End of Life Analysis and Solutions for Dealing with Sewage Sludge and Plastic Waste

by

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ABSTRACT

The topic of this dissertation is the sustainable disposal of waste materials in a way that mitigates risk to human health and the environment. A meta-analysis of organic contaminant concentrations in U.S. sewage sludge highlights the known analytes detected across 106 studies, and juxtaposes these data with a Chinese sludge analysis covering 159 studies, finding that U.S. average concentrations were higher than Chinese concentrations in 26 out of 34 tested organic chemicals. To further investigate the risk that sewage sludge poses when applied on agricultural land mixed with fertilizer as a soil amendment, a sewage sludge risk assessment that for the first time utilized Monte-Carlo simulations was performed to quantify the human health risk of metals present in sewage sludge applied on soils subject to involuntarily ingestion. This study found that while hazard indexes did not indicate a risk to humans for the metals studied, hundreds of other inorganic and organic chemicals are known to be present whose human health risks remain uncertain due to a lack of toxicological data. Among these contaminants are micro- and nanoplastics which contaminate not just sewage sludge but the entire globe. Application of existing models to the world's oceans showed micro- and nanoplastics to constitute an important component of the total global plastic waste inventory, forecasting peak exposures of aquatic organisms (and by extension human populations) to occur in future years irrespective of what policy options will be implemented. A review of disposal options for sewage sludge illustrates the challenge of dealing with waste streams containing persistent or even indestructible contaminants such as perfluorinated organics, mass-produced fossil-fuel derived consumer plastics, and extensively mined toxic metals. The work presented here details the risks, both avoidable and unavoidable, that are

present in the disposal of sewage sludge and plastics. The information presented in this dissertation may inform regulatory actions to promote environmentally responsible disposal and reuse of sewage sludge and highlights the need for industry to transition to the production of more sustainable plastics in order to reduce and ultimately eliminate sources of persistent long-term environmental pollution and their associated adverse human health and ecosystem impacts.

DEDICATION

I would like to dedicate this work first and foremost to my wife, Xiyu (Cora) Li, as well as my family and friends for their continued support throughout my doctoral education. I do not exaggerate when I say that I would never have been able to achieve my goals without your love and encouragement over the years.

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TABLE OF CONTENTS

Page

CHAPTER Page

APPENDIX Page

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

Figure Page

Figure Page

CHAPTER 1

INTRODUCTION

The fate of waste products has been an unresolved environmental challenge for several decades. Many consumer products are designed to be long-lasting and to not break down under physical duress, which is beneficial during the product's useful lifespan and detrimental thereafter when creating long-term pollution. Commonly used products and materials, including toxic metals, mass produced halogenated organics and fossil fuel-based plastics often end up in wastewater which is then conveyed to and processed in municipal wastewater treatment plants (WWTPs). Persistent and nonbiodegradable materials are subject to sequestration in municipal sewage sludge ruing conventional activated sludge wastewater treatment. Since the United States produces about 13.8 million metric tons of dry weight sewage sludge per year (Seiple et al. 2017), the proper disposal of sewage sludge and the contaminants found therein has been a long standing challenge. Prior to the 1980s, sewage sludge was known to contain toxic chemicals and was disposed of primarily by dumping into the coastal water and the ocean. In the late 1980s with passage of the 1988 Ocean Dumping Act banning this convenient disposal option (Environmental Protection Agency 1988b), alternate strategies were needed to deal with the large volume of municipal sewage sludge produced across the United States each year. Banning of the disposal of sewage sludge in the oceans resulted in a diversion of these materials from the aquatic to the terrestrial environment.

1.1 Sewage Sludge Disposal Practices

Since the banning of ocean dumping, the EPA has put forth three alternative disposal methods for sewage sludge, landfilling, incineration and application on land as a soil conditioner and fertilizer. Landfilling of sewage sludge is not a sustainable practice, and any harmful chemicals present in sludge potentially are susceptible to leaching through barriers and to polluting underlying groundwater resources (Dregulo and Bobylev 2021; O'Kelly 2005; Sinha et al. 2010). Incineration, while practiced in both Europe and the U.S., also represents an imperfect solution. While it may be conducted in a fashion that captures and recovers some of the embedded thermal energy, it also is known to create air pollution and climate-impacting carbon dioxide emission (Bauer et al. 2020; Gerstle and Albrinck 1982; Liang et al. 2021; Sullivan and Woods 2000). The last disposal method, application of sewage sludge on land, accounts for just over 50% of modern day sewage sludge disposal practiced in the United States. The premise of land application of sewage sludge is that this material that historically has been considered a hazardous waste, can be converted into a benign and useful material via treatment prior to disposal on land as a soil conditioner and fertilizer. Sewage sludge is rich in phosphorus, nitrogen, carbonaceous organics, and other nutrients that in principle can improve the health of agricultural soils. Yet, there application on soils also can constitute a mechanism of potential pollution due to the large spectrum of persistent and toxic substances that are known to be sequestered therein. These contaminants include both biological and chemical hazards, such as parasites, pathogenic bacteria, viruses, prions, antibiotic resistance genes, as well as toxic metals, pharmaceuticals, personal care products, and thousands of other organic compounds that are known to pose potential

health hazards (Hlisníková et al. 2021; Lassen et al. 2012; Saunders et al. 2008; Sidhu et al. 2019a).

1.2 Legislative History for Sewage Sludge

In order to ensure that sewage sludge in the U.S. is disposed of safely and responsibly, the EPA has performed four national sewage sludge surveys to study the presence of metals and organic contaminants in 1982 (Environmental Protection Agency 1982), 1987-1988 (Environmental Protection Agency 1996), 2001 (Environmental Protection Agency 2002a), and 2006-2007 (Environmental Protection Agency 2009c). However, the only major piece of legislation for which the EPA has utilized these data was the 1993 Part 503 Biosolids Rule, which provided (1) maximum contaminant levels for ten metals in sewage sludge destined for application on land, and (2) minimum treatment technology requirements as a general means to reduce the presence and infectious risk of viable sludge-borne parasites and microbial pathogens (Environmental Protection Agency 1994b). The report that informed this legislation also suggested the use of the term "biosolids" for "treated sewage sludge" meeting the stipulations for legal disposal and application on land, including on agricultural land. The term "biosolids" was selected by wastewater trade associations in a national competition to find a more appealing terminology for a material that previously had been designated a nuisance or even a hazardous waste, municipal sewage sludge (Environmental Protection Agency 1994a). Whereas the terms 'biosolids' and 'sewage sludge' are frequently used interchangeably, an important distinction between the two is that 'biosolids' constitutes not just sewage sludge but specifically treated sewage sludge that complies with current U.S. regulations and can legally be applied on land.

1.3 Data Gaps

Since the implementation of the Part 503 Biosolids rule, a host of new potential human and environmental health hazards have been discovered to be present in sewage sludge, but much research remains to be done to uncover and fully understand the complex chemistry of and risks posed by sewage sludge-borne contaminants that impede or impact the safe disposal and reuse of sewage sludge. One challenge rests in simply compiling all the U.S. sewage sludge data into one, unified database from which researchers can pull information for risk analyses. While a few sewage sludge review studies have been performed over the past few decades, these studies have looked at a limited number of studies ($n < 20$) from the U.S. (Bradley O. Clarke and Stephen R. Smith 2011; Harrison et al. 2006). Since these studies were not comprehensive in their coverage of the U.S., they were limited in their ability to influence U.S. policy. Another important research need is to better understand the impact of Federal legislation and specifically the banning of the production and use of particular chemicals and chemical classes on the composition of sewage sludge and on the concentration of contaminants residing therein. Since sewage sludge constitutes an environmental sink for hydrophobic, toxic chemicals, it can act as a proxy for human and wildlife exposure to harmful chemicals (Venkatesan and Halden 2014c).

Additionally, as has been pointed out by many the U.S. federal (Environmental Protection Agency 2018c), the 1993 EPA Part 503 Biosolids rule has not been updated in decades even though several new biological and chemical threats have been identified and new organic contaminants are known to have been introduced into the environment, wastewater and sewage sludge. While the EPA has produced a significant amount of

concentration data for metals and organic compounds in sewage sludge, they have only performed risk assessments for a small fraction of these compounds, and the risk assessments that were performed were based on data and knowledge that by today's standards frequently are viewed as outdated, inappropriate or both. There exists the potential for more modern approaches to risk assessment to be applied to the most recent concentration data to better understand the risks posed by disposal of sewage sludge on U.S. soils.

One of the more recently discovered health hazards in sewage sludge is plastic waste whether in its originally designed, primary form (e.g., polymeric contact lenses used as vision aids and disposed of into wastewater (REF), or in a modified form and shape brought about by mechanically fragmentation and physical, chemical and/or biological degradation. Of particular concern here are the so-called microplastics, between 1μm and 5mm in length, and nanoplastics, measuring between 1nm and 1μm. Whereas these materials can result from direct chemical manufacturing for use in consumer goods such as cosmetics, building materials, and medical operations (Anderson et al. 2016; Duis and Coors 2016; Hernandez et al. 2017; Koelmans et al. 2015), most of these contaminants are understood to be created as secondary pollutants upon partial destruction of primary macroplastics, such as food containers, drinking bottles and other plastic articles of daily use. As plastics are generally recalcitrant and naturally degrade at extremely slow rates (Gerritse et al. 2020), and at the micro- and nano- scale have toxic properties when ingested (Koelmans et al. 2015), understanding where these particles accumulate and how they may affect human and ecosystem health is of paramount importance. In particular, while some studies have been performed to understand the

concentration of microplastics in the ocean (Erni-Cassola et al. 2019; Lindeque et al. 2020), the inventory of nanoplastics in the global environment has been difficult to quantify experimentally, since capturing equipment such as plastic-trapping nets do not have small enough mesh sizes to reliably retain these sub-microscopic plastics (Lindeque et al. 2020). While some studies have employed models to estimate the total mass of plastic waste entering the ocean (Eriksen et al. 2014; Jambeck et al. 2015), these models have not incorporated the effects of mechanical fragmentation and of other forms of degradation, thereby limiting the applicability and reliability of resultant forecasts. Similarly, many researchers have either modeled or performed experiments to understand mechanical fragmentation and other means of polymer degradation, but the resultant information has not yet been combined and fully integrated into models to inform the inventory and end-of-life of plastics on a global scale (Chubarenko et al. 2020; Kaandorp et al. 2021). Combining these models and experimental data sets would provide valuable insight into potential futures for plastic waste and their impact on the environment based on various approaches to plastic production and use policy that governments could take in the future.

1.4 Primary Goals of This Doctoral Thesis and Research Strategy

With the aforementioned data gaps in mind, the goal of this PhD thesis was to provide insight into the many health hazards posed by the disposal of waste materials in the United States, to summarize the extent of literature on these waste materials, and to arrive at science-based recommendations both for current best practices of waste disposal and needs for additional research.

1.5 Hypotheses

I used the following guiding hypotheses in my doctoral research:

(i) Chapter 2: Because of the increased emphasis on safety, human health, and ecosystem protection in the U.S. relative to the Republic of China, mean concentrations of inorganic and organic chemicals in sewage sludge from the U.S. are lower ($\alpha = 0.05$) than those found in Chinese sludge;

(ii) Chapter 3: Whereas land application of sewage sludge in the U.S. results in an elevated concentration of twelve metals in sludge-amended soils, the resultant overall risk to human health is insignificant and acceptable, as indicated by a hazard quotient analysis for involuntary ingestion of agricultural soils treated with sewage sludge ($HQ << 1$; no significant excess risk);

(iii) Chapter 4: Past and present uses of plastics have created in the world's oceans a large inventory of nanoplastics and microplastics, whose total mass will peak in future years, due to the ongoing continuous disintegration of macroplastics that already have been released into the environment;

(iv) Chapter 5: Revisions are needed for the 503 Rule for Safe Application of Treated Sewage Sludge on U.S. Soils in order to address new threats and new mechanisms of adverse effects that have been uncovered since inception of the 503 Rule.

1.6 Specific Aims

The specific aims for this dissertation were to:

i. Compile data from existing literature on the chemical composition of sewage sludges from China and the U.S., the world's two largest chemical producers;

ii. Perform statistical analyses to understand the difference or lack thereof in organic contaminant loading between U.S. and Chinese sewage sludge

iii. Determine whether attributable human health risk is present in high-risk individuals who involuntary ingest soil that has been treated with sewage sludge based on non-cancerous adverse effects from metals;

iv. Model the impact that plastic production policy has on the fate of both primary and secondary plastic waste in the land and aquatic environment;

v. Identify novel health threats that have emerged in the past few decades regarding the safety of current land application of sewage sludge on agricultural land, and make recommendations for future disposal policy.

TRANSITION 1

This dissertation is focused on the presence of, persistence of, and risk posed by waste materials, specifically municipal sewage sludge applied on U.S. soils and plastic waste extent in the world's oceans.

When this project was first started, only a few review studies existed that had summarized organic contaminant concentrations in the U.S., and none had done a complete assessment of the U.S. history with regard to sewage sludge. Furthermore, a recently published inventory of organic contaminants extant in Chinese sewage sludge offered a unique opportunity to analyze and compare pollutant concentrations present in U.S. and Chinese sewage sludges, two nations representing the largest chemical producers worldwide.

In Chapter 2, organic contaminant concentrations and various metadata from 116 U.S. sewage sludge publications were extracted from their original sources and compiled into a database to make this information available for future research. These data were grouped into standard chemical categories and a select group of 34 analytes which had been studied extensively in both the U.S. and China, thereby allowing for a direct statistical comparison using Welch's *t*-test. A longitudinal analysis also was conducted to better understand the impact (or lack) of government legislation, such as use restrictions or banning of the production of chemicals known to accumulate in municipal sewage sludge.

