough pressures, this gel resistance controls the flux across the membrane, and membrane resistance begins to play a smaller role [41, 116, 145]. Therefore, careful attention must be paid when selecting an operating pressure for these membranes, since the gel layer can have major effects on the flux across the membrane.

A comprehensive literature review demonstrates that UF, NF, and MF are generally effective at removing many biologically recalcitrant PCPPs. UF, NF, and MF literature reviews can be found in Table 4 on page 25.

3. Advanced Oxidation

Advanced Oxidation Processes (AOPs) are utilized to (fully or partially) degrade biologically recalcitrant compounds. In general, AOPs generate a hydroxyl radical to oxidize compounds [106, 151]. Hydroxyl radicals can be produced from Ozone or Ozone/UV process as well as hydrogen peroxide/ozone or hydrogen peroxide/UV processes [106, 151]. All of these processes produce hydroxyl radicals, which have the ability to attack organic compounds of interest. There are other compounds that can be utilized to oxidize compounds (see in Table

Table 11: Oxidation potential of various compounds

Oxidizer	Electrochemical oxidation potential (EOP), Volts	EOP compared to chlorine
F^-	3.06	2.25
OH^-	2.80	2.05
O_1^{-2}	2.42	1.78
O_3	2.08	1.52
H_2O_2	1.78	1.30
MnO_4^-	1.68	1.24
ClO^-	1.49	1.10
Cl^-	1.36	1.00
ClO_2	1.27	0.93
O_2	1.23	0.90

Reproduced from: Metcalf and Eddy, Tchobanoglous, G., Burton , F. L. & Stensel, H. D., 2002. *Wastewater Engineering: Treatment and Reuse*. New York: McGraw-Hill Higher Education.

Added: Crittenden, J. C. et al., 2005. *Water Treatment - Principles and Design*. 2nd ed. Hoboken: John Wiley and Sons Inc..

11), but they have similar mechanisms of actions to one another [106, 151]. When conventional oxidants, such as ozone, oxygen, and chlorine, fail to remove organic compounds, then the use of AOPs may be considered [106, 151]. If a hydroxyl radical attacks organic matter, it will result in H_2O, CO_2, and salts if taken to completion [106, 151]. As a compound is degraded, there are various amounts of completion that occur: 1) Primary, where there are structural change in parent compound; 2) Acceptable, where there are structural changes reducing toxicity; 3) Ultimate, which converts organic carbon to CO_2; and 4) Unacceptable, where the structural changes increase toxicity [106, 151]. If positive reactions (1-3) occur, then hydroxyl radicals will interact with the organic compound and will begin to degrade the compound. In order for this to occur, there must be a production of hydroxyl radicals, or an equivalent molecule. The oxidizer chemistry with key reactions is outlined below [106, 151, 152]:

- Ozone/Hydrogen Peroxide (H_2O_2 accelerates OH^- production)
  - $H_2O_2 + 2O_3 \rightarrow HO^{\cdot} + HO^{\cdot} + 3O_2$
  - $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$
    $O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$
- $UV\ and\ TiO_2$
  - Irradiation with UV yields: $TiO_2 + UV \rightarrow e^- + h$, h is a valance band hole
  - Holes can then form hydroxide radicals by interacting with water or hydroxide:
    $h + H_2O \rightarrow OH^{\cdot} + H^+$
    $h + OH^- \rightarrow OH^{\cdot}$
    $e^- + O_2 \rightarrow O_2^{\cdot}$
    $2O_2^{\cdot -} + 2H_2O \rightarrow H_2O_2 + 2OH^- + O_2$
    $e^- + H_2O_2 \rightarrow OH^- + OH^{\cdot}$
- Hydrogen Peroxide/UV
  - $H_2O_2 + UV\ (\lambda \cong 200 - 280nm) \rightarrow HO^{\cdot} + HO^{\cdot}$
- Chlorine Dioxide
  - Oxidation reduction: $ClO_2 + e^- \rightarrow ClO_2^-$
  - Other key half reactions
    - $ClO_2^- + 2H_2O + 4e^- \leftrightarrow Cl^- + 4OH^-$
    - $ClO_3^- + H_2O + 2e^- \leftrightarrow ClO_2^- + 2OH^-$
    - $ClO_3^- + 2H^+ + e^- \leftrightarrow ClO_2 + H_2Oa$
- Potassium Permanganate
  - $MnO_4^- + 4H^+ + 3e^- \leftrightarrow MnO_2(s) + 4OH^-$
  - Other key half reactions
    - $MnO_4^- + 4H^+ \leftrightarrow MnO_2(s) + 2H_2O$
    - $MnO_4^- + 8H^+ \leftrightarrow Mn^{2+} + 4H_2O$

Many of the starter substances above produce hydroxyl radicals (with the exception of potassium permanganate), but each of these substances can then interact by a hydroxyl-like attack to lead to ultimate degradation.

The mechanism by which compounds are degraded is oxidation, of which, there are four primary means by which hydroxyl attack can occur. Hydroxyl radicals are used to oxidize trace amounts of refractory organic molecules and are not used for disinfection due to their short half-life [106]. The first mechanism of attack is radical addition, which is characterized by the chemical reaction: $R + HO^{\cdot} \rightarrow ROH$ [106]. The second mechanism of attack is hydrogen abstraction, which is characterized by the chemical

reaction: $R + HO^{\cdot} \rightarrow R^{\cdot} + H_2O$ [106]. The third mechanism of attack is electron transfer, which is characterized by the chemical reaction: $R^n + HO^{\cdot} \rightarrow R^{n-1} + OH^-$ [106]. The final mechanism of attack is radical combination, which is characterized by the chemical reaction: $HO^{\cdot} + HO^{\cdot} \rightarrow H_2O_2$ [106]. Each of these mechanisms has potential byproducts of reactions of aldehydes and carboxylic acids, as intermediate products of the degradation of an organic pollutant [106]. As a result, these intermediates can present new pollutants that must be remediated. Therefore, the attack of hydroxyl radicals can occur in multiple ways.

Advanced oxidation has numerous pros and cons associated with its usage that must be considered to determine whether or not to apply the technology. The most prominent advantage of advanced oxidation over alternative technologies is that oxidation is a destruction process. Thus, if taken to completion, there is only H_2O, CO_2, and salts [106, 151, 152, 153]. Additionally, AOPs are more effective than conventional oxidants, due to the high oxidation potential of hydroxyl ions, and AOPs effectively remove many recalcitrant organic compounds [106, 151, 152, 153]. On the other hand, AOPs have numerous disadvantages including: carbonate and bicarbonate in some wastewaters can neutralize the hydroxyl radical produced by AOPs; natural organic matter and reduced metal ions interact with hydroxyl radicals, and kill the reaction; and AOPs are sensitive to pH, suspended materials, residual TOC [106, 151, 152, 153]. Furthermore, the chemicals and equipment needed for AOPs tend to be expensive, and generally there are increased maintenance costs over traditional oxidation with chlorine or ozone [106, 151, 152, 153]. Finally, if a UV process is added, turbidity can affect the effectiveness of the radiation to produce hydroxyl radicals. Therefore, in the proper application, oxidation can be a useful method for complete removal of recalcitrant compounds.

A comprehensive literature review demonstrates that AOPs are generally effective at removing many biologically recalcitrant PCPPs. A literature review can be found in Table 3, on page 23.

4. Ozonation

Ozone is a highly reactive molecule that in the lower stratosphere serves to block UVB light from the sun, but its properties as an oxidant are extremely useful for the treatment of various molecules. Ozone, O_3, is a highly unstable gas that can be utilized to oxidize molecules, and it works by rupturing an organism's cell wall [106, 154]. This mechanism of cell wall rupture is extremely useful in drinking water

disinfection and provides an excellent alternative to chlorine disinfection. Ozone is produced in the atmosphere by UV light and lightening during a thunder storm [106, 154]. Its properties are quite distinct and include, a blue color at 25°C, distinct odor, explosive quality when above 20% by weight in air, solubility governed by Henry's Law (1940-5980 atm/mole [0-30°C]), and greater stability in air than water, but short half-life [106, 154]. Ozone has four distinct decomposition reactions that govern its behavior: 1) $O_3 + H_2O \rightarrow HO_3^+ + OH^-$, 2) $HO_3^+ + OH^- \rightarrow 2HO_2$, 3) $O_3 + HO_2 \rightarrow HO + 2O_2$, and 4) $HO + HO_2 \rightarrow H_2O + O_2$ [106, 154]. Therefore, in order for these reactions to occur and degrade organic compounds, ozone must be successfully generated.

Ozone generation is a multistep process and can occur by various different processes. These generators can either work by cold electrical discharge or UV light, where UV lamps emitting 185nm light split oxygen gas into O^-, which binds to O_2 to stabilize, forming O_3 [106]. The UV process is a substantially less-energy intensive process compared to cold electrical discharge, where this process mimics the atmospheric lightening that is responsible for generating natural ozone in the environment. Due to its short half-life, ozone must be generated onsite, and it can present a health hazard to workers [106]. Air or pure oxygen can be utilized as an input for the generation of ozone and will result in different amounts of ozone produced. First, air that has been dried can produce 1-3% ozone by weight or the air can be enriched with oxygen resulting in a higher yield of ozone [106]. Second, pure oxygen can be utilized and will produce 3-10% ozone by weight, making it an ideal source for producing ozone and allowing for more economical treatment [106]. Therefore, the production of ozone, while expensive, can be accomplished with relatively low cost inputs.

Ozone has numerous pros and cons associated with its usage that must be considered to determine whether or not to apply the technology. As mentioned above, ozone can be utilized to generate hydroxyl radicals, but it can also be an excellent oxidant on its own. Ozone has numerous advantages of its usage including: effective odor elimination, decreased oxygen demand, since one of the decomposition reactions produces oxygen; thereby increasing dissolved oxygen, removal of the bulk of colors, phenolic, and cyanide compounds, and requires a short contact time, 10-30 minutes, for degradation [106, 155, 156, 157, 158]. Furthermore, unlike chlorine, ozone does not form chlorinated disinfection byproducts, non-brominated disinfection byproducts can be removed with biological active filter or carbon column, and

ozone intermediates form are usually short lived [106, 155, 156, 157, 158]. It is crucial that these products can be relatively easily removed, since chlorinated disinfection products are quite resilient and as a result, can be expensive to remove [106, 155, 156, 157, 158]. On the other hand, ozone has numerous disadvantages including: high capital and treatment costs, high demand for electric power for ozone generation, high corrosiveness (steel, iron, and neoprene), high transfer efficiency (>90%) is required for ozone, in order for it to be economical, and high hazard potential from off-gas presents a worker hazard and must be destroyed [106, 155, 156, 157, 158]. Moreover, ozone treatment produces numerous undesirable byproducts including Formaldehyde, Acetaldehyde, Glyoxal, Methyl glyoxal, Acetic acid, Formic acid, Oxalic acid, Succinic acid, Pyruvic acids, Bromate ion, Bromoform, Brominated acetic acids, Bromopicrin, Brominated Acetonitriles, Cyanogen bromide, and hydrogen peroxide [106, 155, 156, 157, 158]. Some of these byproducts are desirable such as hydrogen peroxide, which can serve as an additional oxidant and can help to drive reactions to their completion. Therefore, ozone can be an excellent tertiary treatment for removing difficult compounds.

Improving on traditional ozone treatment methods is the addition of UV light, which improves overall treatment of wastes and allows for enhanced efficiency in the treatment of organic compounds. Combining UV with ozone allows for the advantages of both compounds to be utilized with ozone as a chemical oxidant, and UV radiation able to damage proteins, DNA, and RNA [106, 159]. This combination allows for chemicals to be treated that might otherwise be resistant to conventional ozone treatment. UV radiation can break many covalent bonds including those in PCBs, dioxins, polyaromatic compounds, and BTEX, where ozone oxidation fails to oxidize those compounds [106, 159]. UV radiation has a synergistic effect on the chemical oxidation effects of ozone, and the mechanism is unknown, but further efficiency can be gained by treating with a peroxide module [106, 159]. Few of these systems have been implemented, but they

Table 12: Pros and Cons of adding UV to Ozone Treatment

Advantages	Disadvantages
Low footprint to add UV modules	Pretreatment is often required to remove TDS
No residual toxicity from UV	High capital and treatment costs
UV effectively destroys resistant organics (i.e. NMDA)	UV and Ozone have inherent risks that must be managed
Destructive process that has a larger effect traditionally recalcitrant compounds	High turbidity, solid particles, and heavy metal ions reduce treatment efficacy
Cost of combined system are less than operating UV or ozone individually	

Source: [106].

have shown great promise in research settings and in some commercial settings. The pros and cons of the addition of UV are shown in Table 12.

A comprehensive literature review demonstrates that Ozone is generally effective at removing many biologically recalcitrant PCPPs. A literature review can be found on Table 3, on page 23.

5. Wet air oxidation

Wet Air Oxidation (WAO) is used in high organic content wastewater, and, particularly for toxic or for refractory organic (non-biodegradable) wastewater. WAO operates at 125-320°C and 0.5-20 MPa, where increased temperature and pressure allows for increased oxygen solubility in water and the increased pressure keeps water in liquid form [152, 160]. By utilizing high temperature and pressure, oxidation of organic contaminants is more complete and has the added benefit of little waste product as long as organic material is present to oxidize [152, 160]. If there is inorganic material present, these compounds will be mostly left in solution [152, 160]. WAO results in carbon oxidized to CO_2, nitrogen oxidized to NH_3, and sulfur and halogens converted to inorganic halides and sulfides [152, 160]. The degree of oxidation is a function of temperature, oxygen partial pressure, and reaction rates of pollutants in the waste stream [152, 160]. As a result, there are many operating parameters that can be controlled or optimized to ensure proper degradation of organic compounds.