CHAPTER 2

COMPARATIVE META-ANALYSIS OF ORGANIC CONTAMINANTS IN SEWAGE SLUDGE FROM THE UNITED STATES AND CHINA

ABSTRACT

Characterizing the occurrence of organic contaminants (OCs) of environmental health concern in municipal sewage sludges is essential for safe handling and disposal of these abundant materials. This meta-analysis aimed to (i) summarize the extent of studies performed on the chemical composition of sewage sludges from China and the U.S., the world's two largest chemical producers, (ii) identify chemical groups of priority concern, (iii) quantitatively compare chemical abundance in sludge between nations, (iv) determine longitudinal contaminant accumulation trends in sludge, and (v) identify data gaps with regard to OC concentrations in sludge. A literature search was conducted on concentrations of OCs in U.S. sludges produced during treatment of domestic and industrial wastewater and compared statistically to contaminant levels in Chinese sludge abstracted from a recently established database. Longitudinal trends of OC occurrence were interpreted in the context of national chemical production, usage statistics, and regulations. A total of 105 studies on OCs in U.S. sewage sludge were found, while a total of 159 had been found in China. Among 1,175 OCs monitored for, 23% of all analytes had been monitored in both countries (n = 269), 41% (n = 480) in China only, and the remaining 36% (n = 426) in the U.S. only. On average, concentrations of OCs were 4.0 times higher in U.S. than in Chinese sewage sludge, with the highest detection being observed for alkylphenol ethoxylates. Data from a new binational database on

toxic OCs in sewage sludges suggest and reiterates the need for additional chemical monitoring in both countries, risk assessments for emerging OCs contained in sludges destined for application on land, and stronger enforcement of sludge disposal restrictions in China, where as much as 40% of sludge is currently being dumped improperly.

2.1 Introduction

Sewage sludge is a solid byproduct of the wastewater treatment process, and generally acts as a sink for organic contaminants (OCs) (Bradley O. Clarke and Stephen R. Smith 2011; McClellan and Halden 2010; Patureau et al. 2021; Venkatesan and Halden 2014a). Disposal methods of sludge produced in municipal and industrial wastewater treatment plants (WWTPs) vary significantly depending on the quality of sludge. In the U.S., sludge is disposed of through landfilling, incineration, or as soil amendment (fertilizer), thereby potentially reintroducing these OCs back into the environment. While difficult to estimate, the most recent estimates for dry annual sewage sludge production in the United States and China are 13.84 MT/year and 35.4 MT/year, respectively (Lu et al. 2019; Seiple et al. 2017). Currently, about 47% of U.S. sewage sludges are land applied, and the remaining 53% disposed of either through incineration (15%), or surface disposal (6%) or other methods (32%) (Environmental Protection Agency 2018c). While prior to 2010, about 3% of Chinese sludge was legally applied to land, almost none was incinerated, and over 80% was improperly dumped, China has made significant changes in recent years, with recent data showing about 13% of sewage sludge being used for building materials, 22% being incinerated, 27% landfilled, and just under 40% either land applied or improperly dumped, as it is difficult to distinguish between the two. (Lu et al. 2019; MOHURD 2018; Yang et al. 2015; Zhang et al. 2016).

While the EPA has performed two distinct human health and environmental risk assessments on the disposal of toxic metals and a few classes of organic contaminants in sewage sludge (Environmental Protection Agency 1995, 2002b), there remain 352 pollutants that the EPA has been unable to perform risk assessment for, 61 of which are listed as a hazard or a priority on at least one of the Resource Conservation and Recovery Act hazardous waste listings, the EPA priority pollutant list, or the National Institute for Occupational Safety and Health's list of hazardous drugs (Environmental Protection Agency 2018c). Due to the number of pollutants unevaluated through risk assessment in the U.S. and the continued improper dumping of sewage sludge in China, the monitoring of toxic chemicals in sludge is paramount for environmental practices in both countries.

While many organic compounds degrade easily and have minimal harmful effects on the environment, other more persistent organics have the potential to accumulate in environmental and biological matrices and can eventually cause harm to humans, wildlife, and the environment. In multiple instances, recalcitrant OCs have been found to be taken up from land-applied sewage sludge into plant roots (Engwall and Hjelm 2000; C Wu et al. 2010b; Wu et al. 2012; Wu et al. 2015) and wildlife (Gaylor et al. 2013; Rivier et al. 2019) due to the land application of sewage sludge. In an effort to characterize the presence of OCs in sewage sludge, hundreds of studies have been published worldwide. The U.S. EPA has conducted four major national sewage sludge surveys for organic contaminants in 1982 (Environmental Protection Agency 1982), 1987-1988 (Environmental Protection Agency 1996), 2001 (Environmental Protection Agency 2002a), and 2006-2007 (Environmental Protection Agency 2009c). In the 1987-1988 and 2001 studies, the data was used in part for risk assessments to guide potential

sludge regulation. The 1987 EPA sludge study examined 411 analytes, but later noted that most of the chemicals identified did not have sufficient toxicity data to conduct human health and environmental risk assessments (Environmental Protection Agency 2018b). Of the 50 analytes selected for risk assessment, nine metals were ultimately determined to have concentrations and toxicity levels that merited regulation in final treated sewage sludge. In 2001, the EPA conducted it's third nationwide sewage sludge study, examining 12 polychlorinated biphenyl (PCB) congeners and 17 dioxins and furans in 201 samples from 171 WWTPs, and after performing toxicity studies and risk assessment, the EPA decided that the data did not support a need to regulate the disposal of either PCBs or dioxins in land-applied sewage sludge (Environmental Protection Agency 2003b).

China and the United States are the leading consumers of chemicals and together account for 50 percent of worldwide chemical sales (The European Chemical Industry Council 2014), and therefore are likely to have higher concentrations of OCs in sludge when compared to other countries. Understanding the concentrations of chemicals in sludge from these two countries can also give insight into global trends of OCs in sludge. Past reviews of OCs in sewage sludge have not had access to data from Chinese sewage sludge studies, as over one-third of those studies were published in Mandarin Chinese and were therefore not available to the international research community. In 2016, a comprehensive review of OCs found in Chinese sewage sludge was published (Meng et al. 2016). In this review the sludge data originally published in Mandarin Chinese was compiled and translated into English, allowing the international community access to the data. This database has been utilized by juxtaposing it with a U.S. OC sludge database

that was created for this review, thereby providing a tool by which researchers can compare the OC burden in sewage sludge from the world's two largest chemical consumers.

2.2 Methods

2.2.1 Identification

An existing single-country municipal sewage sludge database was expanded and compared to similar data from a previous study done in China (Meng et al. 2016). To expand on this database, using a modified version of the Preferred Reporting Items for Systematic Reviews and Meta-Analyses guidelines, three different approaches were used to find studies that fit within our criteria (Figure 13). In June of 2019, web searches were performed searches for the Web of Science, Google Scholar, and Arizona State University's OneSearch database using the format ("sewage sludge" OR "biosolids") AND ("pollutant 1" OR "pollutant 2" OR "pollutant 3" . . .), in which the pollutants used were each of the 749 compounds found in the Chinese OC database. Secondly, additional records identified from an existing database on sludge-related articles not captured by the search were included in the preliminary identification. Any study was excluded if it did not include at least one statistical data point for an organic contaminant concentration in U.S. municipal sewage sludge. No limitations on date of publication were utilized. Duplicates between any of the databases searched and the internal sludge article database were removed. As the third approach for finding articles, each of the remaining journal articles were forward- and back-citation checked for additional articles on OCs in U.S. sewage sludge.

The authors are aware of the potential for a lack of rigorous search criteria and methodology to lead to publication bias, wherein the selected journal articles are not representative of the whole field of literature (Sutton 2005). This could be due to the authors choice of databases to search, due to the choice of search terms, or due to the methods for filtering out unrelated publications. While it is certainly not possible for a body of literature to be fully indexed within one search, certain precautions have been taken, including combing through each initial search result by hand to determine eligibility for inclusion. Confirmation bias may also play an important role (Dickersin 2005), although this is potentially mitigated because only the raw chemical data from sewage sludges were used for this publication. Additionally, no statistical tests performed by the studies were included in the final statistical analysis from this study.

From each of these publications, statistical, temporal, and spatial metadata were recorded as available. If the sampling time was not reported, a sample collection date equal to the publication date minus three years was applied, as three years was the average time between sample collection and publication for the publications that included this information. For OCs with non-detects (ND), a concentration of zero was substituted for use in mean and median equations. Typically, a more sophisticated method of interpreting NDs, typically by dividing the method detection limit (MDL) by 2 or the square root of 2, is employed. However, as many of the older studies did not include details on the MDL, the authors decided not to include it in the meta-analysis in instances where provided. The sample locations were recorded at the highest spatial resolution available. All concentrations were converted to units of micrograms per kilogram of dry weight for uniformity, however, the 1982 first EPA nationwide sludge study only

provided wet weight concentrations. To address this, a water content of 90% was assumed to convert to dry weight. Detection frequencies that were missing from the publication were labelled NA. The median was used as a substitute for the mean in a few instances where the mean was not provided. These chemicals were grouped into thirty-two primary groups of chemicals, and the remaining chemicals were placed into an "Other" category. The geometric mean of the U.S. to China average concentration for each OC was used to calculate an overall ratio between the two countries. An estimate of total global publications related to OCs in sewage sludge and biosolids was performed by a year-by-year search of Google Scholar for "organic AND (biosolids OR 'sewage sludge')" Information on U.S. and Chinese sludge regulations was retrieved from the EPA website and from a review paper on Chinese sludge regulations (Yang et al. 2015).

2.2.2 Statistical Analysis

Welch's *t*-test was performed in Microsoft Excel 2016 to compare the means between U.S. and Chinese sewage sludge OC concentrations for each contaminant, which served as the summary statistic for this analysis. This test is a specific application of the Student's *t*-test that is more robust when the sample groups have potentially unequal variances and unequal sample sizes. While significant values of α = 0.05, 0.01, and 0.001 were used to evaluate the difference in mean concentrations of priority pollutants between the U.S. and China, the raw p-values were also provided directly in Figure 4.

2.3 Results

2.3.1 Temporal Distribution of Studies

The preliminary literature search yielded over 1,500 sludge-related journal publications for OCs. After filtering using the prior stated methodology, a total of 105

peer-reviewed publications remained (Figure S1), spanning over 40 years of research and including four national EPA sewage sludge studies (Figure 1A). In contrast, existing international sludge review papers have included no more than 20 USA sludge studies each (Bradley O. Clarke and Stephen R. Smith 2011; Harrison et al. 2006). The earliest available U.S sludge publication on organic contaminants was a 1976 study that analyzed municipal sewage sludges for dieldrin and total PCBs (Furr et al. 1976). The U.S. publication rate for sludge studies has tapered off in recent years, being surpassed by China's publication in the mid-2000s. Between 2011-2015, China maintained a publication rate of 23 studies per annum, almost four times greater than the U.S. annual publication rate (6) for sludge studies on OCs over the same time period. These publications that have data on OC concentrations in sludge were preceded by a general publication interest in OCs in sewage sludge, which increased from 1994 to 2001, and has remained relatively steady since then.

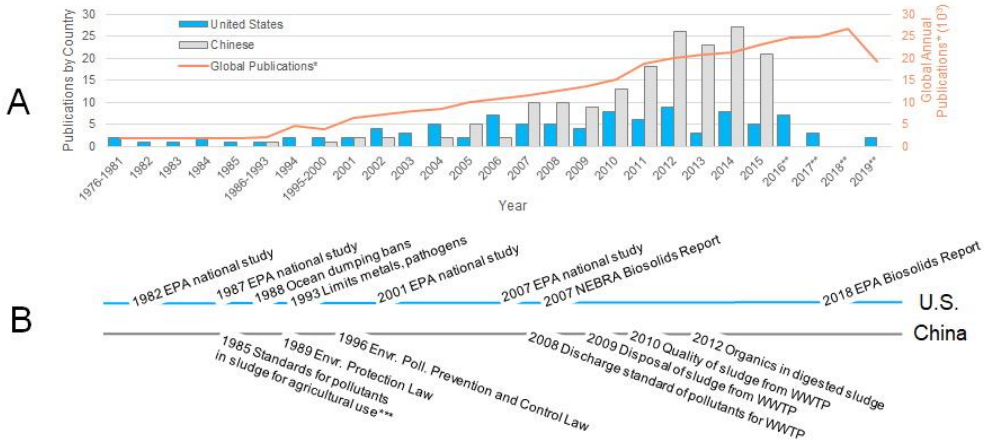

Figure 1. A) Temporal Distribution for Sewage Sludge Studies for Organic Contaminants, and International Trendline for Biosolids Related Studies. B) Timeline for U.S. And Chinese Sewage Sludge Regulations.
NEBRA North East Biosolids and Residuals Association.
*Found searching Google Scholar for "organic AND (biosolids OR 'sewage sludge')"
**No information provided for Chinese studies. U.S. studies through July 2019

***Chinese regulations sourced from Yang et al, 2015

Table 1. Classes of Organic Contaminants (OCs) Analyzed in U.S. Municipal Sewage Sludge

Compound Class	Number of Studies (*N*)	Number of Analytes (*n*)
Antibiotics	10	41
Pharmaceuticals	16	65
Steroids and Hormones	9	35
Benzophenone and Benzotriazole Compounds	2	6
Siloxanes	2	6
Synthetic Musks	10	15
Triclosan, Triclocarban, and Derivatives	33	13
Parabens	2	10
Organochloride Pesticides	6	36
Organophosphate Pesticides	1	45
Polychlorinated Biphenyls	8	158
Polychlorinated Napthalenes	2	1
Alkylphenol Ethoxylates	11	16
Phenol	5	10
Bisphenols	6	18
Polybrominated diphenyl ethers	21	47
Novel brominated flame retardants	4	8
Dechlorance-plus	2	2
Perfluoroalkyl and polyfluoroalkyl substances	8	21
Phthalic acid esters/plasticizers	6	6
Volatile aromatic hydrocarbons	2	23
Aromatic Amines	2	6
Polycyclic Aromatic Hydrocarbons	10	23
Chlorinated Hydrocarbons	2	4
Polychlorinated dibenzo-p-dioxins and -dibenzofurans	6	33
Polybrominated dibenzo-p-dioxins and -dibenzofurans	1	7
Nitrosamines	4	11
Fungicides	6	2
Solvents	2	13
Melamine-based resins	1	4
Other	11	45

2.3.2 Spatial Distribution of Sample Locations

Of the 105 studies found with data from the U.S., about one third (*n* = 37, 35%) were either national studies or did not provide sample locations. The remaining 64 studies were focused on specific geographic areas, with a significant portion from EPA Region 5: the Mid-Atlantic (*n* = 18, 17%), some from EPA Region 3: the Midwest (*n* = 12, 11%), smaller portions for both EPA Region 2 and EPA Region 9: the Southwest (*n* = 11, 11%; *n* = 11, 11%, respectively), and the few remaining studies from each of the other EPA regions. The national studies provide some sample coverage of the less-reached EPA regions, although no studies with samples from Alaska, Hawaii, Puerto Rico, or the U.S. Virgin Islands have been reported. Spatial distribution of the Chinese sewage sludge studies have already been reported in a previous study (Meng et al. 2016).

2.3.3 Sewage Sludge Regulation

The only federal regulations in the U.S. that affect sewage sludge disposal at the federal level are the 1972 Clean Water Act, the 1988 Ocean Dumping ban, and most recently the 1993 40 Code of Federal Regulations Part 503 rule that set the framework for sewage sludge regulations (Environmental Protection Agency 1988b, 1994b; United States 1972). To inform these as well as potential future regulation, the EPA conducted four national sewage sludge studies (1982, 1987, 2001, 2006/2007), but only the 1987 study's data was used in creating the 1993 regulations (Figure 1B). The 2001 study concluded in a decision not to institute limits for PCBs in applied sewage sludge, and the 2006/07 study has had no formal risk assessment performed. In contrast, China has had

36 separate regulations regarding sewage sludge (Yang et al. 2015), but has not had a government-run national survey to inform regulation.

2.3.4 Comparison of Contaminants Studied in US and Chinese Sludge

In U.S. sludge, 310 (43%) of OCs analyzed were non-halogenated (Figure 2A). This is comparable to the Chinese study, in which 335 (45%) of the analytes tested for in sludge were non-halogenated. Almost half of the U.S. chemicals were chlorinated (*n* = 315, 43%), of which more than half (*n* = 158) were PCB congeners tested for in the 2001 EPA sludge study (Environmental Protection Agency 2002b). In contrast, a smaller percentage of chemicals were fluorinated (*n* = 38, 5%) or brominated (*n* = 67, 9%) when compared to the Chinese study (*n* = 83, 11%; *n* = 103, 14%, respectively). This is partially due to the U.S. lack of data for hydroxyl- and methoxylated-polybrominated diphenyl ethers (OH-PBDEs and MeO-PBDEs, respectively), and due to having comparatively less data available for perfluoralkyl and polyfluoroalkyl substances (U.S.: *n* = 21; China: *n* = 37). In addition, a total of eight chemicals (citalopram, fipronil, naled, leptophos, and four of their metabolites), contain more than one kind of halogen and have been detected in U.S. sludge.

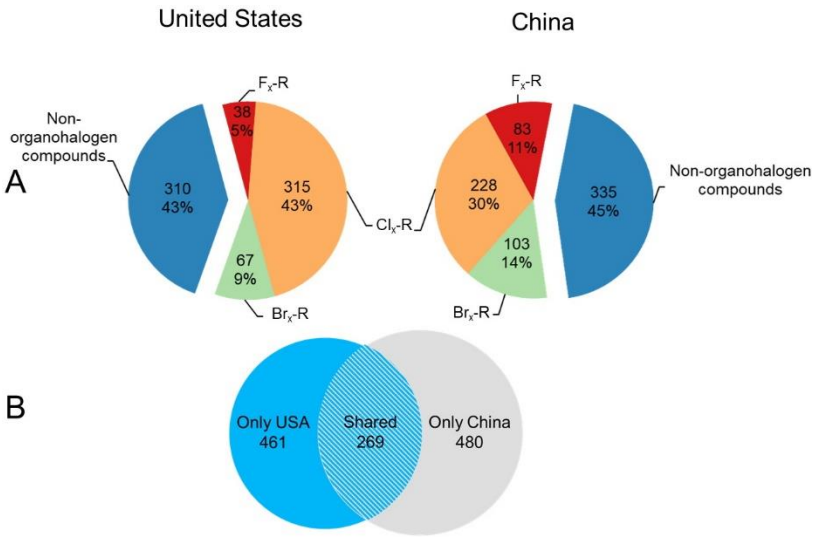

Figure 2. Comparison of a) Halogenation of Organic Contaminants Found in U.S. And Chinese Sewage Sludge. F_x-R: Fluorinated Compounds. Cl_x-R: Chlorinated Compounds. Br_x-R: Brominated Compounds. B) Number of Chemicals Found in U.S. And Chinese Sewage Sludge

A total of 730 organic chemicals belonging to 29 classes in 105 U.S. sludge studies have been found in the literature (Figure 2B). The most studied classes of chemicals were triclosan, triclocarban, and their metabolites (*n* = 34, 32% of studies), polybrominated diphenyl ethers (*n* = 20, 19%), pharmaceuticals (*n* = 16, 15%), alkylphenol ethoxylates (*n* = 11, 10%), antibiotics (*n* = 10, 9%), synthetic musks (*n* = 10, 9%), steroids and hormones (*n* = 9, 9%), polychlorinated biphenyls (*n* = 8, 8%), and perfluoralkyl and polyfluoroalkyl substances (*n* = 9, 9%). Due to many studies including sludge concentration data for more than one chemical class, the sum of *n* is greater than *N* = 105. However, of the 730 chemicals detected in U.S. sludge, only 206 (30%) of these chemicals have been detected both in the U.S. and in China. Chemical groups for which sewage sludge data exists in China but not in the U.S. include the following: OH-PBDEs, MeO-PBDEs, *n*-heterocyclic carbenes, and quaternary ammonium compounds (QACs),

although it is important to note that MeO-PBDEs, while analyzed, have not been detected in Chinese sewage sludge to date. Chemicals and chemical groups for which no data from the past five years exists for U.S. sewage sludges include the following: dechlorance plus, hexabromocyclododecane, most polybrominated diphenyl ethers (PBDE), phenol compounds, steroids and hormones, synthetic musks and fragrances, PCBs, phthalic acid esters (PAEs), volatile aromatic hydrocarbons (VAHs), aromatic amines (AAs), polycyclic aromatic hydrocarbons (PAHs), and dioxins and furans.

2.3.5 Concentration Levels

Five chemicals, octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6), ketoprofen, and PCB-11, were each found to have a mean concentration more than two orders of magnitude higher in Chinese municipal sewage sludge than in the United States. D4, D5, and D6, (U.S.: 6.0, 0.8, 9.4; China: 1189, 1876, 1678 µg/kg, respectively) are cyclic siloxanes, and are widely used in biomedical and cosmetic applications. Ketoprofen, an analgesic and antipyretic, is the only pharmaceutical of the 18 found in both countries that had a difference in mean sludge concentration of more than two orders of magnitude (U.S.: 8.6 µg/kg; China: 1578 µg/kg, respectively). PCB-11 was the only one out of 44 shared PCB congeners that varied by more than three orders of magnitude (U.S.: 11.4 µg/kg; China: 4478.4 µg/kg), having concentrations much higher in Chinese sewage sludge.

Several chemicals were found to have significantly higher concentrations in U.S. sludge than in China. One of the main components of OctaBDE, BDE-196, had mean concentrations of 132.7 µg/kg in the U.S. and 0.8 µg/kg in China. One novel brominated

flame retardant, 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE), had an average concentration of 1762 µg/kg in the U.S. and 0.95 µg/kg in China. Norgestrel, a steroid used in female contraceptives, had average concentrations in the U.S. of 344.5 µg/kg, while concentrations were significantly lower in China (0.091 µg/kg). Chlordane, an insecticide, had an average concentration of 244.5 µg/kg in the U.S. and 1.08 µg/kg in China. Lastly, two musks, galaxolide (HHCB) and tonalide (AHTN), had concentrations over three orders of magnitude greater in the U.S. than in China (U.S.: 25,300 µg/kg and 20,333 µg/kg; China: 27 µg/kg and 6.2 µg/kg, respectively). On average, OC concentrations in U.S. sludge were 4.0 times greater than in Chinese sludge. The resulting power regression equation of the log-log data for Figure 3 was $y = 0.9054x^{0.6772}$ (x = U.S. concentration, y = Chinese concentration, $R = 0.60$). The exponent on x is less than 1, which indicates that on average, OC sludge concentrations are higher in the U.S. than in China (Figure 3).

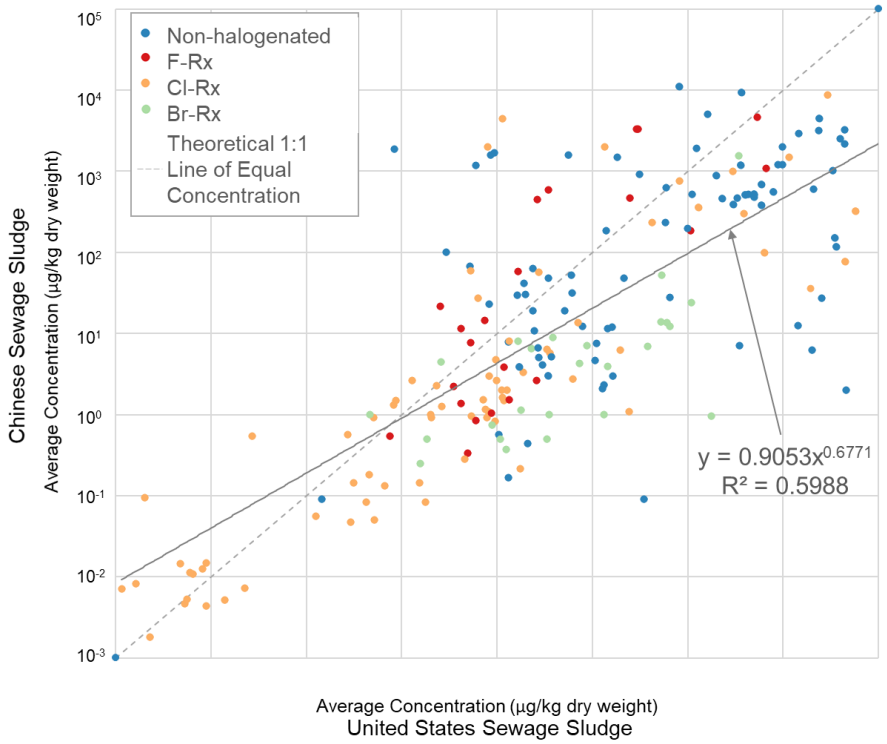

Figure 3. Log-scale Plot of the Average Concentrations for 206 OCs Found in U.S. And Chinese Sewage Sludge

2.3.6 Comparison of Total Concentration Across Chemical Classes

The chemicals with the greatest mean concentrations in U.S. sewage sludge were alkylphenol ethoxylates (APEOs), phthalic acid esters (PAEs), and polycyclic aromatic hydrocarbons (PAHs), while dioxins and furans were the lowest in concentration. Out of the 34 representative chemicals (Figure 4), the United States had higher mean concentrations than China for 26 of these chemicals and was more than an order of magnitude greater than China in 8 of these. Of these 34, the mean concentrations between U.S. and China were significantly different with $p < 0.05$ for seventeen chemicals, $p < 0.01$ for fourteen chemicals, and $p < 0.001$ for ten chemicals. The representative

chemicals that had the greatest difference between U.S. and China were testosterone, BDE-47, and PFDA (U.S.: 131, 610, 26.1; China: 2.3, 13.6, 1.0 µg/kg, respectively).

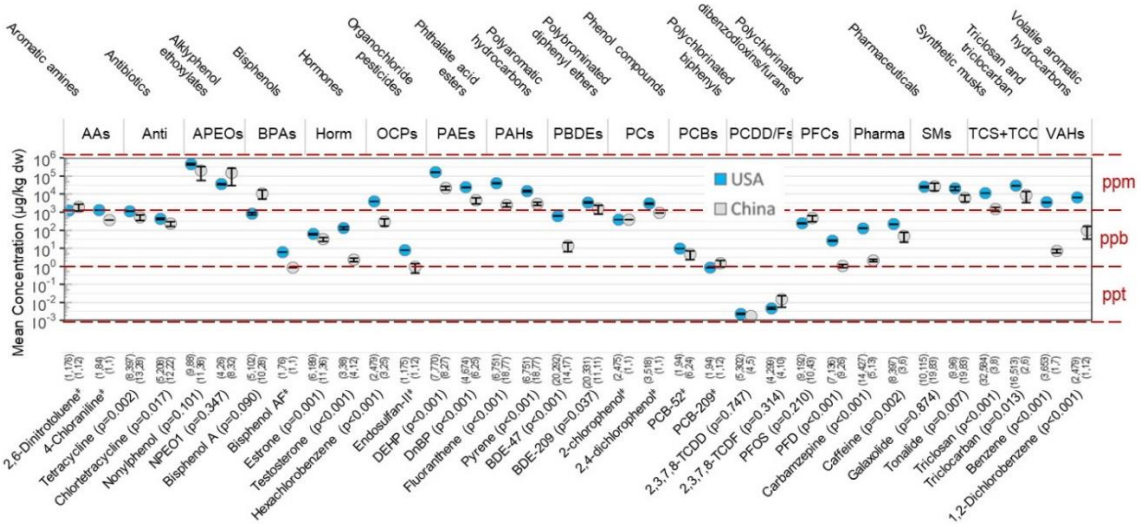

Figure 4. Comparison of Concentrations of Major Contaminants in Sludges from the U.S. (Blue) and China (Gray). (x, y) Indicates a Total of x Studies That Contain Data for a Total of y Samples for That Chemical. Standard Error Bars Shown in Black.
ǂ Unable to Do Statistical Comparison Due to China Having Only One Sample Available

2.4. Discussion

2.4.1 Binational Differences in Publication Rate

A few possible reasons could explain the difference in total number of sludge studies between U.S. (n = 105) and China (n = 159). First, the lack of a Chinese equivalent to the EPA-sponsored national surveys could have driven more studies to be published at the university level to understand OCs in Chinese sludge. Additionally, the trends in government funding for environmental protection are different. Chinese funding for environmental protection projects has increased steadily over the past two decades, increasing from less than 15 billion USD per year prior to 2001, to over 150 billion USD in 2013 (Meng et al. 2016). In contrast, U.S. funding for the EPA has stagnated at about seven to nine billion USD per year for the past 15 years, and is projected to drop to below

six billion USD per year for the following five years (White House Office of Management and Budget 2017). A combination of these can partially explain why China has published over 50% more studies on sewage sludge than the U.S has published. Similarly, differences in government structure result in a difference between the number of federal sludge-related regulations in the U.S. (n = 3) and in China (n = 36). In total, 4 laws, 10 national standards, 15 ministry standards, and 7 technical regulations and guidelines for sludge management have been created by five administrative agents that oversee sludge disposal in China (Yang et al. 2015). This high number is due in part to China having five separate sewage sludge administrative agents, while in the U.S. sludge disposal is regulated primarily by the EPA.