Currently, there is only one commercially available WAO processes, the Zimpro® process. By 1996, 200 units were installed, with greater than 50% of these utilized for sludge treatment [161, 162]. Sludge contains high amounts of organic waste that is not amenable to conventional treatment methods and usually is treated by incineration or landfill disposal [161, 162]. The alternative to this is the Zimpro® process, where the main reactor tends to be a vertical bubble with or without internal baffling, which operates under the following parameters: 1) operating temperatures tend to be 150-320°C, 2) operating pressure is variable and used to control water evaporation, and 3) optimal retention time of 1 hour, but ranges between 20 minutes and 4 hours [161, 162]. One limitation of utilizing this column design is non-

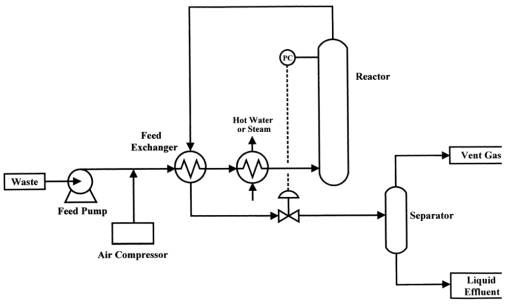


Figure 26: Process schematic of the Zimpro® process. Source: [161].

uniform mixing and residence time, resulting in non-uniform treatment [161, 162]. Therefore, the treatment stream must be examined after treatment to ensure that the degree of treatment achieved is adequate, and if not, further treatment within the reactor maybe necessary. The process diagram for the Zimpro® process is shown in Figure 26. The process is relatively simple and requires an air compressor, heat exchanger, reactor (where oxidation occurs and an exothermic oxidation reaction occurs), feed exchanger, and pressure control valve [161, 162]. The separator is crucial where the effluent is separated into vapor (vented) and liquid effluent, sent for traditional biological treatment as needed [161, 162]. Therefore, the process has two different outputs, each of which can be a highly oxidized waste stream that is substantially less toxic than the original influent. This process is owned by Siemens® Water and has been thoroughly tested and implemented around the world despite some of the disadvantages of this technology.

Wet Air Oxidation has numerous pros and cons associated with its usage that must be considered to determine whether or not to apply the technology. Some advantages of this technology include, a variety of compounds can be treated simultaneously, an effective pre-treatment for high concentration wastewater resulting in biodegradable organics, a potentially large elimination in toxicity and reactivity and COD, and an ability to recycle and/or recover process liquor [161, 162, 163, 164]. Moreover, unlike incineration, the wastes are destroyed in the liquid phase and do not have to be dried out first, which is an extremely energy intensive process [161, 162, 163, 164]. In terms of COD, which can be used to help measure how much energy maybe required to make a process sustainable, WAO requires greater than 20,000 mg/L to be sustainable, whereas incineration requires substantially more at CODs greater than 300,000-400,000 mg/L [161, 162, 163, 164]. Additionally, the WAO process does not produce NOXs and does not contribute significantly to air pollution like incineration does [161, 162, 163, 164]. Therefore, WAO has many advantages over incineration as a treatment method, but it also has many drawbacks. These disadvantages include, high capital costs, waste must be in the liquid phase (excludes solid wastes unless they are dissolvable), treatment is limited to oxidizable wastewater with organic and inorganic compounds (will not work on PCBs for example), and there are safety implications from operating at high temperature and pressure [161, 162, 163, 164]. Therefore, depending on the content of the waste and the air quality requirements, WAO may provide an excellent treatment option.

While WAO has many positives, there are wastes that are not treated easily with WAO and instead are better suited to Supercritical Water Oxidation (SCWO) [152, 165]. Unlike WAO, SCWO operates under supercritical conditions, which occur above 374°C and 22.3 MPa [152, 165]. The supercritical condition allows for a more rapid oxidation over WAO [152, 165]. The removal rate is a temperature dependent process, so for example, at 400-450°C, 99-99.9% conversion in 5 minutes, whereas at 600-650°C, 99.9999% conversion in less than 1 minute [152, 165]. Therefore, depending on how much energy will be invested to raising the temperature in the reactor, will dictate the rates of oxidation reaction within water. Water provides an excellent medium for oxidation since it can dissolve both organic compounds and gases, and the peak efficiency for SCWO is when organics are 1-20% of the waste stream by weight [152, 165]. SCWO works by injecting supercritical wastewater into a reactor and then adding O_2, which results in oxidation of the organics until essentially none remains [152, 165]. Typical wastewaters that are treated with SCWO are pesticide waste, petrochemical processing waste, cyanide containing metal finishing wastes, spent caustic wastewaters, and organic chemical production wastewater [152, 165]. Therefore, as a treatment method for hard-to-treat wastes, SCWO carries the exact same advantages of WAO, and does not contribute to SOX and NOX emissions [152, 165]. These are highly favorable characteristics for the removal of difficult to treat organic wastes, but there are drawbacks to the usage of this technology. The primary drawback of SCWO is corrosion, which is a large problem that must be considered in weighing whether to build a plant or not [152, 165]. Few plants have been built and implemented due to this corrosion issue, and as a result, SCWO remains a virtually untested industrial process.

A comprehensive literature review demonstrates that SCWO is generally effective at removing many biologically recalcitrant PCPPs. A literature review can be found in Table 3, on page 23.

6. Plasma Arc Waste Disposal

Plasma Arc waste disposal is an extremely effective method for reducing all types of waste to basic components and energy. Pyrolysis, which is the underlying mechanism of Plasma Arc waste disposal, occurs in an oxygen-depleted environment and unlike combustion that is exothermic; it is an endothermic process requiring the heat input of hot plasma [166]. Hot plasma is formed by ionized gas in a

strong electrical arc with a power of 2-20 MW producing 2000-6000°C plasma [167]. The plasma is formed by a plasma torch, which is two electrodes, with a carrier gas in between them, which then transfers energy to waste [166]. When waste comes in contact with the plasma, inorganic compounds are melted to form non-toxic dross while the organic components are dissociated into simpler gases of H_2, CO, and CO_2 [167, 166]. The simpler gases, H_2 and CO, form syngas after reaction with water and oxygen, which after purification can be used to generate heat and run a turbine for electrical energy generation [167, 166]. Also, metals can be recovered from the dissociation process and resold, helping to offset cost, while the remaining dross can be used as a construction additive [167]. The dross is essentially vitrified by the process and is non-leachable making it exceptionally useful for hazardous waste that may not be completely destroyed in the process or elements that are toxic in the environment [166]. Therefore, this process is very attractive in situations where lots of waste is generated, metal recovery is attractive, or where environmental concerns over placing materials in a land fill become paramount. This technology has been implemented on smaller scale in the US at Hurlburt Air Force Base in Florida, processing about 10 tons/day and in Arlington, Oregon by InEnTec processing 25 tons/day as a test system [168]. The largest operating systems abroad are found in Utashinai, Japan, which utilizes a 150 tons/day, and a plant just opened last summer in Morcenx, France is processing industrial waste and wood chips [168]. These plants pale in comparison to the planned GeoPlasma facility in St. Lucie County, which would have burned 600 tons/day and produced approximately 220 MW for the grid, but the downturn in the economy, crippled this project [169]. Finally, loans issued for Fulcrum BioEnergy to build a 400 ton/day plant outside Reno, NV to open in 2014, which will stand as the largest plant to date [168]. As more plants are built and more hours are successfully logged, it is clear that the technology has great potential and that financing will be the largest hurdle to successful implementation.

The Plasma Arc waste disposal process is a relatively simple system with four main components. First, the waste feeder, the design of which varies depending on the waste being fed into the system, but typically there is a sealed portion that is pushing the waste into the reactor [166, 170]. Second, is the process chamber or reactor where both AC joule-heating zone and DC arc plasma zone are utilized [166, 170]. The DC plasma arc is created with a potential difference across the electrodes with one being positive and the other being negative, while AC potential is applied directly to glass [167]. By constantly

applying current to the glass, it becomes possible to separate out the components. There are then two mass streams out of the reactor, a solid and a syngas stream. Third, the process gas cleaning is where Syngas is taken from the reactor through a heat recovery steam generator, where steam is then used to drive a turbine [166, 170]. At the same time, as the steam goes to a turn, the syngas goes through a series of filters (three stages: 1) hot particulate removal, 2) wet scrubber removes additional particulates and acid gases, and 3) carbon filter to remove trace elements) to a boiler to produce additional steam to drive a turbine [166, 170]. From the turbine, electrical energy is generated to help power the plant and any remaining energy can be sent to the grid [166, 170]. Finally, the solid mass stream exiting the reactor is where glass and metal recovery occurs. Separate streams are formed for the glass products and metals, which can then be recovered and either sold or used as a construction aggregate [166, 170].

Plasma Arc waste disposal has numerous pros and cons associated with its usage that must be considered to determine whether or not to apply the technology. Plasma Arc waste disposal has many advantages over traditional incineration plants: the quick cooling of produced syngas prevents the formation of dioxins and furans, which are normally a combustion byproduct of incineration; no toxic ash-like incineration to dispose of; <50% of NOX and 5% of SOX and Mercury emissions compared to traditional incinerator; and 300:1 volume reduction as compared to 5:1 for incineration due to ash production [168, 167]. Also, this technology allows for the destruction of hazardous, municipal, medical, and ash wastes including being able to destroy electronics waste, which has no treatment method currently [168, 167]. Additional benefits of Plasma Arc waste disposal include, the filtered Syngas that is produced is as clean as natural gas; clean energy is produced by the process; burning of municipal waste decreases landfill requirements; and the stripping process produces HCl and $NaHSO_4$, which can be resold for industrial purposes [168, 167]. Many of the drawbacks associated with Plasma Arc waste disposal are economically based: high cost since there is a reliance on electrical power and huge upfront capital cost and a lack of willingness to finance these projects (analogous to the capital needed for building a nuclear plant) [168]. Additionally, many critics of this technology point to a perceived lack of reliability [168]. Furthermore, there are concerns about syngas release, which could affect climate change, have public health implications, and potential failure of the liners creating a safety issue.

Methods - Cost Analysis

A cost analysis of potential treatment methods for PCPPs was conducted to ascertain, which of the many technological approaches would be the most cost effective. Modeling was undertaken in Excel® 2010. In order to conduct the modeling, two primary sources of data were utilized including acquiring cost information from the manufacturers when it was available and in the absence of available data, a comprehensive literature review was conducted. For the literature review, two or more sources were utilized to generate high, low, and average costs in order to generate a viable range of values for the modeling exercise.

In order to compare the costs of various treatment methods, cost curves must be constructed for each of the methods for removing PCPPs from wastewater effluents. For this analysis, the treatment methods considered include, filtration (NF and µF), RO, UV, GAC, biological processes, chemical oxidation, ozone, Wet Air Oxidation, and plasma arc waste disposal. The range of flow rates considered include, 10 MGD, 50 MGD, 75 MGD, and 100 MGD to 1.6 BGD of wastewater. These values were selected to represent a range of treatment plant sizes, as well as to reflect the 90% waste volume reduction that would occur as a result of the RO process. The upper range of values is important for processes, like RO, that potentially must treat the entire volume of waste from a WWTP. Three different scenarios were considered for each of the treatment systems, low, average, and high cost scenarios. It was assumed that an interest rate of 10% was applied to any capital costs that had to be finance by loans within calculations of the total cost per unit of treatment. Total costs were assumed to include operations, capital, and maintenance costs when available. Finally, graphs of cost curves were plotted for each of the resulting scenarios with bands to demonstrate the range of potential costs.

Results

A rudimentary cost analysis was performed to compare RO, GAC, Biological, and WAO treatments. The results are shown in Figures 27-29. These results demonstrate that ozone treatment is consistently one of the most expensive treatment options for large volumes of wastewater, whereas conventional biological treatment has been the most cost effective. These results do not include Plasma

Arc Waste Disposal, which is considered separately and has a cost that ranges between $60-$86 per ton of treated municipal solid waste (MSW). These costs must then be applied to the mass content of the wastewater flow in order to determine how much operations would cost. Utilizing this back-of-the-envelope method for calculating costs, a set of cost estimates can be obtained for Plasma Arc Waste Disposal and is presented in Table 13. The costs estimates that were obtained provide a wide range of values and are highly dependent on the water content of the waste. This water content can have the effect of adding 1000 times the cost to the treatment of the wastewater treatment stream.

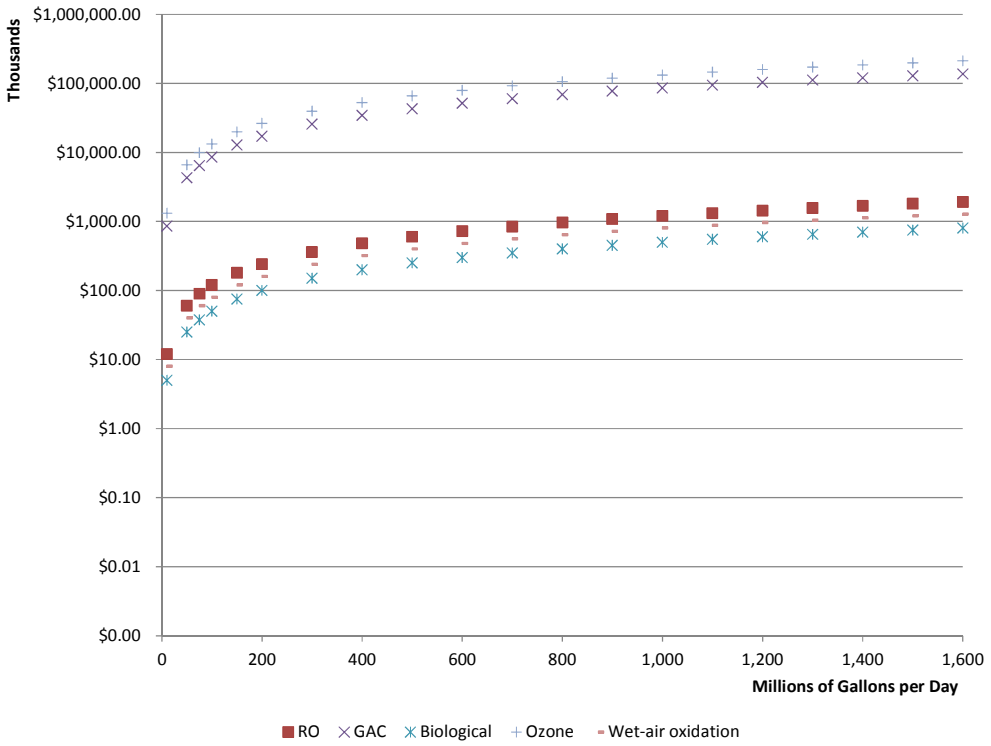


Figure 27: Lowest projected total costs associated with various treatment methods on a daily basis. NOTE: these estimates allow for relative comparisons to be made. Sources: [41, 152, 171, 172].