2.4.2 Binational Differences in Analytes Detected

Halogenation of organic chemicals is a relevant sorting mechanism due to halogenated chemicals generally being more toxic and recalcitrant than their non-halogenated counterparts (Ghosal et al. 1985). The U.S. and China have detected approximately the same percentage of analytes when organized by halogenation. In both countries, about 40% of the chemicals with sludge data are non-organohalogens and belong to a variety of the chemical classes used in this study. China has studied about twice as many fluorinated OCs (U.S.: n = 38, 5%; China: n = 83, 11%), most of which are accounted for in a greater number of antibiotics and per- and polyfluorinated chemicals (PFCs) studied (U.S. n = 41, 21; China: n = 86, 59 respectively). China has also studied 38 more brominated compounds, the majority of which are QACs, OH-PBDEs, and MeO-PBDEs (China: n = 27, 9, and 9 respectively). Of these, MeO-PBDEs have been tested for but not detected in Chinese sludge, but OH-PBDE sludge

concentrations have been found within the same order of magnitude as their parent PBDE congeners. QACs are used as disinfectants, and have been detected in Chinese sludge at concentrations between 38,000 to 154,000 μg/kg (total QACs) (Meng et al. 2016). Even though China has not undertaken a national sludge survey before, China has studied a greater number of OCs in sludge, likely due to China's greater raw number of studies. Just under half (n = 206) of the 461 U.S. chemicals that have not been tested in China belong to just a few classes: pharmaceuticals, steroids and hormones, organochloride pesticides, and PCBs. In contrast, China's unique chemicals are more spread evenly across the chemical classes, even including six classes of chemicals, synthetic phenolic antioxidants (SPAs), short-chain chlorinated paraffins (SCCPs), QACs, n-heterocyclic carbenes, napthenic acids, and organometals, none of which have been tested in U.S. sludge before.

The lack of data on these classes can be partially explained through the EPA national sewage sludge studies, the two most recent of which targeted specific classes of chemicals considered to be higher risk than the above listed classes. In 2001, the EPA national sludge survey targeted dioxin and dioxin-like compounds, and in 2006/07 focused on antibiotics, steroids and hormones, and flame retardants, (Environmental Protection Agency 2002a, 2009c). Thus, while the sample sizes for these studies are significantly higher than other studies in either the U.S. or in China, the breadth of chemical classes analyzed in the U.S. is narrower than in China. This highlights an important difference between the U.S. and Chinese sludge data that is available—China has a greater number of studies (U.S.: n = 105, China: n = 159) and has tested more chemical classes than the U.S. has (U.S.: n = 29, China: n = 35)., but the U.S. has the

benefit of having four national campaigns that offer strong geographic sample distribution and sample sizes ranging from n = 50 to 174, while the largest Chinese study had n = 60 samples (Ruan et al. 2012).

2.4.3 Priority Chemical Classes for the United States

As sewage sludge continues to be applied on land in the United States, it is important to understand as completely as possible the constituents that make up the sludge before application. The United States specifically would benefit from studies characterizing these six chemical classes, SPAs, SCCPs, QACs, n-heterocyclic carbenes, napthenic acids, and organometals, for which the U.S. currently has no data on their presence in sewage sludge. SPAs, and specifically 2- and 3-tert-butyl-4-hydroxyanisole, tert-butylhydroquinone, and 3,5-di-tert-butyl-4-hydroxytoluene, are used extensively in several industries, but primarily the food industry (Perrin and Meyer 2002). SPAs have been demonstrated to be toxic to some animal tissues (Horvathova et al. 1999; Yu et al. 2000), may have additive carcinogenic effects (Hirose et al. 1998), and several of them are listed in the EPA's high-production volume (HPV) database (Liu and Mabury 2018). Organometals would likely be detected in U.S. sewage sludge, as the 2015 U.S. total consumption of organometallics was more than China's total consumption, and the U.S. leads the world particularly in organoaluminums, which are mostly used as catalysts (IHS Markit 2016). While the toxicity of most organometals is not well characterized, several organometals have been shown to be potentially genotoxic, carcinogenic, and neurotoxic (Dopp et al. 2004). SCCPs are used as lubricants and coolants in metal, and have been demonstrated to have chronic toxic effects in both humans and wildlife, and particularly aquatic organisms (Ali and Legler 2010). As of 2007, the total mass of SCCPs and

medium-chain chlorinated paraffins produced in the U.S. was estimated to be 100 million pounds, of which about one-third was SCCPs (Environmental Protection Agency 2009b). Until these are characterized, little risk assessment can be done to understand the potential risk they may pose to humans and the environment through the application of sludge onto agricultural land.

2.4.4 Temporal Trends of Contaminant Concentrations

In some cases, the regulation of OCs can be shown to affect the sludge concentrations over time. The clearest example of this is in total PCBs (Figure 5A). Due to their recalcitrance and toxicity, the EPA banned the production of all PCBs in 1979, and regulated any substance that contains more than 50 ppm of PCBs (Environmental Protection Agency 1979). The effects of this policy were demonstrated in Figure 5A, where a steady decrease can be seen from the first PCB sludge study (Furr et al. 1976), to the most recent PCB data from the third EPA national sludge survey (Environmental Protection Agency 2002a). Another example of production management decreasing sludge concentrations is with PFOS. The United States primary producer of PFOS, 3M, announced a voluntary phase-out of PFOS in their products starting in 2000 due to PFOS's persistence in human and animal tissues (Environmental Protection Agency 2000). As of 2002, 3M had ceased production of PFOS, which is demonstrated by a decrease in U.S. sludge PFOS concentration over time. However, recent data comes from only one Mid-Atlantic WWTP (Armstrong et al. 2016), and thus is not representative of the country as a whole. More recent studies with samples from more locations are required in order to fully understand the current status of PFOS in sludge. Although PFOS has not been reported to be mass-produced in the U.S. since 2002, it may still be

produced in lesser quantities that are not required to be reported, and may be present due to previously made or imported PFOS products (Environmental Protection Agency 2015).

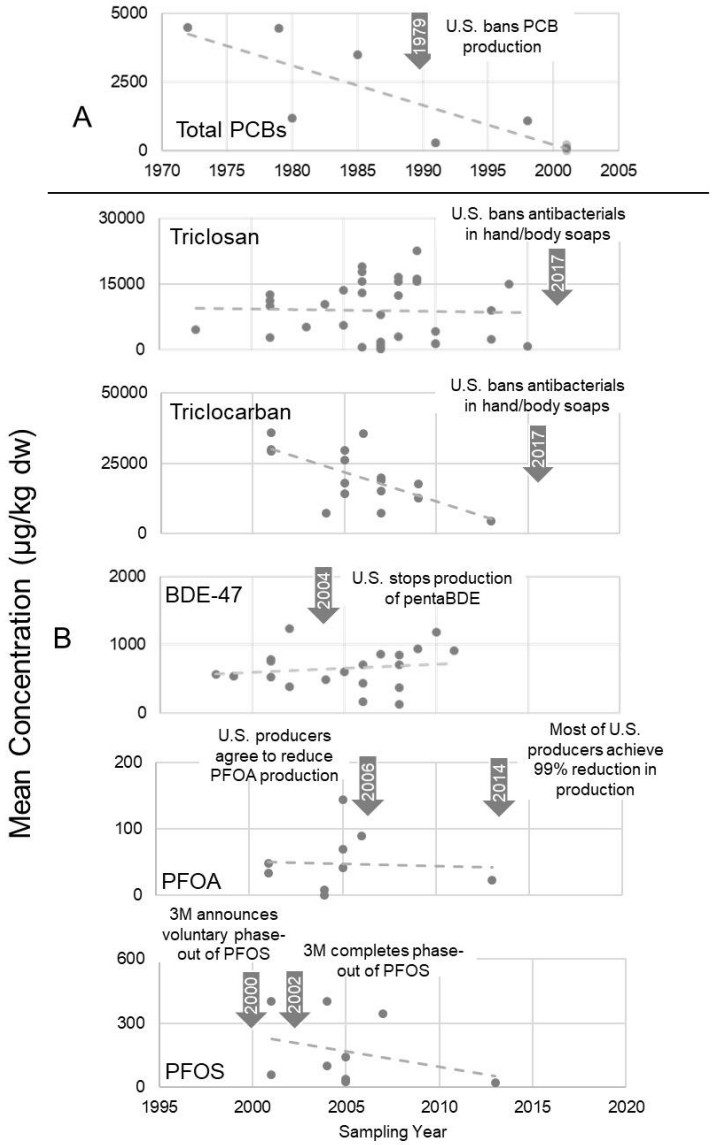

Figure 5. Temporal Trends of Certain OC Concentrations in U.S. Sewage Sludge (Dashed Line Is Trendline; Dots Are Individual Study Results). BDE, Bromodiphenyl Ether; PCB, Polychlorinated Biphenyl, PFOA, Perfluorooctanoic Acid; PFOS, Perfluorooctanesulfonic Acid

However, sometimes regulation has either not made an impact on sludge concentration, or has not had enough time or enough studied samples to see a significant

decrease. In 2006, the eight major producers of PFOA in the U.S. signed an agreement to participate in the EPA's PFOA Stewardship Program, with the goal of reducing PFOA production and emission by 95% by 2010, and end of production and emission by 2015. With the exception of one producer, the participating companies achieved more than 99% reduction in PFOA production and emission by 2014 (Agency for Toxic Substances and Disease Registry 2015). Unfortunately, data for PFOA in sludge is sparse, with only one study being published in the past decade (Figure 5B) (Armstrong et al. 2016). Thus, while data prior to PFOA regulation seem to maintain fairly constant concentrations, the impact of regulation is not clear from the available data. As with PFOS, this could be affected by already existing PFOA products as well as imported PFOA. Similarly, BDE-47 is the primary constituent of pentaBDE, making up between 38 to 42% of the total mass (La Guardia et al. 2006). In 2006, the EPA enacted the Significant New Use Rule, which required any new pentaBDE production pass EPA evaluation prior to manufacture (Environmental Protection Agency 2006). As of 2017, 10 U.S. states have banned or restricted production of pentaBDE (Safer States 2017). Despite these efforts, sludge concentrations of pentaBDE have continued to remain relatively constant since the late 1990s when it was first introduced. This could be due to a combination of its recalcitrance as well as it being formed by the breakdown of higher ordered brominated diphenyl ethers. A previous study has found that through aerobic degradation of PBDE/BDE in sludge, BDE-47 concentrations can increase slightly for the first several months, likely due to debromination of higher-ordered congeners (La Guardia et al. 2006). In one sample, BDE-47 did not significantly decrease over the study period, while other congeners decreased in concentration (Stiborova et al. 2015). The EPA phase-out

for decaBDEs was later than pentaBDE and octaBDE, and took place over a 3-year period ending in 2013 (Environmental Protection Agency 2009d). Thus, it may take more time for PBDE congeners to be shown to decrease in sludge. Lastly, triclosan (TCS) and triclocarban (TCC) are antimicrobials that have shown relatively consistent sludge concentrations over the past decade. In 2016, the FDA issued a ban on these as well as other antimicrobials in hand soaps and body washes (Food and Drug Administration 2016). The ban went into effect in September of 2017, and further tracking in sludge would help elucidate how effective regulation is at mitigating the presence of persistence chemicals such as TCS and TCC. Thus, while existing sludge data can provide insight on the efficacy of regulation of older chemicals such as PCBs, future studies involving these chemicals are needed to shed light on the effect of more recent regulation on their presence in sludge.

2.4.5 Binational Comparison

Chinese sludge concentrations were less than U.S. sludge concentrations for 74% (n = 153) of the 206 chemicals which both countries had detected in sewage sludge. The most notable exception to that is Bisphenol A, which had a mean concentration in Chinese sludge of 10,900 µg/kg, and only 830 µg/kg in the United States. These data came from a few studies (U.S.: n = 5; China: n = 10) with samples collected between 2003 to 2015. Looking at other factors, the opposite mean concentration ratio would be expected to be present. In 2003, the estimated net usage of Bisphenol A in the U.S. was 1.02 million tonnes, while in China it was only 139,000 tonnes (Gao 2003), a ratio opposite to what the sludge concentrations show. The disparity in mean BDE-196 concentration (U.S.: 132.7 µg/kg; China: 0.8 µg/kg) can be largely explained by the fact

that China has never produced or used OctaBDE, for which BDE-196 is one of the primary constituents (Chen et al. 2012). Siloxanes were another group of chemicals for which Chinese sludge had greater concentrations than the U.S. As of 2002, the average annual production for cyclic siloxanes, including D4-D6, was almost twice as large in China as in the U.S. (800,000; 470,000 tons, respectively) (Tran et al. 2015; Xu et al. 2015). The sludge shows an exaggerated version of the same relationship – Chinese sludge concentrations were between 2-3 orders of magnitude greater than the U.S. However, the sludge data for the U.S. was limited to one study in south Florida, and was calculated using measured gaseous phase concentrations and air-water and water-sludge partition coefficients (Surita and Tansel 2014). PCB-11, the congener in which China's concentration is over three orders of magnitude greater than the U.S., is an exception, not a rule for PCBs. In the case of PCB-11, the Chinese concentration is from only one sample near a chemical industry zone, while the U.S. concentration is the average of 94 samples across the U.S. Other PCB congeners tested from the same Chinese sample were similar to U.S. concentrations, and had more samples available for calculations. In addition, recent studies have suggested that PCB-11 can be inadvertently created during the production of yellow pigments (Shang et al. 2014; Vorkamp 2016). Future studies should be concentrated on similar chemicals and should have an increased sample size as well as geographic region covered, before more analysis can be made.

Chlordane, for which the U.S. mean sewage sludge concentration was about 200 times that of China, was banned by the EPA in 1988 (Agency for Toxic Substances and Disease Registry 1994). It makes sense then that U.S. concentrations may be greater than Chinese for chlordane, especially since the U.S. samples tested for chlordane come from

when chlordane was still in use. It was found that norgestrel, used in female hormonal contraceptives, is over three orders of magnitude greater in concentration in U.S. than Chinese sludge. While data about individual contraceptives is hard to obtain, recent pill contraceptive use in women has been about 10 times greater in the U.S., with 1.2% of married or in-union Chinese women using pill contraception, while 16% of U.S. married or in-union women use pill contraception methods (United Nations 2015).

2.4.6 Statistically Significant Differences Between U.S. and China

The power regression equation used to show a linear log-log relationship between these two countries demonstrates one of the main findings of our study: that sludge concentrations in the U.S. are about four times higher than in Chinese sludge. There are several compounding factors that can begin to explain this difference. One possible explanation for the variation in the sludge samples between China and the U.S. is that in most of the U.S. studies, the sludge was taken from domestic wastewater. As of 2004, only about 40 million, (14%) of the U.S. population lived in an area with a combined sewer (Environmental Protection Agency 2004), which would incorporate either rainwater runoff or industrial wastewater into the municipal sewer. However, Chinese municipal wastewater is more commonly mixed with industrial wastewater, with industrial contributions making up about 30% of the total contribution (Feng et al. 2015). This may cause the Chinese sludge concentrations to have a higher level of certain anthropogenic organic pollutants than U.S. sludge. Additionally, the U.S. and China have different sludge treatment methods. As of 2004 in the U.S., about 50% of WWTPs anaerobically digested their sludge before disposal (Environmental Protection Agency 2007). Conversely, while in China anaerobic digestion is acknowledged as a preferred

sludge treatment method, only a few dozen out of 2600 WWTPs nationwide had implemented the anaerobic digestion process for sludge, and only about 20% of sludge is treated at all (Feng et al. 2015). OCs can be degraded through the anaerobic treatment process, and anaerobic treatment removes 50–75% of the volatile organic carbon which can reduce the total dry solids weight, and therefore artificially increase other OC concentrations (Environmental Protection Agency 1978). Thus, the higher concentrations in U.S. sludge when compared to China can be as a result of higher inflow wastewater concentrations, or due to more advanced sludge treatment techniques which sequester a larger portion of OCs into sludge and out of the treated effluent.

2.4.7 Limitations

Comparisons between chemicals from the 1982 EPA study were avoided due to the 1982 national study not providing mean concentrations, and concentrations being reported using wet weight instead of dry weight. Only minimum and maximum concentrations are available from that study, and not enough data was provided about the concentration distribution to accurately estimate the mean concentration. Additionally, except for the EPA studies, limited information was available on the sludge digestion method used for the WWTPs from which the samples were collected. Thus, it is not possible with current data available to make comparisons between various sludge digestion methods, or to account for digestion methods in the statistical analyses.

Another limitation arises from the variation in usage and regulation of chemicals inventoried in this binational database. The United States and China do not have the same regulations in place regarding chemical production and usage, and the regulations currently in place have not been in place across the whole study period. For this reason,

care should be taken in comparing for example, an older study from China to a more recent one from the United States.

Due to a lack of reporting in a significant portion of the sources, the effect of Method Detection Limits (MDLs) was not incorporated into the study analyses. While methods such as the Maximum Likelihood Estimator (MLE) or treating non-detects as the MDL divided by the square root of 2 are preferable (Newton and Rudel 2007), non-detects had to be treated as zero in order to maintain uniformity across the study, and chemicals that had significant numbers of non-detects were not used for detailed comparisons due to the uncertainty that such a comparison would have. While this is a limitation of the study, the margin of error from using zero as a substitute value for the MDL is relatively minimal when the number of non-detects is less than approximately 25% of the total number of samples (Environmental Protection Agency 2003a).

While a spatial analysis of sewage sludge OC concentrations would be valuable to researchers, it is currently difficult to perform due to a lack of available spatial data for any one OC or group of OCs. The largest contributors to this are 1) the lack of spatial variety within and between studies, 2) the fact that the EPA has kept private the key to match sample ID with the wastewater treatment plant location as a measure to protect the participating treatment plants, and 3) the fact that in some cases, a large number of samples were composited prior to analysis, thus losing the spatial component of the samples collected.

2.5 Conclusions

This study has combined a database of U.S. OC sludge concentrations with an existing Chinese database to perform a quantitative review of sewage sludge in the two

countries that produce the largest amount of chemicals in the world. For the past few years, the United States annual sewage sludge OC publication rate has been about one-third of China's and concentrations in the U.S. average 4.0 times higher than China, although factors such as combined sewer systems, contribution from industry, and sludge treatment technology complicate the issue. Prominent chemicals present in higher concentrations in U.S. sludge than in Chinese sludge include chlordane, norgestrel, HHCB, and AHTN, while chemicals found in much greater concentration in Chinese sludge than in U.S. sludge include Bisphenol A, ketoprofen, and some siloxanes. In some cases, these differences can be partially explained through production, usage, or other outside data sources, but in other cases, unknown information such as the type of digestion, sampling methods, and detection methods may be more influential. The data presented in this publication are of value to multiple stakeholders. Policymakers can utilize these data to understand the adequacy of current WWTP technologies in eliminating toxic and recalcitrant OCs from the environment. Those working in the field of public health, agriculture, and wastewater treatment may find this information useful in order to assess the potential risk posed to those handling sludge, although this risk assessment remains to be completed. Sludge concentrations were used to measure the efficacy of regulation of chemicals such as PCBs and PBDEs in the U.S., and can continue to be used in the future to study the effect of new regulations such as the FDA antimicrobial ban in the U.S. In order to address the aforementioned data gaps, the U.S. should increase their breadth of studied chemicals to encompass OCs such as novel-BFRs, *n*-heterocyclic carbenes, quaternary ammonium compounds, and chemicals affected by regulation such as triclosan and triclocarban. Conversely, China should focus

on increasing the sample sizes of their studies, for example by conducting a national sludge survey. Additionally, this new binational database can be leveraged by future researchers to perform risk assessments on the OCs that have been detected in U.S. or Chinese sludge. As the two largest chemical producers in the world, both the U.S. and China need to continue to ensure that their methods for the disposal of sludge preserve both public health and the environment.

TRANSITION 2

While the EPA has made an effort to improve our current understanding of the chemical composition of sewage sludge produced nationwide by performing four National Sewage Sludge Surveys, corresponding risk assessments have only been performed for a limited number of metals. As pointed out in a 2018 report from the EPA Office of the Inspector General, the EPA is lagging behind in analyzing available data. This is presumably due to a variety of reasons, including a lack of both toxicology and exposure data for animals and humans. As new data have emerged over the past 30 years and more sophisticated risk assessment methodologies have been developed, a need has arisen to analyze these new data with available risk assessment tools.

In Chapter 3, I applied contemporary risk assessment methodologies to the most recent data on metal concentration in U.S. sewage sludge to quantify the human health risks posed from one specific exposure pathway – the involuntary ingestion by humans of soil amended with sewage sludge. I performed Monte Carlo simulations to a series of parameter distributions for twelve metals known to be present in sewage sludge to calculate the corresponding hazard quotient for each metal. Hazard quotients were then combined for metals that affected the same organ in the human body to address potential synergistic effects of simultaneous exposure.

CHAPTER 3

ASSESSMENT OF HUMAN HEALTH RISKS FROM INGESTION OF TWELVE TOXIC METALS CONTAINED IN TOPSOIL AMENDED WITH SEWAGE SLUDGE FROM THE UNITED STATES

ABSTRACT

Since the U.S. Environmental Protection Agency ban of ocean dumping of municipal sewage sludge in 1988, the characterization and disposal of sewage sludge have been an ongoing issue of regulatory and public concern. Depending on the disposal method used for sewage sludge, health threats removed from wastewater can be reintroduced into the environment and can cause exposure to humans and wildlife through multiple pathways. This study used Monte Carlo and Maximum Likelihood Estimator methods to answer two questions: (i) what risk do twelve metals (antimony, barium, beryllium, boron, cadmium, chromium, manganese, molybdenum, nickel, selenium, silver, and zinc) investigated in the 2006/07 U.S. EPA National Sewage Sludge Survey (NSSS) individually pose to humans via Pathway 3, i.e., the ingestion of sludge-amended topsoil, and (ii) do these risks change when combined additively based on the bodily systems affected by these metals? Study results indicate that while hazard quotients never surpassed the threshold value of 1 in the Monte Carlo simulations, hazard quotients (HQ) for antimony, cadmium, chromium, and manganese were elevated and within the safety margin of 0.1 to 1 for children impacted by soil pica who regularly ingest large amounts of soil. Hazard quotients for metals that affected the same bodily system were combined into hazard indexes (HIs), which were found to be in the 0.1 to 1

range for the hematologic, nervous, and urinary, and other bodily systems. The methodology adopted in this work demonstrates how more modern approaches can be leveraged to arrive at more robust risk assessments for sewage sludge that take into sources of known variance in the risk assessment process and the combined effects of multiple threat agents on the same bodily system..

3.1. Introduction

Sewage sludge, a byproduct of wastewater treatment, is currently disposed in the U.S. via several methods, including land application, incineration, and landfilling. Depending on the disposal method, metals removed from municipal wastewater during activated sludge treatment can be reintroduced into the environment to cause exposure of humans and wildlife through multiple exposure pathways. Many of these metals are toxic or carcinogenic (e.g., cadmium, mercury, lead, arsenic), and thus can pose a risk to ecosystems and human health upon application of treated sewage sludge (biosolids) on soils.

The 1972 EPA Clean Water Act (United States 1972) laid the groundwork for wastewater pollution regulations that later led to the 1988 Ocean Dumping Ban (Environmental Protection Agency 1988a), which stipulated that U.S. wastewater treatment plants (WWTPs) could no longer directly dump sewage sludges into the ocean. This legislative action necessitated a sudden need to identify and alternative methods of sewage sludge disposal such as land application upon additional treatment of sludges as well as landfilling, and incineration. The increase in usage of these three disposal methods compelled the EPA to conduct both a chemical risk assessment and quantitative microbial risk assessment for each of these disposal methods that was published in 1995

(Environmental Protection Agency 1995). This risk assessment used deterministic risk assessment models to consider the potential need for regulating up to 411 analytes identified in 174 sewage sludge samples collected throughout the U.S. between 1988 and 1989. These compounds covered a variety of chemical classes, including dioxins, furans, metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, pesticides, and phthalates. However, during the pre-screening for the risk assessment, chemicals were excluded from consideration if they were (1) currently banned in the U.S., (2) not manufactured in the U.S., or (3) detected at a frequency less than 5%. For target chemicals that passed the pre-screening, a total of fourteen risk assessment pathways were considered, but a focus was placed on the *Highly Exposed Individual*, a term used to describe children with soil pica who eat farm soil, and gardeners who apply biosolids on home soil. The results from the risk assessment led to the currently active EPA Part 503 Biosolids Rule (Environmental Protection Agency 1994c), which stipulates maximum pollutant loadings for 10 metals and in addition requires the use of certain pathogen treatment technologies as a function of the disposal methods used for sewage sludge and treated sewage sludge (biosolids).

Beyond the risk assessment that led directly to the 1993 EPA Part 503 Biosolids Rule, several risk assessments have been performed on the disposal of sludge both from a QMRA perspective by looking at risk posed by human enteric viruses (Brooks et al. 2012; Eisenberg et al. 2008; Gerba et al. 2002b; Grant et al. 2012; Hamilton et al. 2020) and a chemical risk perspective by looking at metals and organic contaminants (Bradley O Clarke and Stephen R Smith 2011; Clarke et al. 2018; Dudka and Miller 1999; Navarro et al. 2018; O'Connor et al. 2001; Sidhu et al. 2019b). While metal analyses have

generally agreed with the EPA's results from the 1988/89 study, the risk assessments for organic contaminants generally cannot be compared to the EPA risk assessment due to the EPA lacking the toxicology data to properly model risk from organic contaminants at the time (Bradley O Clarke and Stephen R Smith 2011; Clarke et al. 2018; Environmental Protection Agency 1995; Navarro et al. 2018; Sidhu et al. 2019b). In fact, as a 2018 EPA report on biosolids pointed out, the lack of toxicological data for organics has been and continues to be an issue preventing wide-scale risk assessments from being performed on existing sewage sludge data (Environmental Protection Agency 2018c).

To the authors' knowledge, to date no stochastic modeling has been applied to the chemical risk assessment for biosolids application on U.S. agricultural land. The goal of this study therefore was to improve on the EPA risk assessment methodology by using stochastic methods, specifically Monte Carlo simulations, and to apply this more robust approach to data on metal concentrations obtained in the 2006/07 EPA National Sewage Sludge Survey. As this data has not been formally analyzed before, the results from this study have the potential to inform regulations on the disposal of sewage sludge in the U.S. The two primary research questions for this study were: (1) what risk do twelve of the metals studied in the 2006/07 U.S. EPA sludge survey individually pose to humans via Pathway 3 (soil ingestion of biosolids/soil mixture), and (2) do these risks change when combined additively based on the bodily systems affected by these metals?

3.2 Methods

3.2.1 Data Sources

To this end, a non-carcinogenic chemical risk assessment was performed on the 2006/07 U.S. EPA national sewage sludge survey concentration data for 28 metals. Due

to the fact that in the 1993 EPA risk assessment, Exposure Pathway Number 3: biosolids application to topsoil > child eats topsoil was often the limiting factor for determining regulatory limits, this study focused on Pathway 3 (Environmental Protection Agency 1994c). Risk assessment was only applied to the twelve metals, antimony, barium, beryllium boron, cadmium, chromium, manganese, molybdenum, nickel, selenium, silver, and zinc, as these are the only data for which references doses and affected systems data were available in the EPA's IRIS database (Table 1)(Environmental Protection Agency 2018b). Topsoil concentration data was retrieved from the EPA Ecological Soil Screening Level (Eco-SSL) dataset(Environmental Protection Agency 2018a).