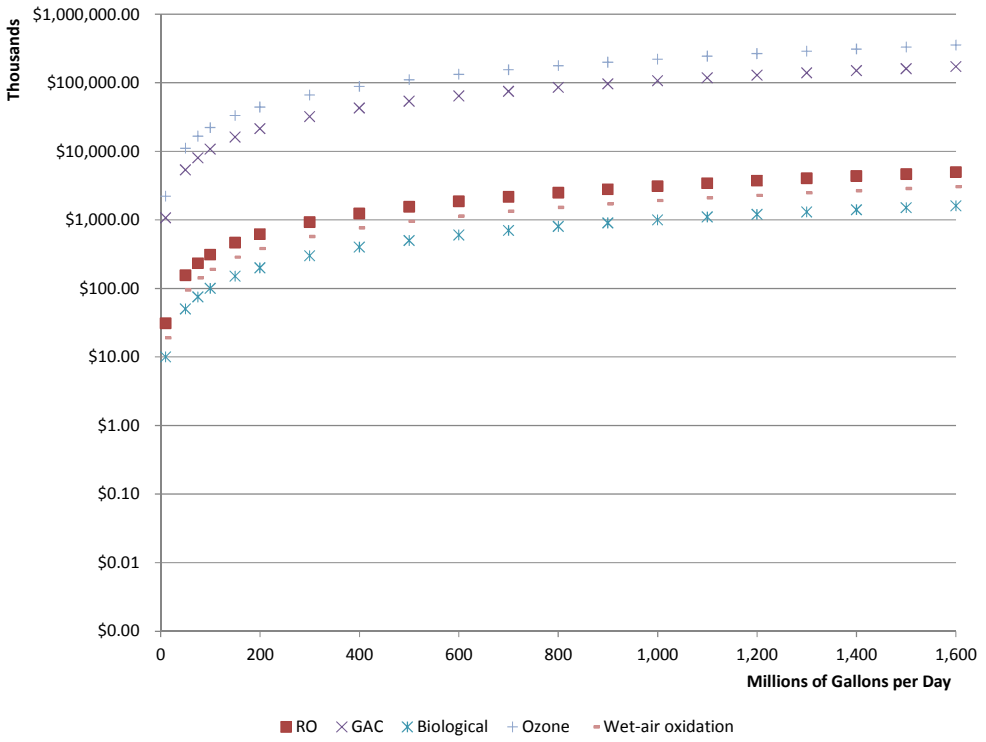


Figure 28: Average projected total costs associated with various treatment methods on a daily basis. NOTE: these estimates allow for relative comparisons to be made. Sources: [41, 152, 171, 172].

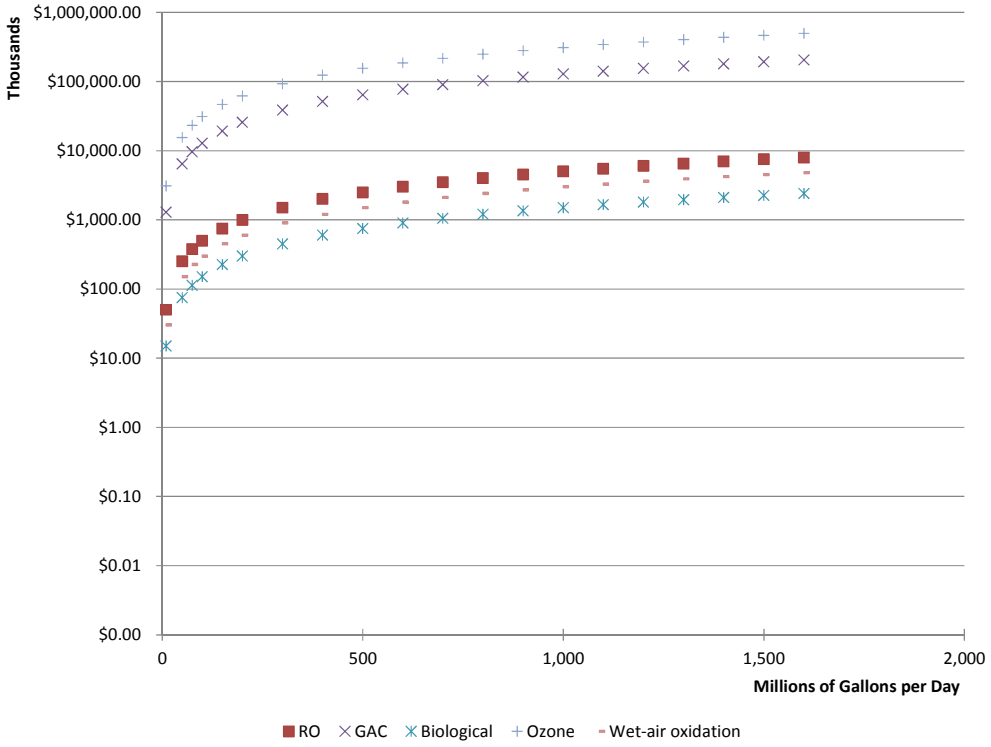


Figure 29: Highest projected total costs associated with various treatment methods on a daily basis. NOTE: these estimates allow for relative comparisons to be made. Sources: [41, 152, 171, 172].

Table 13: Daily **c**ost estimate of Plasma Arc Waste Disposal Treatment including Capital, Operations, and Maintenance costs. NOTE: that water content in this rough analysis is assumed to be either 0% or 100% and thus the additional weight would be responsible for adding cost. Source: [173, 174].

MGD	1	10	100
Low Cost (with water)	$ 320,000	$ 3,207,000	$ 32,068,000
High Cost (with water)	$ 360,000	$ 3,591,000	$ 35,910,000
Low Cost (without water)	$ 420	$ 4,230	$ 42,300
Low Cost (without water)	$ 475	$ 4,740	$ 47,370

Discussion of Practicality

Several trends and limitations can be noted about the cost analysis that was conducted above. First, limited data was available for the cost analysis, and therefore, there is a need for increased data availability to hone in on the actual costs. In addition, full lifecycle cost estimates are largely unavailable. The implications of this lack of data availability are that the results must be used with caution and should not be used as absolute values. Therefore, further research is necessary to develop a fuller picture of the costs associated with these treatment methods. This could be accomplished if corporations would be willing to aggregate their processes into a database, which could mask the individual corporation's proprietary processes. Several trends with implications were noted from the modeling exercise, which can be used to make decisions on which type of technology should ultimately be applied for the removal of PCPPs from wastewater. Firstly, biological is always the cheapest, and ozone is always the most expensive treatment process. Secondly, Wet Air Oxidation, which is considered to be an expensive process, is surprisingly more cost effective than is perceived in the industry. Thirdly, activated carbon is also an expensive process, and as was shown in the previous chapter, susceptible to competitive effects of the dominant species, and is dependent upon the dose of carbon added. As the carbon dose increases, the cost increases. Finally, as the volume of waste to be treated increases, the slope decreases eventually coming to a sort of plateau in cost. This reflects the economies of scale principle, where the cost to add a unit of output decreases, thereby making larger scale plants more cost-effective than their smaller scale counterparts. Hence, Wet Air Oxidation in terms of a cost-benefit analysis is the most favorable, and generally as all of the plant types get larger, they become more cost effective.

In terms of cost-effective treatment, the methods discussed in this chapter are not likely to be cheap enough for widespread application. From a practicality standpoint, more research must be conducted

on Plasma Arc Waste Disposal. It is unlikely that this technology will be applied directly to a wastewater treatment stream due to its cost, but rather, it may be utilized to generate electricity from MSW. Furthermore, as discussed previously, biological and GAC processes will not be likely to treat PCPPs on the scale of a WWTP. Therefore, the highest potential for direct application to wastewater stream would be Wet Air Oxidation, which has numerous technological and environmental advantages with its implementation.

Conclusions

1. Implications of research: ethical, moral, legal

The combination of ethics, morality, and legal arguments will provide a potential impetus for action. For example, when considering climate change, water is becoming an increasingly valuable resource, and the population and climate pressures being applied to areas of the world are causing new and reusable sources of water to be explored. As a result, the usage of technologies such as water recycling and RO will become more commonly deployed. Additionally, a blend of ethical, moral, legal, and business considerations will be crucial for helping to shape public opinion and legislative agendas in the face of new scientific discoveries.

From the perspective of the morality and ethics, the precautionary principle and concern for future generations will help to drive society's views and demands for the regulation of PCPPs. John F. Kennedy Jr. said, "Our most basic common link is that we all inhabit this small planet, we all breathe the same air, we all cherish our children's futures, and we are all mortal" [175]. While this quote spoke to the arms race and threat of nuclear war between the Soviet Union and the United States, it is just applicable to environmental issues 50 years later. Water is a fundamentality scarce resource, and it is being redistributed across the globe creating pressure. Therefore, if humanity is able to adapt appropriately and provide fresh sources of water for future generations (giving them the same opportunities as our generation was afforded), then there is an ethical obligation to ensure that as a society, there is not a depletion of resources. As a result, society is called to investigate and implement emerging technologies like RO, water recycling, and aquifer recharge to ensure that future generations have access to safe water. Without this, there will be an injustice that may threaten our children's future. Finally, the precautionary principle dictates that the

deployment of advanced, albeit expensive technologies like plasma arc waste disposal, should be undertaken to avoid the associated dangers of PCPPs. For example, estrogenic compounds in the environment pose a threat to environmental and public health, and while at their current concentrations these compounds do not pose a risk to humans, there is the potential for adverse effects to occur. Therefore, a novel technology should be applied to remediate these water supplies. While the potential application of ethical frameworks like the precautionary principle could help to motivate the public and employ action, there is still a lack of legal framework that could help to regulate PCPPs.

The legal entity that is responsible for regulating PCPPs is the Federal Drug Administration (FDA), which with adaptation of the current legal framework, could be able to consider the environmental and potential public health consequences of accumulation of these compounds in the environment. In its current form, the FDA prioritizes public health as the primary consideration of drug approval while completely disregarding environmental protection [176]. While this is the current state of affairs, it is conceivable that current statutes could be applied to the FDA and pharmaceutical companies to at a bare minimum consider the environmental impacts of PCPPs, or even to prevent their release into the environment. The main laws that may be pivotal in this role would be the National Environmental Policy Act (NEPA), Clean Water Act (CWA), Safe Drinking Water Act (SWDA), Resource Conservation and Recovery Act (RCRA), and Toxic Substances Control Act (TSCA) [176, 177]. Potential mechanisms of regulation within the relevant laws are shown in Table 14.

Table 14: Summary of current statutes, which could be adapted to regulated PCPPs

Law	Potential Implications and Effects
NEPA	• Apply law to FDA and require Environmental Impact Assessment (EIS and EA) process • Do not categorically exclude pharmaceuticals (concentration at point of entry less than 1 bbp)
CWA	• Apply technology forcing mechanism under Section 301(b)(2)(A) • Consider PCPPs as toxic pollutants by classifying them as such
SWDA	• Utilizes a health based rationale, and this law is not as useful since "little is known about the impacts of exposure at low concentrations of pharmaceuticals over long periods of time" • Still offers EPA a potential regulatory mechanism for EPA by promulgating standards
RCRA	• Governs land disposal of hazardous waste, but exempts domestic sewage or anything from domestic sources • Flushed PCPPs are outside the purview of the act • Hospitals and nursing homes are subject to RCRA's provisions
TSCA	• Explicitly excluded pharmaceuticals from its coverage

Source: [176, 177]

While there are many environmental laws on the books, the most promise for regulating micropollutants is with RCRA, SWDA, SWA, and NEPA. With that said, these laws would place a large strain on the pharmaceutical industry and WWTPs. Further research would need to be conducted to ascertain which type of technology would qualify as the best available (BAT – under the CWA) without becoming so cost prohibitive as to make either of these industries overly burdened. Additionally, the public health benefit must remain at the forefront of this decision process as laws and regulations potentially could become promulgated.

It is likely that PCPPs will become regulated in some form or another over time and therefore, it will be necessary to utilize emerging and established technologies to remove these contaminants. The implementation of different technologies will then generate new types of wastes that will need to be disposed of. For example, the use of filtration processes results in membranes that must be disposed of; the use of ozone processes creates the potential for air pollution issues and regulation under the CAA; and the use of adsorption processes generate potentially hazardous waste from activated carbon that cannot be regenerated. SDWA, RCRA, and CWA all become potentially become applicable with new treatment technologies and may place additional costs and concerns slowing enactment. Therefore, the

implementation of new treatment methods will necessitate further application of existing statutes, causing an increase in costs and adding potentially new environmental harms to be concerned about. With this said, the value of removing micropollutants from discharges to the environment may offset the concerns over new hazardous waste generation.

Finally, new environmental regulation could be developed specifically aimed at preventing environmental impact and adverse public health impact from endocrine disrupting compounds and micropollutants. This act like would take a form similar to the CWA and would set effluent limits from point sources to help protect human health and the environment. While no such regulation or statute is being considered, it is highly probably that if the US were to adopt the Precautionary Principle as it applies to environmental issues, then this sort of act could come into fruition within the next few decades. The implications of such an act would be tremendously favorable for the protection of health, but would likely increase the costs of treatment of water and wastewater. Therefore, the enactment of such a statute would need to be carefully considered in the context of costs and benefits.

This work recommends such a statute be enacted, not only due to the moral imperatives of the precautionary principle, and the moral imperatives of affording future generations the same opportunities that our generation was afforded, but also for the potential economic and technical stimulus that such a large scale implementation would spur.

2. Paths forward

Given the expense associated with each of the various tertiary treatment methods outlined above, it is highly unlikely that a combination of them would be employed and thus the optimal treatment method to move forward with would have the ability to remove biologically recalcitrant molecules, be energy efficient, and be acceptable from a cost and benefit analysis. In terms of what effectively removes the most PCPPs, there are only a few contenders including, Wet Air Oxidation, Plasma Arc Waste Disposal, and UV/Ozone treatments. With that said, each of these pieces of technologies each have their own pros and cons associated with them. In terms of capital cost, Plasma Arc Waste Disposal is the most expensive, while biological treatment is the cheapest. On the other hand, in terms of overall versatility and minimization of environmental impacts, Plasma Arc Waste Disposal does the most good. Therefore, it is

recommended that Plasma Arc Waste Disposal be utilized for the final treatment of PCPPs after RO removes a majority of the contaminants of wastewater effluent. A close second treatment option would be Wet Air Oxidation. The recommended treatment methods in this thesis are shown in Figure 30 on page 104.