Table 2. Availability of ECOSSL Topsoil Baseline Concentrations for Metals Analyzed in 2006/07 EPA National Sewage Sludge Survey, and Human Bodily System Affected According to EPA IRIS Toxicological Data.
Source: (Environmental Protection Agency 2009a, 2018a, b).

Element		Al	Sb	As	Ba	Be	B	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mg	Mn	Hg	Mo	Ni	P	Se	Ag	Na	Tl	Sb	Ti	V	Y	Zn
EPA Biosolids Concentrations		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Human Bodily System Affected	dermal																				✓	✓							
	developmental						✓																						
	hematologic		✓																		✓								✓
	immune																												✓
	nervous																				✓								
	urinary				✓			✓										✓											
	other					✓				✓						✓			✓										
ECOSSL Topsoil Concentration		✓		✓	✓			✓		✓	✓	✓	✓	✓		✓	✓		✓		✓								✓

3.2.2 Governing Equations

The average daily dose was calculated using the following equation:

$$\boldsymbol{ADD = CS\ x\ IS\ x\ BC\ /\ BW}$$

The **ADD** (mg/kg-day) is the Average Daily Dose during an exposure period, **CS** (mg/kg dry weight) is the concentration of the target analyte in biosolids, **IS** (mg/day) is the Soil Ingestion rate for the analyzed scenario, **BC** is the estimated percent composition of biosolids in the final tilled soil after application, and **BW** (kg) is the Body Weight of the

human subject analyzed. The point estimate for BC was calculated using the below equation

$$BC = \frac{BL * 907\frac{kg}{ton} * 1000\frac{g}{kg}}{43560\frac{ft^2}{acre} * TD * 28316.8\frac{cm^3}{ft^3} * SD}$$

The **BL** (tons/acre), Biosolids Loading rate, **TD** (ft), Tilling Depth, and **SD** (g/cm3)**,** Soil Density were estimated from literature values as shown below. Once the ADD was estimated using the Monte Carlo model, the hazard quotient was calculated through a simple quotient as follows:

$$HQ = ADD/RfD$$

Here, HQ, the hazard quotient, has no units, and **RfD**, the Reference Dose is in mg/kg-day. If the HQ is less than 1, the risk assessment concludes that that particular metal independently evaluated does not pose a health risk to the case scenario being studied. To account for synergistic effects, the hazard quotient values for metals that are known to affect the same system (Table 1) were combined additively into an Hazard Index (HI), formally calculated as shown below:

$$HI = \sum HQ_i$$

The HI was evaluated using the same rubric from HQ. An HI value greater than or equal to one would be considered a health risk to the individual due to the combined effect of multiple metals on the same bodily organ.

Table 3. Model Parameters for Monte Carlo System.

Parameter	**Symbol**	**Value**	**Type**	**References**

Reference Dose and Affected Systems	RfD	Varied	Point estimate	(Environmental Protection Agency 2018b)
Concentration	CS	Varied	Distribution	(Environmental Protection Agency 2009a)
Soil ingestion rate	IS	Varied	Distribution	(Environmental Protection Agency 2011)
Biosolids fractional composition in soil	BC	0.0074	Point estimate	(Brown 2018; National Research Council 2002)
Body Weight	BW	Varied	Distribution	(Environmental Protection Agency 2011)

3.2.3 Model Design

To obtain parameters for the Monte Carlo model, searches were performed in both Web of Science and Google Scholar to look for typical loadings for biosolids on farmland. To estimate the percent biosolids concentration in soil, a biosolids loading, BL, of 7.5 tons (dry weight)/acre (National Research Council 2002) was used. An average tilling soil depth of 0.5 ft was estimated based on the author's understanding of how biosolids are incorporated into soil, it was assumed that tilling biosolids-applied soil evenly distributes the biosolids throughout the 0.5 ft depth of the soil. An average soil density of 1.5 g/cm^3 was utilized, although this value can vary geospatially (Brown

2018). Using these values, a biosolids fractional composition in soil (BC) of 0.74% was determined. Body weight and soil consumption distribution data were retrieved from the EPA Exposure Factors Handbook (Environmental Protection Agency 2011), and were categorized into categories for children, adult, and children with soil pica.

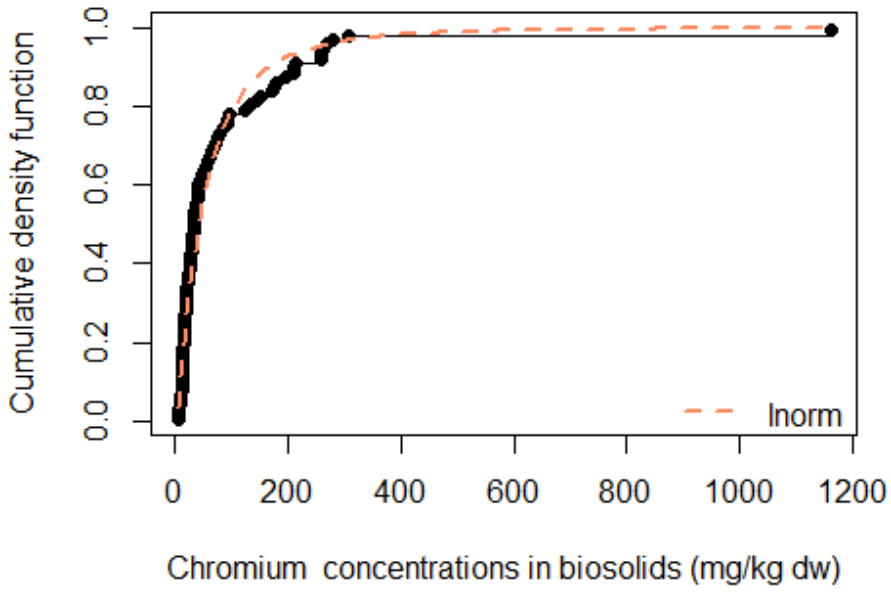

Figure 6. Application of the Log-normal Model to Chromium Concentrations in Biosolids.

The reference doses were collected from the EPA's Integrated Risk Information System (IRIS) (Environmental Protection Agency 2018b) for each of the 28 metals as available. Only 12 of the 28 metals provided reference doses that could be used in the model. For affected bodily systems not explicitly indicated in the EPA's IRIS database, a pooled "Other" system category was used as a conservative estimate to measure risk to these other affected systems. Lognormal models for the concentrations of each metal in sewage sludge were fit using the Maximum Likelihood Estimator method, an example of

which is shown in (Figure 1). Model analyses were performed in R 3.5.1 and R-studio 1.1.453 using the mc2d software package.

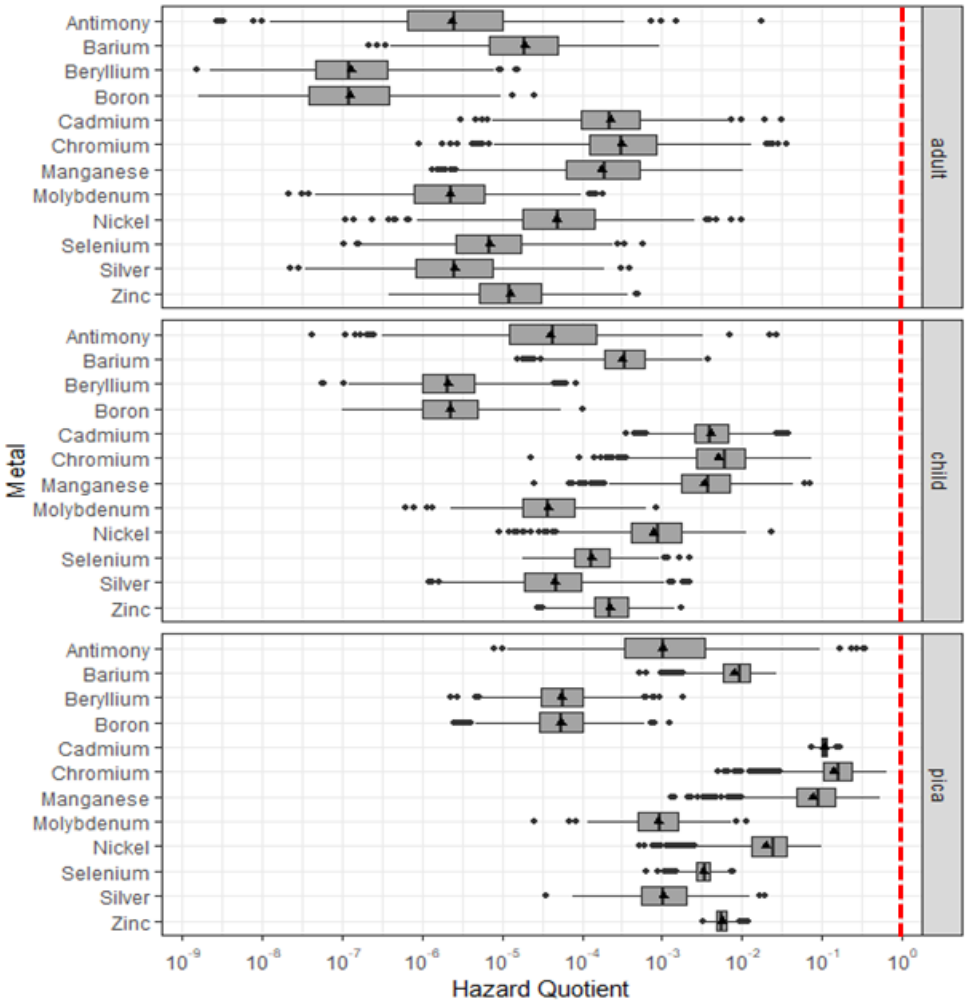

Figure 7. Risk Assessment Results Showing Hazard Quotients for Twelve Metals to Adults, Children, and Children with Soil Pica. Hazard Quotient of 1 Shown in Red.

3.3 Results

3.3.1 Monte Carlo Model Results by HQ

The risk assessment model results showed no calculated HQ greater than one, although the simulations yielded a median HQ between 0.1 and 1 for cadmium chromium, and manganese for children with soil pica (Figure 2, bottom panel).

Antimony, barium, molybdenum, nickel, selenium, silver, and zinc each yielded median HQ values between 10^{-3} and 10^{-2} for children with soil pica, while beryllium and boron posed the least risk, having median HQs below 10^{-4}. As expected, comparatively lower risks were posed to adults and children without soil pica (top and middle panels, respectively).

The HIs from the Monte Carlo simulations showed similar results, with the nervous, urinary, and other bodily systems yielding median HIs between 0.1 and 1 for children with soil pica (Figure 7, bottom panel). The dermal, hematologic, and immune systems yielded median HIs between 10^{-3} and 10^{-2}, and the developmental system was least affected, with median HIs below 10^{-4}. Similar to Figure 8, the adults and children without soil pica were much less affected in the model, showing risks much lower than that of the children with soil pica group.

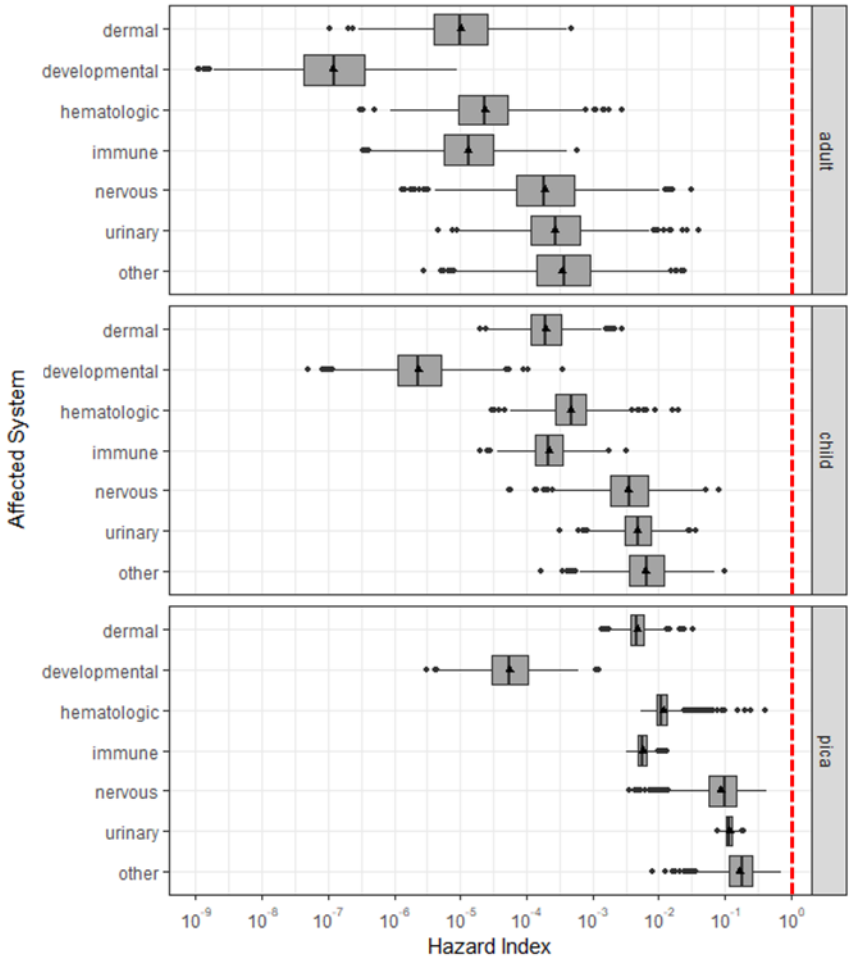

Figure 8. Risk Assessment Results Showing Hazard Indexes for Seven Bodily Systems Affected by Metals in Adults, Children, and Children with Soil Pica. Critical Hazard Index of Unity (1) Is Shown in Red for Reference.