There are numerous benefits to treating the retentate of RO with Plasma Arc Waste Disposal. First, in the retentate stream, there are many different valuable metals that can be recovered with this technology which can be resold to help offset treatment costs [167, 166]. Additionally, the retentate contains many biologically recalcitrant PCPPs, which can be completely degraded along with other organics to form syngas. Any other inorganic toxics will be vitrified and will be impermeable conferring a huge advantage over incineration where toxic ashes are still generated. Furthermore, the 300:1 volume reduction that will not need to be disposed of in another fashion and the water will be vaporized for syngas production. Water will come back into the process during the combustion process primarily in the form of CO and H_2 with some impurities. This process may present problems, since Plasma Arc Waste Disposal was originally designed for the destruction of solid wastes and not liquid wastes so it is unclear whether this could actually be implemented. Further research would be required to determine whether the syngas products that would come from a process that is occurring in water.

On the other hand, Plasma Arc Waste Disposal can be utilized to generate electrical energy from MSW and used to power WAO to degrade micropollutants. This would be the ultimate combination of technology since the input of MSW into the Plasma Arc Waste Disposal would produce electrical energy, keep MSW out of landfills preventing carbon emissions, and would provide a metal resale to help offset the huge capital that would be needed for this unique operation. With the electrical energy requirements met, WAO could be conducted on the effluent from the

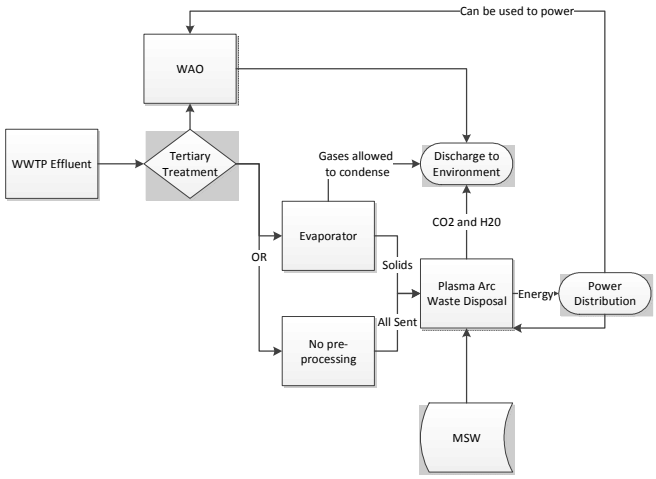


Figure 30: Ideal treatment methods for the removal of PCPPs

WWTP. This would not only decrease the COD of the effluent entering the environment, but also the water would be saturated with oxygen. Finally, the oxidation of organics would help to keep micropollutants out of the environment.

With the high promise of treatment with WAO and Plasma Arc Waste Disposal, further research and development must be conducted to allow for widespread implementation of this technology, which is believed to be one of the best solutions for removing PCPPs from wastewater. The treatment scheme suggested for the removal of PCPPs is shown in Figure 30. Unlike, WAO which is a liquid phase process, Plasma Arc Waste Disposal is a solid phase process, so the organics and metals amenable to treatment must be consolidated into a solid phase or research must be conducted on the feasibility of applying this treatment method to the liquid phase. One potential mechanism of consolidating the liquid effluent is to utilize an evaporator, although this does create the need for further energy production. On the other hand, it may be more cost effective to apply WAO and utilize only the energy from Plasma Arc Waste Disposal to run this process via the pyrolysis of waste products. Either of these options present feasible alternatives to solving the issues associated with PCPPs being discharged into the environment and will decrease the burden on the environment in terms of landfill requirements. In order to proceed with this kind of recommendation further research and development must be conducted in Plasma Arc Waste Disposal and its application to the liquid phase treatment, feasibility and characterization of end products from the liquid phase, and improvement on reactor materials (utilize research from fusion) to extend plant life. Additionally, financing will need to be extended to allow for plants to be built, but it is unlikely that banks will extend financing for these high capital cost plants. Therefore, either federal or private equity firms are envisioned to finance the loans for these massive capital expenditures. Furthermore, it is predicted that as climate change becomes a larger issue and carbon offsets become more of a reality, the application of Plasma Arc Waste Disposal will become a more and more attractive disposal methodology.

3. Future Research and Approaches

There are many different potential approaches that could be utilized to help treat biologically recalcitrant PCPPs that are not yet technologically or economically feasible. This thesis has examined many different treatment methods, but there is still not a technology that can be easily applied at all scales

of WWTPs. Therefore, continued research and development in conjunction with technological innovation and financing will be needed to help address the removal of micropollutants in the coming years.

The first set of solutions to the micropollutant problem involves conditioning or engineering of algae or bacteria that could be added within the WWTP. In the past, bioaugmentation was touted as a method for the removal of undesired compounds in a WWTP. The implementation of bioaugmention requires that bacteria be grown and conditioned to the compounds that are desired to be removed, and thus high concentrations of the compounds are utilized to acclimatize these bacteria [178]. Once sufficient yields are obtained, the bacteria are freeze dried for transportation to their final implementation site, usually a WWTP [178]. These conditioned bacteria are then added to the biological treatment process during wastewater treatment [178]. The bacteria utilized for these treatment processes is usually a blend of species or strains that are proprietary and has been utilized for WWTP, cleaning of grease traps, biological treatment of industrial waste products, and degradation of hydrocarbons and petroleum distillates [178]. Biotechnology and genetic engineering may prove useful in designing microbes for the degradation of selected compounds, and this is an area where genetic engineering may prove useful. The application of these microbes to the removal of PCPPs would require the usage of advanced techniques in genetic engineering that have not previously been needed in wastewater treatment. Naturally occurring or classically selected microbes have been able to treat many of the compounds of interest, but "there are, however, some situations where biotechnology offers potential advantages: for example, to engineer a naturally occurring derivative pathway so that it is continuously active in the bacteria, even in the absence of a molecule ordinarily needed to activate the pathway…" [179, pp. 271-275]. While past experience with many bioaugmentation strategies has not produced highly favorable results, observed increases in efficiency were actually due to improvements in plant operations and not due to the addition of the conditioned bacteria, there is still room for this technology to have an impact on the removal of micropollutants. A related strategy that can be applied is algae treatment via biotransformation of organic chemicals like DDT, napthaline, and phenol into less toxic substances [180]. It should be noted that algae are rarely capable of complete degradation, although partial degradation can be expected with some biotransformation [180]. Therefore, there is a potential to modify algae utilizing genetic engineering to create natural pathways for the degradation of organic compounds including PCPPs. Another potential

source of degradation of these compounds could be reverse engineering the bacteria that produce many of these pharmaceutical agents. Further research should be conducted on algae and bacteria to effectively degrade PCPPs, as the addition of these compounds would provide a biologic method for their removal. Another potential method would be to isolate the enzymes that are responsible in bacteria or algae for degradation and mass produce them. These enzymes could then be added during the wastewater treatment process to degrade micropollutants of concern that do not respond to conventional biological treatment. It could also be imagined that algae or bioaugmentation would provide an excellent means of removing PCPPs.

In terms of pros and cons, there are numerous different potential reasons for implementing bioaugmentation or algae to degrade micropollutants. One of the largest drawbacks associated with the implementation of bioaugmentation or algae is the costs of developing these particular processes. Genetic engineering processes are expensive and can be largely a trial and error process to get to the exact set of pathways necessary to allow for algae or bacteria to degrade substances of interest. Additionally, the implementation of bioaugmentation requires that the bacteria be conditioned at high concentrations of the compounds to be degraded. Pharmaceutical compounds are remarkably expensive, and conditioning bacteria with high concentrations will be extremely expensive. Furthermore, considering the amount of bacteria needed to treat micropollutants for a single treatment plant, a substantial operation would need to be established in order to yield enough conditioned bacteria. On the other hand, treatment with algae or bioaugmentation has the advantage of being easy to implement (freeze dried bacteria can be added to the WWTP), requires no additional capital expenditures for equipment at the WWTP, and *in situ* treatment has shown that bioaugmentation is an effective strategy for degrading organic compounds. Therefore, algae and bioaugmentation should be further investigated for the removal of PCPPs, and if feasible, could be a viable method for removing these compounds.

Another attractive set of solutions revolve around the usage of sorption processes by utilizing novel methods. New materials could be utilize for sorption processes that address the expense associated with regenerating the sorbent and making the sorbent specific to the micropollutants of interest. One possible means of removing micropollutants, comes from biomaterials research, where surfaces can be coated with different receptors, antigens, etc. to allow for molecules to bind or not bind to a surface [181].

In a similar fashion to medical devices, novel materials could be devised with the receptors that PCPPs bind to within the human body, thereby making the sorbents highly specific. For example, if the removal of Esterone is desired, then placing an estrogen receptors or estrogen G protein-coupled receptors on the surface of the sorbent would be a means of selectively removing Esterone compounds [182]. While it is likely that these surfaces would not be easily regenerated, research could be done to address the possibility of these types of surfaces. Additionally, to improve surface area, which improves sorption efficiency, nanoparticles coated with these receptors could be utilized to remove compounds of interest. Another novel material that may prove to be useful for water treatment technology is graphene. Membranes composed of graphene have already been proposed as an alternative to RO for desalting water, allowing for improved flux across the membrane [183]. Also, the role that functional groups play on a nanoporous graphene filter, demonstrate a degree of customizability while preserving that flow can still occur [183]. These types of materials definitely have the potential to revolutionize water treatment and become the breakthrough that is needed to address sorption and filtration as a potential means of removing micropollutants. Therefore, while not technologically developed yet, research and development should be directed at novel sorbents and membranes like graphene to aid in the removal of PCPPs. It should be noted that a similar problem to RO will be encountered in the reject stream where there will be a concentrating effect and that will need to be treated. Finally, a novel material for sorption could be discovered that is easily regenerated and has tight reversible binding. Future research should be directed towards these novel adsorbents along with the fabrication of graphene, so that adsorption becomes a more viable treatment methodology for treating micropollutants.

In terms of pros and cons, there are numerous different potential reasons for implementing graphene, nanotechnology, or developing a novel sorbent to remove micropollutants. First, graphene is a high potential technology that in the future could be utilized to remove PCPPs. Currently, graphene is still so new that fabrication costs are high and future uncertain, so it remains unclear how to mass-produce this material. This is the largest drawback, in conjunction with it is a largely unproven technology, but with time will become more studied. On the other hand, graphene has many positives: it provides higher flux than RO allowing for smaller modules and less energy needed to generate pressure differentials to drive filtration, and the surface is modifiable to improve flux rates. Additionally, the structure of the graphene

without punching holes into it is impermeable to even helium, making the material extremely attractive as a filter that operates on the size exclusion principle [183]. While graphene holds great promise, another potential technology to be utilized is nanotechnology where the receptors of interest are covering nanoparticles. Nanotechnology for water treatment has many disadvantages over other approaches including: receptors must be isolated and reproduced, which is an expensive process, high cost due to shear number of molecules that have to be manufactured, and large processing costs. On the other hand, nanotechnology has many potential benefits including: high specificity for the compounds of interest, won't remove minerals from the water like RO, and there is a wealth of knowledge that can be utilized in generating these types of particles from biomaterials research. Finally, if society follows previous paths, depending on a novel material to be discovered to bail us out of the problems associated with PCPP is a potential option. Waiting for a novel material to be developed has many shortcomings such as, basic research and development is slow and costly, research and development advances are sporadic, research and development costs are huge and there is no certainty in that a breakthrough will be found in a given timeframe. Alternatively, a breakthrough could revolutionize the industry, and may allow for cost-effective and seamless removal. Many of the compounds of interest do theoretically adsorb, so this method of removal holds promise. Therefore, sorption processes hold promise especially with graphene processes, and as a result, continued research should be conducted in this area to increase the probability that a major breakthrough could occur.

Additional methods also revolve around the application of currently available industrial and chemical processes to the treatment of PCPPs. Multi-stage flash distillation (MSF) has been used as an alternative to RO for producing desalted water. MSF works by flashing a small amount of water into steam in multiple stages, running past cold water resulting in a countercurrent heat exchanger [184]. The largest demand of this technology is energy; so many times the plant is coupled to a cogeneration facility where the heat can be used to heat the influent water of the MSF [184]. While desalting is the traditional usage for this particular technology, it could be imagined that the flash distillation process would be useful for the removal of PCPPs from wastewater. The result of applying this technology would be a very high quality effluent which would be largely devoid of micropollutants, unless these compounds possessed large vapor pressures or were able to become volatilized. Therefore, MSF may hold promise as a technology for the

removal of micropollutants from wastewater. Another potential mechanism of removal of PCPPs is Chromatography. The mobile phase is where compounds of interest are dissolved, while these compounds move through the stationary phase within an instrument [185]. Different compounds will move at different speeds, causing a separation of these compounds based off the compound's partition coefficient [185]. As a result, given that there is a large degree of variation in partition coefficients of PCPPs; chromatography could be utilized hypothetically to separate these compounds. Research and development would be needed to scale up these processes to the size of a WWTP, but the separation needed for this process would not be extremely high in resolution, which should help to drive down potential costs. Finally, molecular differentiation could be utilized as another means of removing micropollutants from wastewater. While not perfectly related, density overlap sorting recently has been utilized to separate plastics for recycling. This process allows for mixed plastics to be separated on the basis of multiple variables (temperature, pressure, shear, and mass) [186]. This novel process allows for significant waste reduction by sorting by density. Therefore, if this process were applied to the removal of PCPPs, it may be possible to separate these particles based off shear, pressure, temperature, and mass difference. While this application would require further research, it potentially would be very worth exploring considering the success that the plastics industry has experienced with this technology.