3.4 Discussion

3.4.1 Research Implications

This study featured an innovative approach by applying for the first time a stochastic model for chemical risk assessment of sewage sludge in the form of Monte Carlo analysis. Qualitatively, the results are in alignment with previous risk assessment studies on metals in sewage sludge; yet, a better understanding of the contribution of each Monte Carlo parameter allows researchers to more comprehensively understand the data behind each hazard quotient and hazard index, and to focus future research on high

impact, high uncertainty parameters. Currently, only 12 of the 28 originally studied metals have a recommended IRIS RfD datapoint. The other 16 metals either lack toxicological data, or the EPA believes that the toxicology literature is inconclusive and does not allow one to assign a reference dose. Additionally, these analytes only represent a fraction of the over 400 total analytes for which the EPA has tested U.S. sewage sludge. While it is unrealistic to expect the EPA and the scientific community to collect enough toxicological data to run risk assessments for every possible analyte in every conceivable scenario for the land application of biosolids, there is still a large gap between harmful metals and organic contaminants that have been detected in sewage sludge, and those that have also had formal risk assessments conducted for. As novel threats including prions, viruses, antibiotic resistance genes, and endocrine- and neurodisruptors continue to be recognized and detected in sewage sludge and biosolids, it is imperative that the research community obtain a better understanding of this complex mixture of threat agents and the potential risks posed from application of sewage sludge on agricultural soil in the U.S.

3.4.2 Limitations

While this study attempted to analyze human health risk from an affected systems perspective, a simple additive approach was adopted, and further research should be done to better understand how multiple analytes' effects' on a body's systems can be most accurately modeled in aggregate. A more sophisticated, multi-analyte model could improve future risk assessment in this way. Importantly, the background soil concentration of a metal has a large influence on the final concentration after the soil has been amended with sewage sludge, and background concentration data were not available in the ECOSSL database for arsenic, beryllium, boron, molybdenum, and silver,

indicating the risks for these metals may be underestimated. Lastly, this study only considered non-carcinogenic health risk, so a carcinogenic approach should be analyzed as well in the future.

3.4. Conclusion

Sewage sludge is an inevitable by-product of effective contemporary wastewater treatment. While sewage sludge and biosolids resulting from additional treatment contain several potential health risks, the sludge matrix itself, absent of the threats, represents a latent resource for reuse to advance sustainability. From this Monte Carlo study, it is concluded that the twelve metals studied do not pose a non-carcinogenic health risk to the affected individuals in the test scenarios considered, whether analyzed individually or cumulatively based on the bodily system affected. However, this study also highlights the existence of a large gap between potential health threats detected in biosolids and the extent to which the necessary risk assessments for these threats actually have been completed. Toxicological data is lacking on synergistic effects of the metals considered here and maybe more importantly, no data are available for the most of the 400+ organic contaminants that thus far have been identified in biosolids through the EPA's National Sewage Sludge Surveys and allied efforts by other agencies and research groups. Moving forward, more sophisticated models in risk assessment will continue to need to incorporate newer toxicology data on the ever expanding spectrum of threat agents contained in sewage sludge to ensure the environmentally safe land application of treated sewage sludge (biosolids) on U.S. soils.

TRANSITION 3

Plastics are a newly recognized human health and environmental threat that is detected not only in wastewater and sewage sludge, but throughout the global aquatic and terrestrial environment. Much of the perceived health risks from plastic waste are due to micro- and nano-plastics, which are at small enough sizes to enter bodily organs such as the liver, kidney, lungs and gut, potentially causing serious adverse biological effects ranging from mild inflammation to cancer in animals, and potentially also in humans. Beyond human health risks, micro- and nanoplastics also pose significant risks to aquatic wildlife, which has motivated scientists to study the effects of plastic pollution in the oceans on biota and a potential transfer of pollutants up the food chain into humans. Available scientific literature does inform to a decent extent on the rates at which environmental plastic waste mechanically fragments and degrades, but these data have not been integrated yet into a mathematical model of a global scale in order to inventory and predict the current and future extant of pollution from microplastics and nanoplastics in the world's oceans.

In Chapter 4, I used existing experimental data and small-scale plastic pollution models to integrate into a global environmental box model the transport of plastic waste from land to sea and its subsequent fragmentation. I modeled the mechanical fragmentation and degradation of plastic using best estimates of parameters from recently published studies. Three scenarios were then run on the resulting model to understand extreme cases for plastic pollution in the ocean, specifically: (1) unlimited continued growth (2) the current goal of plastic manufactures, (3) a hypothetical flat line starting in

2022, (4) a pragmatic phase-out of plastic production by 2100, and (5) an immediate abandoning of plastic production.

CHAPTER 4

MODELLING THE DISINTEGRATION OF PLASTICS IN THE WORLD'S OCEANS

ABSTRACT

Microplastics (MPs) and nanoplastics (NPs) are newly recognized health threats whose current and future inventories in the world's oceans are presently unknown. This modeling study integrated the transport and fragmentation of environmental plastics in an environmental box model to inform on the inventory of plastic waste of different dimensions in the world's oceans. To understand possible futures of oceanic pollution with plastic waste, five scenarios of plastic consumption were considered from 2000 through the year 2100: (1) unlimited continued growth; (2) halving the rate at which plastic production currently is increasing (3) capping future plastic use at the production quantity of 2022, (4) a straight-line phase-out of plastic production by 2100, and (5) an immediate termination of production and use of contemporary plastics. Based on these scenarios, the maximum mass of MPs and NPs in the ocean by 2100 are projected to equal 74.2 ± 14.8 and 38.9 ± 7.8 M tonnes, respectively. If annual plastic production was limited to current 2022 levels, the resultant mass of MPs and NPs in the oceans would peak at 25.1 ± 5.0 M and 12.7 ± 2.5 M tonnes, respectively, in the year 2055. If plastic production were to be immediately halted starting in 2022, the mass of MP and NP waste would peak at 10.7 ± 2.1 and 5.5 ± 1.1 M tonnes in the years 2023 and 2025, and would decrease back to 2010 levels by the years 2054 and 2059, respectively. This study shows that the present day inventory of MPs and NPs in the world's oceans is considerable and that even the most draconian voluntary or regulatory steps would not prevent this

inventory from increasing at least for a number of years and, more realistically, for decades to come.

4.1 Introduction

Estimates of global macroplastic pollution in the ocean have been well documented by both modelling and experimental studies (Eriksen et al. 2014; Lebreton et al. 2019), whereas microplastics (MPs), whether in primary MP form as manufactured, or in secondary MP form as degraded or fragmented from larger macroplastics, have only recently received attention from scientific researchers (Kaandorp et al. 2021; Lindeque et al. 2020). Nanoplastics (NPs), which can both be directly produced or result as a consequence of degradation or mechanical fragmentation of larger primary plastic waste in the environment, constitute a relatively unstudied threat, due in part to a lack of practical detection and enumeration methods for use in field studies (Gaylarde et al. 2021; Kögel et al. 2020). Since plastics that are larger than MPs are non-absorbable, and plastics that have broken down to sizes smaller than NPs (such as oligomers and monomers) do not appear to have large adverse effects on humans or wildlife, MPs and NPs are thought by researchers to be responsible for much of the human health and environmental risk posed by plastic pollution (Figure 9) (Gasperi et al. 2018; Gaylarde et al. 2021; Kögel et al. 2020; Lavoie et al. 2021).

To better characterize the state of plastics in various compartments throughout the world, an environmental box model has been developed by international researchers (Kaandorp et al. 2021; Lebreton et al. 2019). Typically, this model is then coupled with a fragmentation, degradation, or transport models (Hinata et al. 2020; Menna et al. 2017), and then is applied to local areas throughout the world (Kaandorp et al. 2021). To our

knowledge, no study has attempted to apply these models together to the entirety of the world's ocean, a task performed in the present study.

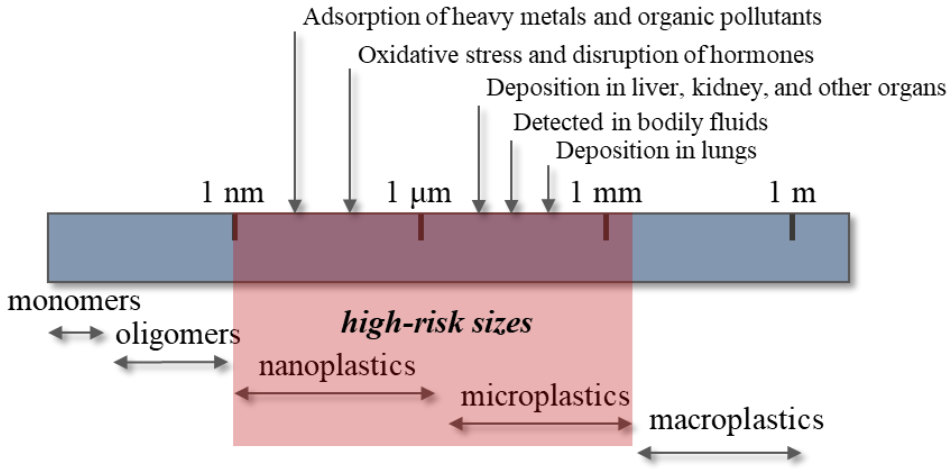

Figure 9. Distribution of Plastic Sizes and the Known Health Hazards Posed to Humans and Wildlife. High-risk Plastic Sizes Shaded in Red.
Sources: (Burns and Boxall 2018; Cox et al. 2019; Deng et al. 2017; Luo et al. 2022; Manikkam et al. 2013; Pauly et al. 1998; Zhang et al. 2020).

Since the magnitude of plastic pollution has and is expected to continue to increase in the ocean, environmental scientists have continued to study the adverse effects of plastic pollution on the oceanic ecosystem. Due to a number of recent discoveries regarding the hazards posed by micro- and nanoplastics (Kögel et al. 2020; Lavoie et al. 2021), it is imperative to determine the global inventory of MPs and NPs in the world's oceans and to assess how differing interventions may aid in reducing potential adverse ecosystem and human health impacts. We know that plastic pollution poses many risks to various levels of flora and fauna (Gaylarde et al. 2021), but to what degree those risks are inevitable, and to what degree they are preventable through modern reduction of plastic production and use is not thoroughly documented. To fill this knowledge gap, this study builds on previous plastic modeling studies and applies

fragmentation and degradation models in combination with an environmental box model (Figure 10) to understand: 1) the present day inventory of MPs and NP inventories in the world's oceans, and 2) the predicted change in these inventories as a result of voluntary or mandatory reductions in plastic production.

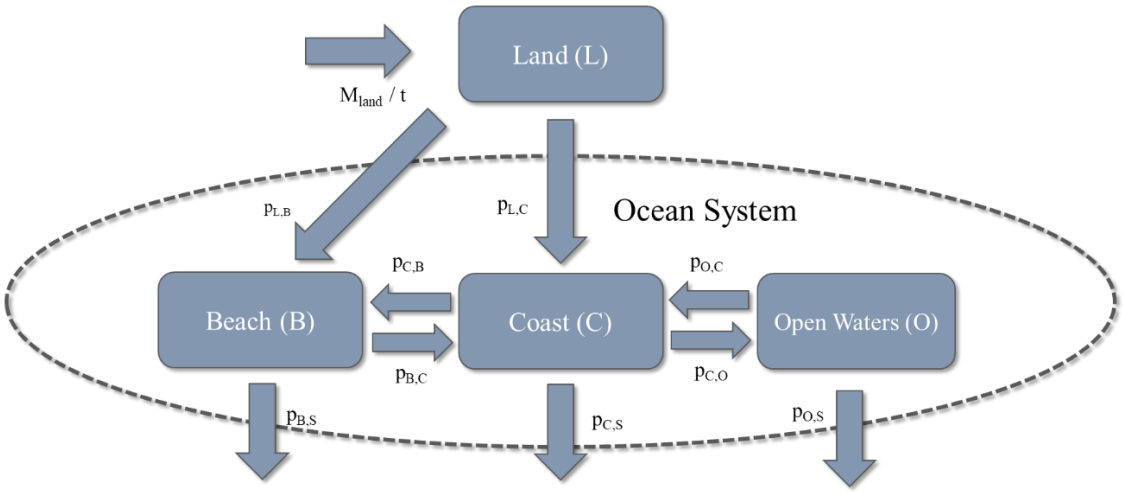

Figure 10. Conceptual Model Used in This Study Showing the Movement of Plastic Waste from Terrestrial into Aquatic Environments. The Model Was Derived by Combining Environmental Fate Models for Plastics Published Previously by Other Research Groups.
Sources: (Kaandorp et al. 2021; Lebreton et al. 2019).

4.2 Methods

4.2.1 Environmental Box Model

This study utilized an environmental box model, a tool that has previously been applied to smaller geographies across the world to understand plastic mass transfer (Kaandorp et al. 2021; Lebreton et al. 2019). The four boxes utilized in this model were land, the beach, coastal waters, and open waters. For each time step of one week, plastic particles in each box were modeled as having probabilities to do one of the following: 1) transfer to other boxes, 2) remain in the current box, or 3) be removed from the system

entirely. These probabilities, shown in Table 4, are based on previous plastic transport models (Cózar et al. 2015; Hinata et al. 2020; Kaandorp et al. 2021; Menna et al. 2017). The box model relies on a few key assumptions about the system studied, namely that the probability of particle transfer between any two compartments is independent of the particle size and time-independent. The land compartment was considered the only source for plastic waste, with estimates for plastic production and transfer rates from land to the beach and coast taken from previous modeling studies (Jambeck et al. 2015; Wayman and Niemann 2021). While annual plastic production over the past two decades has not increased in a perfectly linear manner, a linear model using the most recent plastic production data (Jambeck et al. 2015; Wayman and Niemann 2021) was utilized for the extreme scenario of increased plastic production, as these estimates are only important to give a general understanding of the predicted state of plastic pollution in the ocean.