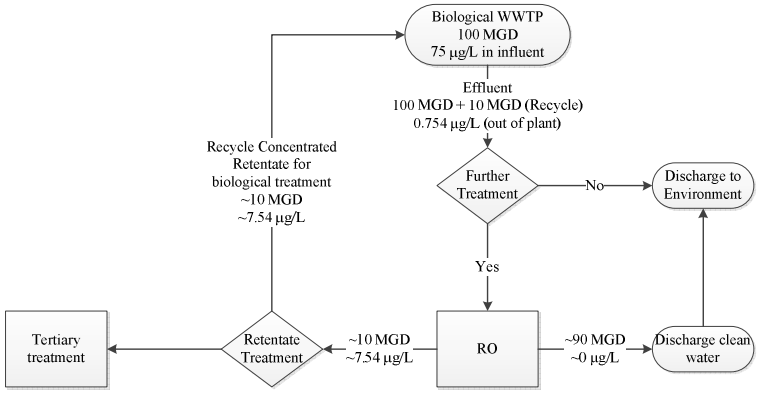
In terms of pros and cons, there are numerous different potential reasons for implementing MSF, chromatography, or density overlap sorting for the removal of PCPPs. MSF has numerous pros including being a straight forward process, has no reduced heat transfer due to scaling in the reactor, and the presence of suspended solids do not affect the process [184]. On the other hand, MSF is energy intensive, the steam is partially consumed during the process, has the recurring problem of having a left over substance to treat that is now highly concentrated in the liquid phase, and the output stream will not necessarily be completely devoid of PCPPs [184]. An alternative technology is the application of chromatography to remove micropollutants of interest. One of the most promising technologies is density overlap sorting, which has the pros of utilizing pressure, temperature, and shear to differentiate materials, where most technologies only utilize one of these factors [186]. This technology also has a lower capital investment than other similar processes and allows for high quality final products to be produced [186]. Like many separation technologies, density overlap sorting is highly energy intensive and as a result, the recovered

products must be quite valuable to offset a part of this cost. Finally, chromatography holds promise with its ability to separate out mixtures effectively, but it is ultimately not very cost effective and is somewhat slow depending on the complexity of the feed mixture [185]. Although, with further research, a fast system, much like the quick gas chromatography used in airports to screen for bomb materials, could be developed to remove PCPPs from wastewater [187]. Therefore, while these applications would require further research, there is the potential, especially with density overlap separation, to remove many of the PCPPs of interest.

Finally, truly novel processes and treatment methods could be developed to treat micropollutants and will require truly out of the box thinking to address these recalcitrant compounds. Materials research will be necessary, along with processing engineering for any new process to be implemented to remove PCPPs. There are three relatively new technologies that potentially could be utilized in the treatment of water to remove PCPPs including, fabric filtering with novel materials that could repel undesired organics, capsular perstraction ("enveloping of pre-selected organic solvents within a porous hydrogel membrane to form liquid-core microcapsules") [188], and nanotechnology of some form. To construct filters, a novel hydrophobic material is required. One such material can repel water and adsorb oil, while another material has been discovered and considered for use in rain jackets that are both breathable and lightweight [189]. There is the potential for these materials to be adapted for the removal of PCPPs by utilizing these compounds successful rejection of water and adsorption of hydrophobic compounds, to trap the PCPPs in the hydrophobic portion and thereby generate clean water. Further research and development would be required in order to even demonstrate the potential for implementing this type of technology. Additionally the usage of nanotechnology and capsular perstraction may hold promise as strategies for the removal of PCPPs from water [188, 190]. Whelehan et al. demonstrated the viability of capsular perstraction for rapidly removing seven PCPPs of interest, but these experiments would need to be repeated in the context of wastewater effluent to ascertain the role of competitive substrates amongst other factors. Like any of the potential nanotechnology efforts, these methods will be expensive and will require large scale manufacturing to allow for the treatment of wastewater at the scale of a WWTP. Therefore, further research should be undertaken to determine how nanotechnology could play a role in potentially removing micropollutants, as well as into methods for mass producing these particles. Additionally, nanotechnology

in the form of nanoparticles may hold promise for the ability to remove PCPPs from water [190]. Again further research would need to be conducted as to the type of nanoparticles would be suitable for effectively, rapidly, and cost effectively removing micropollutants. Therefore, truly novel processes and treatment methods may hold a plausible solution for the removal of PCPPs from water, but these techniques are so new that it is extremely difficult to predict if and when they could be available for usage in the field.

If prioritization of research funding must occur, then the most promising technologies to remove PCPPs from water should preferentially be funded over those that are more of a stretch. As a result of the analysis in this work, the funding potential should go to Plasma Arc waste disposal, Wet Air Oxidation, reverse osmosis, bioaugmentation, and grapheme filters. The rest of the technologies that are outlined in this work still have the potential to be a part of the solution for removing micropollutants from water, but they will require heavy investment in research and development prior to becoming viable. With that said, these solutions should not be discounted and should still be funded.



Point in System	Concentration ($\mu g/L$)	Volume (MGD)	Mass Total (lbs)
Biological WWTP Effluent	75	100	6245931
RO retentate and Recycle	7.5	10	62459
Combined Recycle and Retentate (1 pass)	68.86	110	6308390
Effluent out of 2nd Pass of WWTP	0.69	110	63084

Figure 31: With the addition of the recycle loop from the retentate, the concentration of the influent increases, thereby increasing the likelihood that biological degradation will occur.

4. Model plant design

In order to effectively remove PCPPs from wastewater utilizing current technology, there a numerous different paths that could be taken to remove these compounds effectively. It should be noted that while there are numerous treatment technology combinations that could accomplish this task, the costs

are disregarded. As part of a theoretical exercise, the plant design paths are meant to establish which technologies could accomplish the removal. The various design paths are shown in Figure 32 (page 114). One optimal treatment path relies on tertiary treatment of WWTP effluent in the form of Wet Air Oxidation to ultimately degrade the PCPPs of interest. This would require the Wet Air Oxidation module, likely a Zimpro® process, to be scaled to the size of the treatment plant (100-1000 MGD). One of the advantages of this path is that utilizes established technology and that as the technology becomes more widely implemented, the capital cost is likely to decrease. Another likely treatment path utilizes Reverse Osmosis as the first step in the treatment sequence of effluent. From here Plasma Arc Waste Disposal can be used to generate energy for the RO process and the tertiary treatment process or with additional research could be directly applied to the retentate. A final treatment scheme would be to recycle the retentate of RO to the biological WWTP. This would increase the mass flow of PCPPs into the biological process, thereby potentially allowing for these substances to be degraded (see Figure 31, page 112). By recycling the retentate stream into the treatment plant, an additional 10 MGD of water will flow into the plant at an average concentration of 7.54 µg/L. The effect of treatment in this fashion is a 10 fold reduction in the mass load to the environment, which potentially avoids adverse environmental impacts. Therefore, by selecting an optimal treatment scheme, there is the potential to avoid adverse effects and to remove many of these PCPPs of concern.

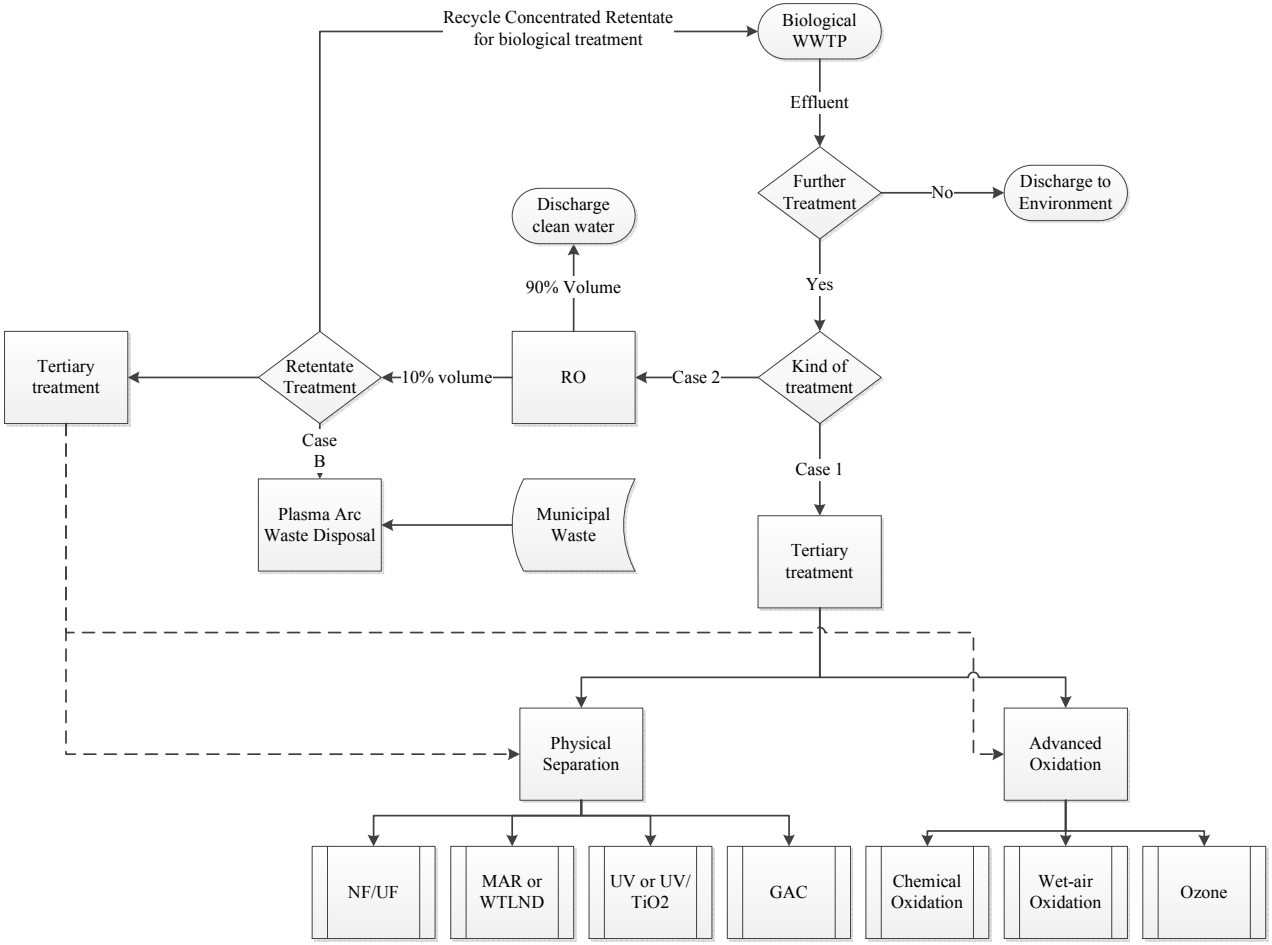


Figure 32: Potential treatment methods demonstrate that there are numerous paths for the removal of PCPPs. Each of the different paths will have different costs and benefits associated with it and will achieve different levels of removal. The least expensive path will involve a recycle loop of the rententate for biological treatment, which could be powered by Plasma Arc Waste Disposal (produces energy from municipal and industrial wastes).

5. Final Thoughts

Currently there are not any viable technologies to treat these recalcitrant compounds in terms of applicable technology, cost-effectiveness, or scalability to current WWTP volumes. First off, biological treatment, either as plug-flow or CSTR, for many of the PCPPs is not going to occur due to the competitive effects associated with the many compounds present at higher concentrations in the WWTP. Secondly, PCPP adsorption density will be a dose dependent process and with the costs associated with activated carbon, it is highly unlikely this technology will be able to be implemented in the field. Additionally, the higher concentration species will be more competitive and be sorbed preferentially over PCPPs. Therefore, both sorption processes and biological treatment have similar shortcomings with respect to higher concentration species being preferentially removed due to competitive kinetics.

There are currently available technologies, that if scaled correctly, which could adequately remove PCPPs from water, but technological breakthroughs may make implementation more cost-effective and likely. The current best available technology, barring a major technological breakthrough is Wet Air Oxidation in combination with Plasma Arc Waste Disposal. In this treatment scheme, the addition of RO could be considered and then Plasma Arc Waste Disposal could be utilized to treat the retentate. However, the addition of RO will still present the challenge of membrane fouling which must be solved in order for RO to be a viable technology. Finally, technological breakthrough will be crucial to successfully removing micropollutants from WWTP's effluent. Technologies that hold the most promise include: Wet Air Oxidation, RO, bioaugmentation, and grapheme filters. Specifically, there is optimism surrounding graphene filters as a breakthrough, which could drastically reduce the costs associated with RO and prevent membrane fowling. As a result, then applying Wet Air Oxidation to the retentate might be a good method of removal. Future research will be needed to advance technologies to the point of large scale implementations and to drive down the large capital costs associated with many of the potential treatment technologies.

As a society, we have a moral obligation to ensure that there are adequate sources of fresh water for future generations. By implementing technologies such as Plasma Arc Waste Disposal, there is the ability to fulfill the obligation to future generations for water and to help impact climate change in a positive fashion by making sure that less trash is destined for landfills. Additionally, by further purifying

the water destined for the environment, the negative consequences of PCPPs to the environment will be avoided and further degradation of water supplies will be avoided. While there are many positives and cause for optimism, there should always be a cautionary undertone. The lessons drawn from nuclear power plants, which like many of the proposed alternative technology implementations are capital intensive, demonstrated that there is resistance to funding such large upfront capital expenditures. Generally, economics tend to drive policy, and thus, there will need to be further research to determine how to drive down the capital costs of alternative treatment methods that are able to effectively remove PCPPs from wastewater. Therefore, while the economics may be prevailing most decision, hopefully society's ethical and moral framework will prevail and chose to implement new technologies to remove PCPPs from wastewater; thereby, improving water quality for future generations and preventing additional environmental damage.

Appendix I: Freundlich Literature Values

Compound	n	K_f	Original K_f units	Converted K_f (mg/g)(mg/L)^n	Carbon	Author
Phenol	0.69	0.22	(mg/g)(mg/L)^(n)	0.22	EFB 500	[130]
	0.3	2.79	(mg/g)(mg/L)^(n)	2.79	EFB 800	[130]
	0.616	6.193	(mg/g)(mg/L)^(n)	6.193	GAC, NS	[131]
	2.525253	0.851	(mg/g)(mg/L)^(n)	0.851	RGM1	[132]
	2.267574	0.863	(mg/g)(mg/L)^(n)	0.863	RB2	[132]
	2.336449	1.452	(mg/g)(mg/L)^(n)	1.452	ROW0.8supra	[132]
	2.380952	0.209	(mg/g)(mg/L)^(n)	0.209	Cgran	[132]
	0.54	21	(mg/g)(mg/L)^(n)	21	Fitrasorb 300	[133]
	0.037	0.371	(mg/mg)(mg/L)^(1/n)	37	GAC	[134]
	1.694915	2.11	(mg/g)(mg/L)^(n)	2.11	Modified Bentonite, ph 4	[135]
	2.272727	3.72	(mg/g)(mg/L)^(n)	3.72	Modified Bentonite, ph 7	[135]
	3.030303	8.35	(mg/g)(mg/L)^(n)	8.35	Modified Bentonite, ph 12	[135]
	2.47	0.04177	(mol/L)*(L/g)^n	38.097	PX-21	[202]
	0.1912	89.43	(mol/L)*(L/g)^n	89.43	Filtrasorb-400	[136]
	3.142	53.985	(mg^(1-1/n))*(L^1/n)/g	53.985	GAC	[137]
	0.56	0.17	L/mg	0.17	GAC-70	[138]
	0.42	0.32	L/mg	0.32	Com GAC-70	[138]
	0.37	0.6	L/mg	0.6	GAC-80	[138]
	2.380952	37	(mg/g)(L/mg)^(1/n)	37	GAC	[138]
	3.134796	36.3	(mg/g)(L/mg)^(1/n)	36.3	F-400	[138]
	0.4	0.046	(moles/g)*(L/mole)^n	44.355	Coconut shell Activated Carbon	[247]
	0.38	0.021	(moles/g)*(L/mole)^n	25.461	Coconut shell Activated Carbon	[138]
	0.167	0.008	(moles/g)*(L/mole)^n	111.207	Coconut shell Activated Carbon	[138]
	0.117	0.011	(moles/g)*(L/mole)^n	271.093	Coconut shell Activated Carbon	[138]

	3.846154	50	mg/g	50	Filtrasorb-400	[119]
2-CP	2.066116	2.512	(mg/g)(mg/L)^(n)	2.512	RGM1	[132]
	2.178649	2.518	(mg/g)(mg/L)^(n)	2.518	RB2	[132]
	2.439024	3.75	(mg/g)(mg/L)^(n)	3.75	ROW0.8supra	[132]
	2.717391	0.667	(mg/g)(mg/L)^(n)	0.667	Cgran	[132]
	28.57143	169.2	(mg/g)(L/mg)^(1/n)	169.2	SA4	[140]
	3.875969	39.3	(mg/g)(L/mg)^(1/n)	39.3	CA1	[140]
	31.25	155.4	(mg/g)(L/mg)^(1/n)	155.4	PKDA	[140]
	0.286	35.4	(mg/g)(L/mg)^(1/n)	35.4	Cagran	[140]
	2.841	0.916	(mg/g)(mg/L)^(n)	0.916	Modified Bentonite	[141]
	2.302	0.566	(mg/g)(mg/L)^(n)	0.566	Modified Bentonite	[141]
	2.793	57.795	(mg^(1-1/n))*(L^1/n)/g	57.795	GAC	[137]
4-CP	1.872659	3.034	(mg/g)(mg/L)^(n)	3.034	RGM1	[132]
	1.972387	3.076	(mg/g)(mg/L)^(n)	3.076	RB2	[132]
	2.040816	4.256	(mg/g)(mg/L)^(n)	4.256	ROW0.8supra	[132]
	2	0.955	(mg/g)(mg/L)^(n)	0.955	Cgran	[132]
	3.593	0.03458	(mol/L)*(L/g)^n	134.341	PX-21	[202]
	3.737	101.504	(mg^(1-1/n))*(L^1/n)/g	101.504	GAC	[137]
DCP	1.828154	6.934	(mg/g)(mg/L)^(n)	6.934	RGM1	[132]
	1.960784	5.794	(mg/g)(mg/L)^(n)	5.794	RB2	[132]
	2.293578	9.333	(mg/g)(mg/L)^(n)	9.333	ROW0.8supra	[132]
	1.858736	1.75	(mg/g)(mg/L)^(n)	1.75	Cgran	[132]
	0.144033	220.9557	???	220.956	Filtrasorb-400	[136]
	3.925	128.728	(mg^(1-1/n))*(L^1/n)/g	128.728	GAC	[137]
TCP	1.934236	13.37	(mg/g)(mg/L)^(n)	13.37	RGM1	[132]
	2.159827	9.55	(mg/g)(mg/L)^(n)	9.55	RB2	[132]

	2.109705	13.8	(mg/g)(mg/L)^(n)	13.8	ROW0.8supra	[132]
	1.620746	2.965	(mg/g)(mg/L)^(n)	2.965	Cgran	[132]
	1.25	22.04	(mg/g)(L/mg)^(1/n)	22.04		[143]
	1.219512	31.48	(mg/g)(L/mg)^(1/n)	31.48		[143]
	1.190476	35.42	(mg/g)(L/mg)^(1/n)	35.42		[143]
	0.1512	588.7	???	588.7	Filtrasorb-400	[136]
	6.821	284.41	(mg^(1-1/n))*(L^1/n)/g	284.41	GAC	[137]
PCP	3.236246	28.84	(mg/g)(mg/L)^(n)	28.84	RGM1	[132]
	2.688172	26	(mg/g)(mg/L)^(n)	26	RB2	[132]
	3.134796	31.33	(mg/g)(mg/L)^(n)	31.33	ROW0.8supra	[132]
	2.132196	14.12	(mg/g)(mg/L)^(n)	14.12	Cgran	[132]
p-Nitrophenol	2.358	1.1824	(mg/g)(mg/L)^(n)	1.1824	Modified Bentonite	[141]
	4.235	0.0302	(mol/g)(mol/L)^n	190.211	PX-21	[202]
	0.1494	166.5	-	166.5	Filtrasorb-400	[136]

Appendix II: EasyFitXL Distributions

Bernoulli	Error Function	Geometric	Levy	Pareto	Reciprocal
Beta	Exponential	Gumbel Max	Logarithmic	Pareto 2 (Lomax)	Rice
Binomial	F	Gumbel Min	Logistic	Pearson 5	Student's t
Burr	Fatigue Life	Hyperbolic Secant	Log-Gamma	Pearson 6	Triangular
Cauchy	Frechet	Hypergeometric	Log-Logistic	Pert	Uniform
Chi-Squared	Gamma	Inverse Gaussian	Log-Pearson 3 (LP3)	Poisson	Wakeby
Dagum	Generalized Extreme Value	Johnson SB	Lognormal	Phased Bi-Exponential	Weibull
Discrete Uniform	Generalized Gamma	Johnson SU	Negative Binomial	Phased Bi-Weibull	
Erlang	Generalized Logistic	Kumaraswamy	Nakagami	Power Function	
Error	Generalized Pareto	Laplace	Normal	Rayleigh	
Source: http://www.mathwave.com/products/easyfit_desc.html#dist					

Appendix III: Final Data Distributions

33%, Ce = 0.01mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
1	Beta	0.36315	1	34.211	28	N/A	
22	Gen. Pareto	0.36563	2	14.499	6	N/A	
15	Frechet	0.36991	3	23.69	14	15.153	42
40	Pearson 5	0.37237	4	46.465	29	17.717	43
41	Pearson 5	0.37238	5	46.465	30	17.717	44
33	Log-Logistic	0.38241	6	22.829	12	6.4607	24
35	Lognormal	0.38301	7	26.776	17	5.9629	19
36	Lognormal	0.38301	8	26.776	16	5.9629	18
14	Fatigue Life	0.38385	9	31.866	24	1.9923	7
	⋮		⋮		⋮		⋮
19	Gen. Extreme Value	0.45275	24	13.442	3	2.7576	9

#	Distribution	Parameters
19	Gen. Extreme Value	k=-1.456 σ=0.003 μ=0.00694
20	Gen. Gamma	k=19.379 α=0.01887 β=0.01044
21	Gen. Gamma	k=0.33402 α=1.1094 β=0.00225
22	Gen. Pareto	k=-4.8204 σ=0.06708 μ=-0.00518

33%, Ce = 0.1 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
40	Pearson 5	0.3742	1	39.388	28	8.9734	39
39	Pearson 5	0.37422	2	39.388	29	8.9742	40
35	Lognormal	0.37432	3	27.454	17	6.2157	31
34	Lognormal	0.37432	4	27.454	16	6.2157	30
21	Gen. Pareto	0.38013	5	14.338	5	N/A	
15	Frechet	0.38285	6	24.604	13	16.494	43
12	Fatigue Life	0.38619	7	32.231	22	2.0282	6
13	Fatigue Life	0.38619	8	32.231	21	2.0282	5
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.44318	23	12.643	2	2.9572	8
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.47845	31	33.335	27	3.6362	15

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.5454 σ=2.7898E-4 μ=7.1357E-4
19	Gen. Gamma	k=20.628 α=0.02092 β=0.00103
20	Gen. Gamma	k=0.35502 α=1.2229 β=2.0507E-4
21	Gen. Pareto	k=-5.2424 σ=0.00737 μ=-5.3399E-4

33%, Ce = 0.2 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
35	Lognormal	0.37176	1	27.634	16	4.4225	23
34	Lognormal	0.37176	2	27.634	15	4.4225	22
39	Pearson 5	0.38489	3	40.759	29	9.3973	40
40	Pearson 5	0.3849	4	40.759	28	9.3977	41
15	Frechet	0.38641	5	24.935	13	28.027	44
13	Fatigue Life	0.38692	6	32.35	22	2.0395	7
12	Fatigue Life	0.38692	7	32.35	21	2.0395	8
21	Gen. Pareto	0.38721	8	14.369	5	N/A	
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.43852	22	12.346	2	2.008	6
	⋮		⋮		⋮		⋮
19	Gen. Gamma	0.66962	47	72.096	40	1.8318	3

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.5871 σ=1.3466E-4 μ=3.6093E-4
19	Gen. Gamma	k=21.02 α=0.02161 β=5.1074E-4
20	Gen. Gamma	k=0.361 α=1.2616 β=9.9428E-5
21	Gen. Pareto	k=-5.4476 σ=0.00385 μ=-2.7125E-4

33%, Ce = 0.5 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
47	Rice	0.36863	1	71.713	42	N/A	
35	Lognormal	0.37275	2	27.843	16	4.4976	23
34	Lognormal	0.37275	3	27.843	15	4.4976	22
25	Inv. Gaussian	0.37739	4	42.476	31	7.9263	36
12	Fatigue Life	0.38779	5	32.494	21	2.053	8
13	Fatigue Life	0.38779	6	32.494	22	2.053	9
3	Burr	0.38837	7	32.556	23	5.7467	32
15	Frechet	0.39078	8	25.403	13	25.974	43
21	Gen. Pareto	0.39707	9	14.5	6	N/A	
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.43204	21	12.024	2	1.239	4
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.46896	30	33.604	26	3.8207	17

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.6444 σ=5.1268E-5 μ=1.4651E-4
19	Gen. Gamma	k=21.666 α=0.02247 β=2.0288E-4
20	Gen. Gamma	k=0.37063 α=1.3129 β=3.8531E-5
21	Gen. Pareto	k=-5.7383 σ=0.00163 μ=-1.1106E-4

33%, Ce = 1 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
25	Inv. Gaussian	0.37257	1	42.231	27	8.8598	36
34	Lognormal	0.38573	2	28.079	14	4.484	24
35	Lognormal	0.38573	3	28.079	15	4.4839	23
13	Fatigue Life	0.38837	4	32.599	19	2.0621	10
12	Fatigue Life	0.38837	5	32.599	20	2.0621	9
15	Frechet	0.39409	6	25.722	12	25.555	41
48	Uniform	0.39491	7	54.794	35	N/A	
45	Rayleigh	0.39881	8	65.302	36	7.1163	34
	:		:		:		:
21	Gen. Pareto	0.40511	11	14.655	5	N/A	
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.42726	19	11.844	1	0.60012	1
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.46405	28	33.667	22	3.9154	19

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.6861 σ=2.4691E-5 μ=7.3957E-5
19	Gen. Gamma	k=24.261 α=0.02185 β=9.9738E-5
20	Gen. Gamma	k=0.38489 α=1.3683 β=1.8894E-5
21	Gen. Pareto	k=-5.9569 σ=8.5356E-4 μ=-5.6464E-5

33%, Ce = 2 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
25	Inv. Gaussian	0.38518	1	42.518	28	9.0684	37
13	Fatigue Life	0.38893	2	32.685	19	2.071	11
12	Fatigue Life	0.38893	3	32.685	20	2.071	12
49	Uniform	0.39237	4	54.545	35	N/A	
35	Lognormal	0.39316	5	28.179	14	4.5579	28
34	Lognormal	0.39316	6	28.179	15	4.5579	27
46	Rayleigh	0.39443	7	62.282	36	7.2828	35
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.41933	13	14.876	5	N/A	
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.42368	18	11.857	1	0.6536	1
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.46377	30	33.719	22	3.9862	21

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.7254 σ=1.1934E-5 μ=3.7339E-5
19	Gen. Gamma	k=24.316 α=0.02288 β=4.9812E-5
20	Gen. Gamma	k=0.39304 α=1.4051 β=9.3181E-6
21	Gen. Pareto	k=-6.1683 σ=4.4541E-4 μ=-2.8784E-5

33%, Ce = 4 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
25	Inv. Gaussian	0.38243	1	31.41	18	7.6824	36
13	Fatigue Life	0.38937	2	32.761	21	2.0779	11
12	Fatigue Life	0.38937	3	32.761	22	2.0779	10
49	Uniform	0.39014	4	54.562	36	N/A	
46	Rayleigh	0.39052	5	59.33	38	7.4093	35
34	Lognormal	0.39686	6	28.264	15	4.6312	28
35	Lognormal	0.39686	7	28.264	14	4.6312	27
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.41979	12	11.875	1	0.65068	2
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.4257	17	15.08	5	N/A	
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.4752	32	33.733	25	4.0515	22

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.7596 σ=5.7831E-6 μ=1.8806E-5
19	Gen. Gamma	k=24.409 α=0.02396 β=2.4848E-5
20	Gen. Gamma	k=0.40183 α=1.4437 β=4.5936E-6
21	Gen. Pareto	k=-6.3559 σ=2.3076E-4 μ=-1.4606E-5

33%, Ce = 6 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
46	Rayleigh	0.38821	1	57.651	38	7.4291	35
49	Uniform	0.38877	2	54.661	37	N/A	
13	Fatigue Life	0.38949	3	32.804	21	2.0798	10
12	Fatigue Life	0.38949	4	32.804	20	2.0798	11
34	Lognormal	0.39859	5	28.326	14	4.6539	28
35	Lognormal	0.3986	6	28.326	15	4.6539	27
25	Inv. Gaussian	0.40015	7	30.873	18	7.1864	34
15	Frechet	0.40044	8	26.902	12	30.323	42
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.41687	12	11.869	1	0.49355	1
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.4303	17	15.252	5	N/A	
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.47946	33	33.724	23	4.0869	22

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.7787 σ=3.7776E-6 μ=1.2560E-5
19	Gen. Gamma	k=24.964 α=0.02432 β=1.6468E-5
20	Gen. Gamma	k=0.40871 α=1.4716 β=3.0310E-6
21	Gen. Pareto	k=-6.463 σ=1.5653E-4 μ=-9.7883E-6

33%, Ce = 8 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
46	Rayleigh	0.38641	1	56.443	38	5.5147	37
49	Uniform	0.38761	2	54.738	37	N/A	
12	Fatigue Life	0.38981	3	32.83	25	2.0847	13
13	Fatigue Life	0.38981	4	32.83	24	2.0847	14
40	Pearson 5	0.39432	5	43.44	33	9.5284	39
39	Pearson 5	0.39432	6	43.44	34	9.5284	40
25	Inv. Gaussian	0.39858	7	30.842	20	5.2938	36
34	Lognormal	0.39905	8	28.361	17	4.681	31
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.40638	13	14.527	4	N/A	
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.41154	15	11.652	1	0.70955	2
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.48099	37	33.702	27	4.1271	25

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.7847 σ=2.8060E-6 μ=9.4204E-6
19	Gen. Gamma	k=25.312 α=0.02461 β=1.2299E-5
20	Gen. Gamma	k=0.41365 α=1.4915 β=2.2566E-6
21	Gen. Pareto	k=-6.4969 σ=1.1766E-4 μ=-7.3042E-6

33%, Ce = 10 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
46	Rayleigh	0.38579	1	55.565	38	5.5099	36
49	Uniform	0.3874	2	54.786	37	N/A	
12	Fatigue Life	0.38982	3	32.851	21	2.085	13
13	Fatigue Life	0.38982	4	32.851	22	2.085	14
25	Inv. Gaussian	0.39795	5	114.07	45	5.2948	35
34	Lognormal	0.39884	6	28.383	15	4.7022	30
35	Lognormal	0.39884	7	28.383	16	4.7022	29
15	Frechet	0.40183	8	27.245	14	0.0252	1
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.41412	14	11.922	1	0.56352	3
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.42521	16	15.356	5	N/A	
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.48169	34	33.69	25	4.1403	26

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.7999 σ=2.2241E-6 μ=7.5771E-6
19	Gen. Gamma	k=25.344 α=0.02498 β=9.8626E-6
20	Gen. Gamma	k=0.4169 α=1.5048 β=1.8041E-6
21	Gen. Pareto	k=-6.5827 σ=9.6090E-5 μ=-5.9309E-6

50%, Ce = 0.01 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
41	Pearson 5	0.37273	1	39.363	27	11.524	42
40	Pearson 5	0.37274	2	39.363	28	11.524	43
33	Log-Logistic	0.37655	3	19.023	11	13.416	45
22	Gen. Pareto	0.38202	4	14.351	6	N/A	
36	Lognormal	0.38888	5	20.735	14	0.64475	6
35	Lognormal	0.38888	6	20.736	15	0.64475	7
15	Frechet	0.38921	7	20.467	13	19.286	48
32	Log-Logistic	0.39288	8	22.071	16	7.3125	37
50	Uniform	0.40373	9	58.017	38	N/A	
	⋮		⋮		⋮		⋮
19	Gen. Extreme Value	0.44349	17	12.835	3	3.0677	15
	⋮		⋮		⋮		⋮
21	Gen. Gamma	0.5031	38	26.604	22	3.1923	18

#	Distribution	Parameters
19	Gen. Extreme Value	k=-1.5287 σ=0.05349 μ=0.13415
20	Gen. Gamma	k=19.882 α=0.01481 β=0.19817
21	Gen. Gamma	k=0.29072 α=1.0316 β=0.03943
22	Gen. Pareto	k=-5.1617 σ=1.3689 μ=-0.10049

50%, Ce = 0.1 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
33	Log-Logistic	0.38575	1	17.97	11	17.094	44
32	Log-Logistic	0.39655	2	19.914	16	3.5967	24
50	Uniform	0.39673	3	54.511	37	N/A	
1	Beta	0.39798	4	10.925	1	16.815	43
41	Pearson 5	0.40041	5	42.87	30	12.861	40
40	Pearson 5	0.40042	6	42.87	31	12.862	41
22	Gen. Pareto	0.4038	7	14.57	6	N/A	
16	Frechet	0.4039	8	19.047	12	15.13	42
35	Lognormal	0.40391	9	19.398	13	7.5495	37
	⋮		⋮		⋮		⋮
19	Gen. Extreme Value	0.43065	15	12.009	2	1.3211	12
	⋮		⋮		⋮		⋮
21	Gen. Gamma	0.50119	36	25.169	22	1.1065	11

#	Distribution	Parameters
19	Gen. Extreme Value	k=-1.6631 σ=0.00477 μ=0.0139
20	Gen. Gamma	k=19.286 α=0.01514 β=0.0199
21	Gen. Gamma	k=0.28185 α=1.0541 β=0.00361
22	Gen. Pareto	k=-5.8356 σ=0.15762 μ=-0.01059

50%, Ce = 0.2 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
27	Kumaraswamy	0.36706	1	11.539	1	25.292	41
25	Inv. Gaussian	0.37014	2	113.3	43	8.1505	34
40	Pearson 5	0.38284	3	32.206	25	9.3147	35
39	Pearson 5	0.38285	4	32.206	26	9.3149	36
31	Log-Logistic	0.38969	5	18.278	11	16.809	40
49	Uniform	0.39408	6	54.284	36	N/A	
32	Log-Logistic	0.39983	7	20.227	16	3.6698	23
14	Frechet	0.40507	8	19.435	12	25.74	42
15	Frechet	0.40637	9	19.703	13	32.327	43
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.42592	15	11.875	2	0.69251	7
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.50777	37	25.47	21	1.1294	10

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.7051 σ=0.0023 μ=0.00702
19	Gen. Gamma	k=19.884 α=0.01516 β=0.00989
20	Gen. Gamma	k=0.28495 α=1.0734 β=0.00177
21	Gen. Pareto	k=-6.0585 σ=0.08233 μ=-0.00539

50%, Ce = 0.5 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
43	Pert	0.37477	1	43.276	34	N/A	
25	Inv. Gaussian	0.38141	2	59.369	39	7.78	30
39	Pearson 5	0.38461	3	31.97	28	9.3859	31
40	Pearson 5	0.38464	4	31.97	29	9.3873	32
49	Uniform	0.39075	5	54.377	38	N/A	
13	Fatigue Life	0.39368	6	26.251	26	31.248	38
12	Fatigue Life	0.39368	7	26.251	27	31.248	39
31	Log-Logistic	0.39371	8	18.435	11	25.603	37
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.41993	16	11.807	2	0.69775	7
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.42048	17	15.001	6	N/A	
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.50862	39	25.332	22	53.156	43

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.7582 σ=8.7415E-4 μ=0.00284
19	Gen. Gamma	k=20.282 α=0.01669 β=0.00392
20	Gen. Gamma	k=0.30337 α=1.1339 β=6.8854E-4
21	Gen. Pareto	k=-6.3483 σ=0.03479 μ=-0.0022

50%, Ce = 1 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
39	Pearson 5	0.36384	1	30.485	26	8.5794	28
40	Pearson 5	0.36661	2	30.501	27	8.6832	29
49	Uniform	0.38844	3	54.598	38	N/A	
31	Log-Logistic	0.3986	4	18.869	10	27.713	34
23	Gumbel Min	0.40589	5	12.872	2	1.2257	10
32	Log-Logistic	0.40646	6	20.764	16	1.2486	11
15	Frechet	0.40702	7	20.203	13	34.317	35
14	Frechet	0.41184	8	19.994	12	27.672	33
	⋮		⋮		⋮		⋮
18	Gen. Extreme Value	0.41566	11	11.83	1	0.69009	9
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.42718	12	15.234	5	N/A	
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.51844	39	25.801	23	0.11747	6

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.796 σ=4.2162E-4 μ=0.00143
19	Gen. Gamma	k=20.642 α=0.0164 β=0.00196
20	Gen. Gamma	k=0.30106 α=1.1395 β=3.3800E-4
21	Gen. Pareto	k=-6.561 σ=0.01808 μ=-0.00112

50%, Ce = 2 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
40	Pearson 5	0.37183	1	30.436	27	5.9	32
39	Pearson 5	0.37184	2	30.436	28	5.8997	31
49	Uniform	0.38634	3	54.87	39	N/A	
25	Inv. Gaussian	0.39097	4	122.15	46	5.4626	30
23	Gumbel Min	0.40246	5	13.061	2	1.3189	13
31	Log-Logistic	0.40258	6	19.121	11	27.2	36
15	Frechet	0.40877	7	20.409	13	33.844	43
32	Log-Logistic	0.40925	8	21.002	16	1.282	12
18	Gen. Extreme Value	0.41162	9	11.901	1	0.67146	9
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.43352	13	15.487	5	N/A	
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.52129	39	25.895	22	26.786	35

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.8319 σ=2.0354E-4 μ=7.2075E-4
19	Gen. Gamma	k=21.098 α=0.01712 β=9.7295E-4
20	Gen. Gamma	k=0.311 α=1.1768 β=1.6592E-4
21	Gen. Pareto	k=-6.7675 σ=0.00937 μ=-5.6610E-4

50%, Ce = 4 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
50	Uniform	0.3859	1	52.771	38	N/A	
24	Gumbel Min	0.39939	2	13.228	2	1.4167	14
33	Log-Logistic	0.40669	3	19.428	10	29.489	41
19	Gen. Extreme Value	0.40773	4	11.997	1	0.63963	11
15	Frechet	0.40937	5	20.662	13	0.06595	3
32	Log-Logistic	0.41278	6	21.337	16	14.334	38
46	Rayleigh	0.41283	7	40.904	35	4.8615	31
36	Lognormal	0.41373	8	21.094	14	31.15	42
35	Lognormal	0.41373	9	21.094	15	31.15	43
	⋮		⋮		⋮		⋮
22	Gen. Pareto	0.43964	16	15.751	5	N/A	
	⋮		⋮		⋮		⋮
21	Gen. Gamma	0.52265	39	26.17	23	11.363	34

#	Distribution	Parameters
19	Gen. Extreme Value	k=-1.8668 σ=9.8243E-5 μ=3.6273E-4
20	Gen. Gamma	k=21.533 α=0.01756 β=4.8431E-4
21	Gen. Gamma	k=0.3171 α=1.2068 β=8.1283E-5
22	Gen. Pareto	k=-6.9728 σ=0.00485 μ=-2.8641E-4

50%, Ce = 6 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
46	Rayleigh	0.38535	1	38.791	35	5.8209	33
49	Uniform	0.39412	2	52.439	39	N/A	
23	Gumbel Min	0.39775	3	13.311	2	1.479	14
18	Gen. Extreme Value	0.40545	4	12.053	1	0.20987	6
31	Log-Logistic	0.40891	5	19.577	10	29.198	40
15	Frechet	0.40927	6	20.782	12	0.43605	10
35	Lognormal	0.41297	7	21.282	13	33.944	41
34	Lognormal	0.41297	8	21.282	14	33.944	42
32	Log-Logistic	0.41471	9	21.528	15	5.5804	32
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.44321	17	15.911	5	N/A	
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.52236	39	26.303	23	27.631	38

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.8874 σ=6.4108E-5 μ=2.4272E-4
19	Gen. Gamma	k=21.809 α=0.01787 β=3.2201E-4
20	Gen. Gamma	k=0.32101 α=1.2272 β=5.3442E-5
21	Gen. Pareto	k=-7.0961 σ=0.0033 μ=-1.9213E-4

50%, Ce = 8 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
46	Rayleigh	0.39034	1	37.748	36	5.8692	27
23	Gumbel Min	0.39664	2	13.362	2	1.5271	9
49	Uniform	0.39964	3	52.339	40	N/A	
18	Gen. Extreme Value	0.4038	4	12.088	1	0.19605	4
15	Frechet	0.40902	5	20.87	12	0.42972	5
31	Log-Logistic	0.41048	6	19.686	10	28.993	39
35	Lognormal	0.41429	7	21.425	14	33.778	41
34	Lognormal	0.41429	8	21.425	13	33.778	42
32	Log-Logistic	0.41618	9	21.679	15	14.38	32
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.44581	16	16.027	5	N/A	
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.52188	40	26.415	24	27.476	37

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.9024 σ=4.7319E-5 μ=1.8253E-4
19	Gen. Gamma	k=22.0 α=0.01808 β=2.4104E-4
20	Gen. Gamma	k=0.32342 α=1.2418 β=3.9636E-5
21	Gen. Pareto	k=-7.1873 σ=0.00251 μ=-1.4469E-4

50%, Ce = 10 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
46	Rayleigh	0.39335	1	36.957	35	5.908	27
23	Gumbel Min	0.40035	2	13.397	2	1.5669	10
27	Kumaraswamy	0.40179	3	15.849	4	N/A	
18	Gen. Extreme Value	0.4025	4	12.112	1	0.1833	5
49	Uniform	0.4032	5	52.305	40	N/A	
15	Frechet	0.40868	6	20.901	13	0.42507	6
31	Log-Logistic	0.41163	7	19.735	11	28.844	38
35	Lognormal	0.41528	8	21.509	15	33.719	39
34	Lognormal	0.41528	9	21.509	14	33.719	40
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.44786	17	16.119	6	N/A	
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.52069	39	26.417	24	27.295	36

#	Distribution	Parameters
18	Gen. Extreme Value	k=-1.9144 σ=3.7370E-5 μ=1.4633E-4
19	Gen. Gamma	k=22.158 α=0.01851 β=1.9241E-4
20	Gen. Gamma	k=0.32813 α=1.2617 β=3.1410E-5
21	Gen. Pareto	k=-7.2605 σ=0.00203 μ=-1.1610E-4

67%, Ce = 0.01 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
53	Uniform	0.3797	1	54.341	42	N/A	
34	Log-Logistic	0.38913	2	16.378	11	24.05	37
35	Log-Logistic	0.38938	3	16.066	10	15.597	32
30	Kumaraswamy	0.39196	4	15.859	9	N/A	
18	Frechet	0.39477	5	18.469	19	30.575	39
37	Lognormal	0.39492	6	16.525	12	17.354	33
38	Lognormal	0.39492	7	16.525	13	17.354	34
21	Gen. Extreme Value	0.39666	8	11.611	1	1.5644	1
24	Gen. Pareto	0.40067	9	14.033	5	N/A	
26	Gumbel Min	0.40142	10	12.113	2	2.6737	4
	⋮		⋮		⋮		⋮
22	Gen. Gamma	0.48613	39	20.586	23	26.198	38

#	Distribution	Parameters
21	Gen. Extreme Value	k=-1.6378 σ=0.91861 μ=2.6116
22	Gen. Gamma	k=0.35941 α=1.2162 β=0.68286
23	Gen. Gamma	k=20.493 α=0.02034 β=3.6565
24	Gen. Pareto	k=-5.7044 σ=28.928 μ=-1.9675

67%, Ce = 0.1 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
36	Lognormal	0.38954	1	17.803	12	28.878	31
35	Lognormal	0.38955	2	17.803	13	28.878	32
50	Uniform	0.38956	3	48.396	41	N/A	
30	Levy	0.39525	4	30.653	32	2.1718	7
31	Levy	0.39526	5	30.653	33	2.1719	8
15	Frechet	0.39826	6	19.982	19	16.241	24
32	Log-Logistic	0.40317	7	17.035	9	14.859	23
24	Gumbel Min	0.40771	8	12.394	3	1.4564	4
	⋮		⋮		⋮		⋮
19	Gen. Extreme Value	0.41233	10	11.482	1	0.71351	3
	⋮		⋮		⋮		⋮
22	Gen. Pareto	0.43325	12	15.153	6	N/A	
	⋮		⋮		⋮		⋮
21	Gen. Gamma	0.49119	38	21.125	23	25.544	27

#	Distribution	Parameters
19	Gen. Extreme Value	k=-1.829 σ=0.07608 μ=0.27269
20	Gen. Gamma	k=21.949 α=0.0247 β=0.35872
21	Gen. Gamma	k=0.39471 α=1.4392 β=0.05852
22	Gen. Pareto	k=-6.7504 σ=3.4828 μ=-0.20656

67%, Ce = 0.2 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
51	Uniform	0.38667	1	45.346	40	N/A	
36	Lognormal	0.38891	2	18.159	12	30.947	34
37	Lognormal	0.38891	3	18.159	13	30.947	35
24	Gumbel Min	0.40301	4	12.437	2	1.6986	5
19	Gen. Extreme Value	0.40572	5	11.285	1	0.60534	1
34	Log-Logistic	0.40695	6	17.333	8	14.65	25
15	Frechet	0.40792	7	20.493	23	15.972	26
33	Log-Logistic	0.41506	8	18.396	14	12.213	24
39	Normal	0.43548	9	14.403	3	2.6393	10
	⋮		⋮		⋮		⋮
22	Gen. Pareto	0.44406	13	15.512	6	N/A	
	⋮		⋮		⋮		⋮
21	Gen. Gamma	0.4876	37	21.225	24	49.837	40

#	Distribution	Parameters
19	Gen. Extreme Value	k=-1.8979 σ=0.03529 μ=0.13812
20	Gen. Gamma	k=22.435 α=0.02663 β=0.17822
21	Gen. Gamma	k=0.4077 α=1.5357 β=0.02753
22	Gen. Pareto	k=-7.1596 σ=1.8547 μ=-0.1045

67%, Ce = 0.5 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
51	Uniform	0.38773	1	42.45	40	N/A	
36	Lognormal	0.38967	2	18.768	13	34.845	27
37	Lognormal	0.38967	3	18.768	14	34.845	28
19	Gen. Extreme Value	0.39535	4	15.091	4	N/A	
24	Gumbel Min	0.39612	5	12.504	2	2.067	11
1	Beta	0.40222	6	17.093	9	N/A	
42	Pearson 5	0.40756	7	30.445	35	1.4059	5
41	Pearson 5	0.40758	8	30.446	36	1.4057	4
34	Log-Logistic	0.41294	9	17.867	11	26.784	23
	⋮		⋮		⋮		⋮
22	Gen. Pareto	0.45992	26	16.128	8	N/A	
	⋮		⋮		⋮		⋮
21	Gen. Gamma	0.48263	37	21.617	28	46.485	37

#	Distribution	Parameters
19	Gen. Extreme Value	k=-1.997 σ=0.01261 μ=0.05616
20	Gen. Gamma	k=23.111 α=0.02845 β=0.0708
21	Gen. Gamma	k=0.41586 α=1.6504 β=0.01008
22	Gen. Pareto	k=-7.7803 σ=0.81024 μ=-0.04239

67%, Ce = 1 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
19	Gen. Extreme Value	0.3869	1	15.031	4	N/A	
36	Lognormal	0.38843	2	19.215	12	34.17	28
37	Lognormal	0.38843	3	19.215	13	34.17	29
24	Gumbel Min	0.39157	4	12.566	2	0.66243	3
51	Uniform	0.39177	5	42.107	40	N/A	
41	Pearson 5	0.40324	6	30.119	37	1.4399	14
42	Pearson 5	0.40324	7	30.119	38	1.4399	13
34	Log-Logistic	0.41727	8	18.274	10	24.338	26
	⋮		⋮		⋮		⋮
22	Gen. Pareto	0.47282	30	16.71	8	N/A	
	⋮		⋮		⋮		⋮
21	Gen. Gamma	0.48349	35	21.915	27	43.886	34

#	Distribution	Parameters
19	Gen. Extreme Value	k=-2.077 σ=0.00573 μ=0.02841
20	Gen. Gamma	k=23.649 α=0.02989 β=0.03522
21	Gen. Gamma	k=0.42149 α=1.7443 β=0.0047
22	Gen. Pareto	k=-8.3111 σ=0.43423 μ=-0.0214

67%, Ce = 2 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
18	Gen. Extreme Value	0.378	1	14.996	3	N/A	
36	Lognormal	0.39026	2	19.646	12	0.39047	7
35	Lognormal	0.39026	3	19.646	13	0.39047	8
50	Uniform	0.39349	4	39.653	39	N/A	
23	Gumbel Min	0.39438	5	12.64	1	0.29232	5
41	Pearson 5	0.40127	6	29.878	36	1.4324	15
40	Pearson 5	0.40127	7	29.878	37	1.4324	14
25	Inv. Gaussian	0.40985	8	39.938	40	2.272	16
32	Log-Logistic	0.4214	9	18.679	10	23.879	21
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.48177	33	22.21	27	46.126	35
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.48641	36	17.403	8	N/A	

#	Distribution	Parameters
18	Gen. Extreme Value	k=-2.1612 σ=0.00258 μ=0.01436
19	Gen. Gamma	k=24.213 α=0.03137 β=0.01753
20	Gen. Gamma	k=0.42678 α=1.844 β=0.00219
21	Gen. Pareto	k=-8.8997 σ=0.2333 μ=-0.0108

67%, Ce = 4 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
19	Gen. Extreme Value	0.36869	1	14.988	3	N/A	
24	Gumbel Min	0.39441	2	12.739	1	0.39529	4
51	Uniform	0.39527	3	39.285	40	N/A	
37	Lognormal	0.39902	4	20.056	13	4.6627	15
36	Lognormal	0.39903	5	20.056	14	4.6628	16
42	Pearson 5	0.40269	6	29.771	36	1.3762	13
41	Pearson 5	0.4027	7	29.771	37	1.3762	12
1	Beta	0.40306	8	17.964	9	N/A	
34	Log-Logistic	0.4253	9	19.078	11	24.422	23
	⋮		⋮		⋮		⋮
21	Gen. Gamma	0.47843	31	22.496	28	48.455	35
	⋮		⋮		⋮		⋮
22	Gen. Pareto	0.50053	41	18.212	10	N/A	

#	Distribution	Parameters
19	Gen. Extreme Value	k=-2.2488 σ=0.00115 μ=0.00725
20	Gen. Gamma	k=24.805 α=0.03289 β=0.00872
21	Gen. Gamma	k=0.43187 α=1.9489 β=0.00102
22	Gen. Pareto	k=-9.5472 σ=0.12558 μ=-0.00545

67%, Ce = 6 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
18	Gen. Extreme Value	0.36308	1	14.996	3	N/A	
23	Gumbel Min	0.39344	2	12.812	1	35.241	22
50	Uniform	0.39825	3	39.398	40	N/A	
35	Lognormal	0.40308	4	20.286	12	4.612	12
36	Lognormal	0.40308	5	20.286	13	4.6121	13
40	Pearson 5	0.40769	6	26.638	34	34.312	21
41	Pearson 5	0.41641	7	26.821	37	35.571	23
25	Inv. Gaussian	0.42465	8	55.189	45	0.53249	8
32	Log-Logistic	0.42743	9	19.306	9	24.173	19
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.47602	30	22.656	28	0.34121	6
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.50899	41	18.741	8	N/A	

#	Distribution	Parameters
18	Gen. Extreme Value	k=-2.3014 σ=7.1777E-4 μ=0.00486
19	Gen. Gamma	k=25.165 α=0.03379 β=0.0058
20	Gen. Gamma	k=0.43487 α=2.0122 β=6.5091E-4
21	Gen. Pareto	k=-9.9538 σ=0.08748 μ=-0.00366

67%, Ce = 8 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
18	Gen. Extreme Value	0.35902	1	15.007	3	N/A	
28	Kumaraswamy	0.38749	2	16.926	7	N/A	
23	Gumbel Min	0.39447	3	12.873	1	34.913	19
50	Uniform	0.3996	4	39.518	40	N/A	
35	Lognormal	0.40545	5	20.287	15	0.37563	8
36	Lognormal	0.40545	6	20.287	14	0.37563	9
40	Pearson 5	0.40789	7	26.705	37	34.443	17
41	Pearson 5	0.4079	8	26.705	38	34.444	18
25	Inv. Gaussian	0.42285	9	55.773	45	0.53755	10
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.47198	29	22.506	28	0.32248	7
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.51506	41	19.143	9	N/A	

#	Distribution	Parameters
18	Gen. Extreme Value	k=-2.3392 σ=5.1205E-4 μ=0.00366
19	Gen. Gamma	k=29.943 α=0.03142 β=0.00427
20	Gen. Gamma	k=0.4523 α=2.1337 β=4.7434E-4
21	Gen. Pareto	k=-10.255 σ=0.06771 μ=-0.00275

67%, Ce = 10 mg/L

#	Distribution	Kolmogorov Smirnov		Anderson Darling		Chi-Squared	
		Statistic	Rank	Statistic	Rank	Statistic	Rank
18	Gen. Extreme Value	0.35584	1	15.019	2	N/A	
1	Beta	0.36408	2	16.992	6	N/A	
23	Gumbel Min	0.39559	3	12.926	1	34.656	24
49	Uniform	0.40029	4	39.625	38	N/A	
35	Lognormal	0.40712	5	20.564	13	5.9801	15
36	Lognormal	0.40712	6	20.564	14	5.9802	16
40	Pearson 5	0.40816	7	26.761	34	34.576	22
41	Pearson 5	0.40837	8	26.764	35	34.605	23
28	Kumaraswamy	0.41451	9	17.929	9	N/A	
	⋮		⋮		⋮		⋮
20	Gen. Gamma	0.47485	30	22.845	27	0.32169	9
	⋮		⋮		⋮		⋮
21	Gen. Pareto	0.5198	42	19.469	10	N/A	

#	Distribution	Parameters
18	Gen. Extreme Value	k=-2.3688 σ=3.9380E-4 μ=0.00293
19	Gen. Gamma	k=25.633 α=0.03495 β=0.00347
20	Gen. Gamma	k=0.43885 α=2.0939 β=3.7130E-4
21	Gen. Pareto	k=-10.495 σ=0.05552 μ=-0.00221

Appendix IV: Matlab Code for Adsorption Processes

```
function [Ce, kvec, nvec, C0vec, FinalCe, FinalQe] = CeGeneratorFinal(z)
%% UNTITLED Summary of this function goes here
%   Detailed explanation goes here

%%Initialize variables
load kandm.mat
Ce = zeros(size(kandm,1),1);
kvec = zeros(size(kandm,1),1);
nvec = zeros(size(kandm,1),1);
C0vec = zeros(size(kandm,1),1);
Qe=zeros(size(kandm,1),1);
options=optimset('Display','off');

%% Find a given Se for all values
for j=1:length(z)

   m=z(j)

   for i=1:size(kandm,1)
      Kf=kandm(i,2);
      n=kandm(i,1);

            C0 = 0.000004547; %(5%: 0.000004547, 33%: 0.000085941, 50%: 0.001624175, 67%:
0.030695007, 95%: 0.580099709)
            C0vec(i)=C0;

         Ce(i) = real(1000*fsolve(@(x) (C0-x-(Kf*m*x^(1/n))), C0/2, options));
     Qe(i)=(C0*1000-Ce(i))/m;
   end
   FinalCe(:,j)=Ce(:,1);
   Ce = zeros(size(kandm,1),1);
   FinalQe(:,j)=Qe(:,1);
   Qe=zeros(size(kandm,1),1);
end

end
```

Running the program for each percentile influent concentration:

```
clear all
z=[0.0001,0.001,0.01, 0.1, 0.2, 0.5, 1, 2, 4, 6, 8, 10];
z=z*1000;
[Ce, kvec, nvec, C0vec, FinalCe, FinalQe] = CeGeneratorFinal(z);
```

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