4.2.2 Fragmentation and Degradation

A time step of one week was used for this model. Mechanical fragmentation was applied to all plastics in the beach and coast compartments, but was ignored in the ocean compartment as plastics in the ocean generally do not physical collide enough to have significant fragmentation rates (Kaandorp et al. 2021; Wayman and Niemann 2021). As studies have been inconclusive with regard to the significance of biodegradation on plastics, the effect was ignored for this model (Jacquin et al. 2019; Oberbeckmann and Labrenz 2020; Zettler et al. 2013). Photooxidation rates were based on recent studies (Wayman and Niemann 2021; Zhu et al. 2020), and were applied to the beach and coast compartments, as well as a fraction of the ocean compartment based on the approximate

percentage of ocean plastics (Erni-Cassola et al. 2019) with a lower density than 1.025 g/cm^3, that of seawater, (Nayar et al. 2016), thus keeping those plastics afloat and within range of sunlight penetration.

Table 4. Parameters for Plastic Waste Inputs, Environmental Box Model, and Fragmentation

Parameter	Description	Value	Reference
$p_{O,O}$	Ocean to ocean transfer	0.72	Kaandorp et al (2020)
$p_{O,C}$	Ocean to coast transfer	0.27	Kaandorp et al (2020)
$p_{C,O}$	Coast to ocean transfer	0.034	Kaandorp et al (2020)
$p_{C,C}$	Coast to coast transfer	0.83	Kaandorp et al (2020)
$p_{C,B}$	Coast to beach transfer	0.13	Menna et al (2017), Kaandorp et al (2020)
$p_{B,C}$	Beach to coast transfer	0.032	Hinata et al (2017)
$p_{B,B}$	Beach to beach transfer	0.96	Hinata et al (2017)
$p_{B,S}$; $p_{C,S}$; $p_{O,S}$	Removal from system	0.0051	Kaandorp et al (2020)
M_{land} / t	Global terrestrial plastic production	275 M tonnes/y (2010) 359 M tonnes/y (2018)	Jambeck et al (2015) Wayman and Niemann (2021)
$p_{L,BC}$	Fraction of terrestrial plastic contributed to beach + coast	1.7% - 4.6% / y	Jambeck et al (2015)
r_{BC}	Ratio of beach:coast input from land	1 to 1	Best estimate
r_{frag}	Plastic fragmentation rate	0% - 26% / y	Gerritse et al (2020)
r_{ox}	Photooxidation rate	0.8%, 27%, and 46% / y	Wayman and Niemann (2021)

4.2.3 Scenario Analysis

In order to address the impact of potential policy changes on a global scale, five scenarios were run in this model with regard to the input rate of plastics into the land compartment after the year 2022 (Figure 11). These scenarios were 1) an increasing annual plastic production rate throughout the time range based on literature projections,

2) a tapered increase at 50% of the current increase per year in annual plastic production, 3) a hypothetical flat line maintaining a constant 2022 production rate, 4) a pragmatic decrease in plastic production starting in 2022 and phasing out by 2100, and 5) an immediate abandoning of plastic production. Each of these scenarios were run separately to understand potential outcomes of global plastic production policy.

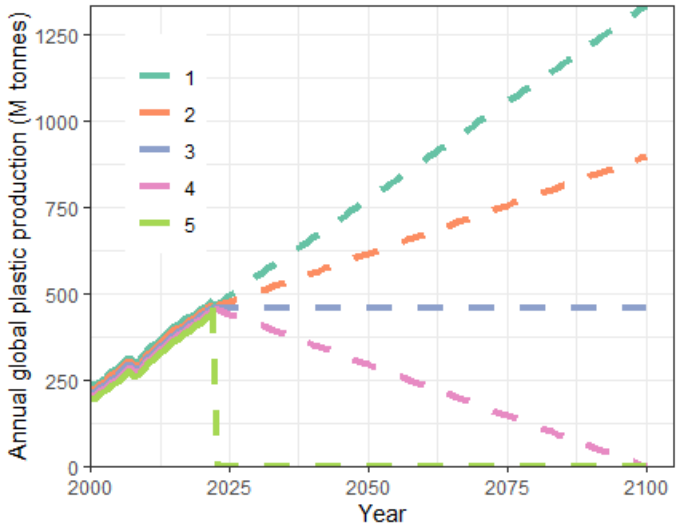

Figure 11. Annual Plastic Production Input into Land Compartment over Model Analysis Period for (1) Unlimited Continued Growth; (2) Tapered Production, (3) Freezing Plastic Production at 2022 Levels; (4) Linear Phase-out of Plastic Production by Year 2100; (5) Immediate Abandoning of Plastic Production.

4.3 Results

Based on the results from Scenario 1, if annual plastic production continues to increase at the current rate, by 2100 the total mass of MPs and NPs in open waters will be 74.2 ± 14.9 and 38.9 ± 7.8 M tonnes, respectively (Figure 12). In Scenario 2, where plastic manufactures slow the historic rate of plastic production increases, the mass of MPs and NPs in open waters would reach 48.1 ± 9.6 and 22.1 M ± 4.4 tonnes by 2100. If plastic production would be capped at the 2022 annual rate (Scenario 3), the

corresponding inventory of plastic waste in the oceans would reach steady-state conditions around the year 2055, with 25.1 ± 5.0 and 12.7 ± 2.5 M tonnes of MPs and NPs, respectively. If an aggressive reduction in plastic production were undertaken to completely phase out the production of contemporary plastics by the year 2100 (Scenario 4), oceanic inventories of MPs and NPs in open water would peak at 23.6 ± 4.7 and 12.2 ± 2.4 M tonnes by the year 2063. Lastly, even given an extreme case of plastic use policy (Scenario 5), which assumed a complete global cease of plastic production starting in 2022, MP and NP peak masses of 10.7 ± 2.1 and 5.5 ± 1.1 M tonnes would still not be reached until the years 2023 and 2025, respectively. Maybe even more concerning, in this scenario, MP and NP levels would not decrease back down to the 2010 estimates of 3.6 ± 0.7 M and 1.5 ± 0.3 M tonnes until the years 2054 and 2059, respectively. It is important to note that Scenario 5 still involves plastic waste input from land after 2022, as ceasing production of plastic does not prevent already produced plastic waste currently residing in terrestrial settings to enter ocean beaches and coastal zones.

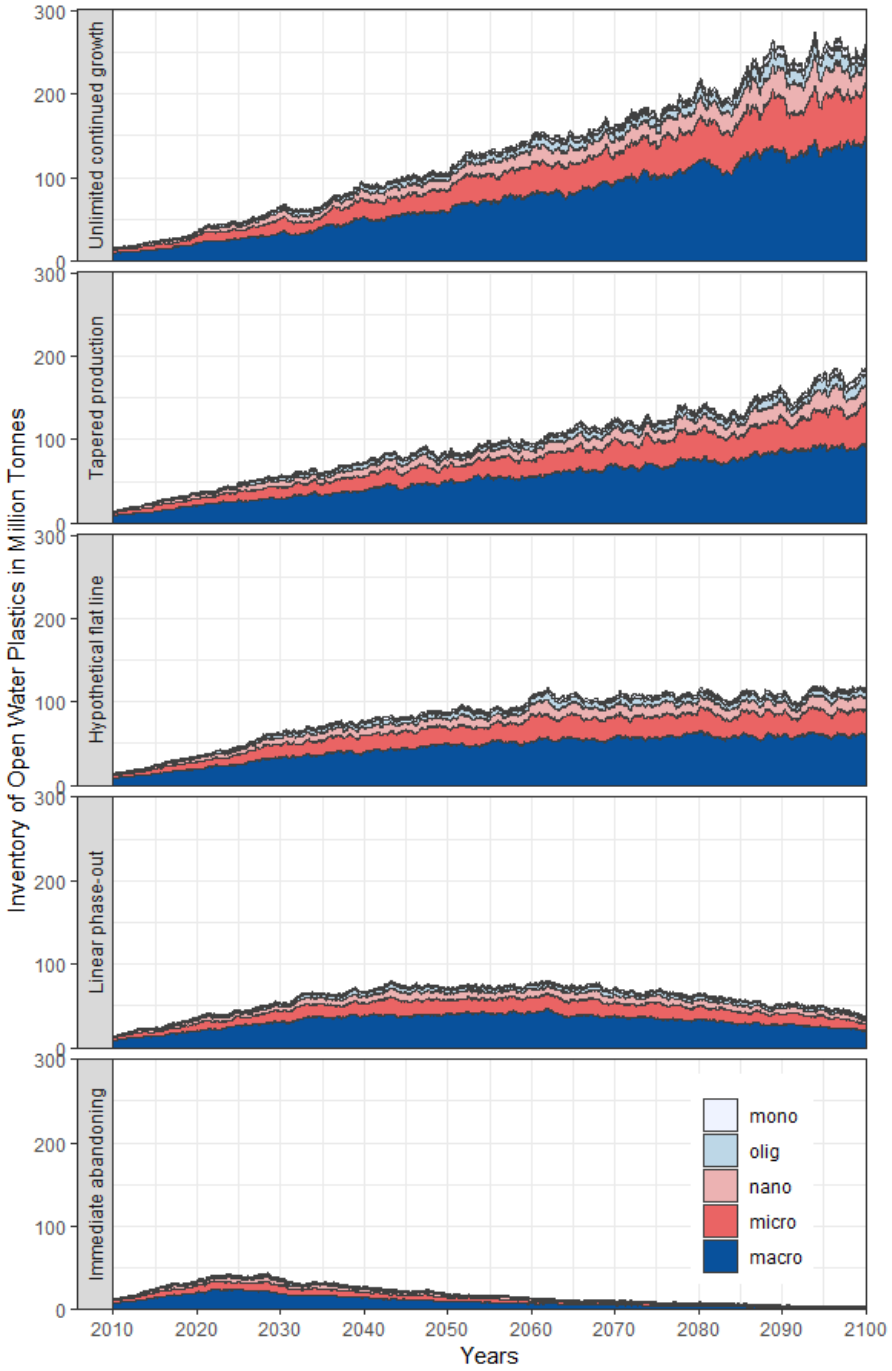

Figure 12. Scenario Analysis Comparing Plastic Production Policies (1) Unlimited Continued Growth (2) Current Goal of Plastic Manufactures, (3) Hypothetical Flat Line, (4) Pragmatic Phase-out of Plastic Production by Year 2100, (5) Immediate Abandoning of Plastic Production, and Their Impact on Plastic Concentrations in the Ocean for Monomers, Oligomers, Nanoplastics, Microplastics, and Macroplastics from 2010 to 2100.

4.4 Discussion

4.4.1 Comparison to Other Plastic Studies

Due to differences in chronological and geographical scope, as well as differences in treatment of factors such as degradation and fragmentation, it is difficult to do a perfect comparison of these model results to those from similar studies. Jambeck et al. estimated 4.8 to 12.7 M tonnes of plastic entering the ocean in 2010 (Jambeck et al. 2015). According to Eriksen et al, 270,000 tons of plastic were floating in major plastic gyres across the world in 2014, although this does not take into account the fraction below the surface or in the rest of the ocean surface (Eriksen et al. 2014). Kaandorp et al. estimated 176 years for 99% of plastic mass to disappear from surface water and beaches (Kaandorp et al. 2021), which is comparable to the slow rates at which the plastic waste at various sizes decreased in each of the scenarios modeled in this study.

4.4.2 Toxicological Impact of High-risk Plastics

Over the past decade, MPs, NPs have been studied to understand their effect on humans and wildlife at various tropic levels. These high-risk plastics have been demonstrated to be neurotoxic, to induce oxidative stress, to disrupt metabolism, and to inhibit immune function in both humans and marine creatures (Deng et al. 2017; Manikkam et al. 2013; Sana et al. 2020).

Given that the spatial distribution of plastics in the ocean is not homogeneous, it is difficult to quantify the exact impact a certain mass of high-risk plastics would have on wildlife as it is highly dependent on the distribution. One study suggested that the

predicted no-effect concentration of nanoplastics on marine wildlife was 72 μg L^{-1} (Yang and Nowack 2020), a number several orders of magnitude above the modeled concentrations of high-risk plastics in this study assuming a perfectly homogeneous distribution of plastic. However, as plastics are unlikely to remain stationary in the middle of the ocean water column, there is the potential for plastic concentrations to be much higher near the surface or the ocean floor depending on the density of the particular type of plastic. Additionally, researchers have pointed out the tendency of plastics to aggregate in gyres across the world's oceans, where much higher concentrations can be expected(Eriksen et al. 2014; Law et al. 2010).

4.4.3 Limitations

While this model may serve as a general estimate for potential plastic pollution outcomes in the coming decades, there are many parameters on which this model relies that are not fully understood. These include the probability for exchange between compartments, photodegradation rates and fragmentation parameters. Many of these parameters came from localized geographies and may not extrapolate well to the global scale, as climate variables such as temperature, wind speed, and cloud cover are heterogeneous throughout the ocean, and affect degradation and fragmentation rates. Additionally, biodegradation and chemical degradation may play a role in the fate of plastic in the ocean, but inconclusive research on the matter make it difficult to include in a model. While the 5th scenario, the immediate abandonment of plastic production, may seem unrealistic, it serves as a baseline for the minimum mass of high-risk plastics in the ocean over the next several decades without any clean-up efforts.

4.5. Conclusions

Some of the motivation for cleaning up plastic pollution in the ocean is aesthetic – large pieces of plastic floating in the ocean help demonstrate the extent to which plastic pollution is a global issue, but macroplastics are not the greatest source of human and environmental risk. Quantifying the cumulative mass of plastic in the high-risk range of MPs and NPs is challenging due to NPs being too small to physically collect in mesh nets. This study employed recent fragmentation, biodegradation, and environmental box models to quantify the effect of five approaches to plastic production on the estimated mass of high-risk plastics in the ocean until the year 2100.

TRANSITION 4

New threat agents and mechanisms of potential harm have been recognized since inception of the Part 503 Rule, including prions, viruses, endocrine- and neurodisruptors, micro- and nanoplastics, antibiotic resistance genes, and synergistic toxicity. As has been pointed out by researchers, the National Research Council, and the Inspector General (Environmental Protection Agency 2018c; Gianico et al. 2021; National Research Council 2002), the EPA has been slow in addressing these threats, leading state and local municipalities to be in a position where they are underinformed as to best practices regarding environmentally responsible sewage sludge treatment methodology. In theory, the land application of sewage sludge as a fertilizer to agricultural land might be the most sustainable disposal method for sewage sludge, but this same sewage sludge was identified by the EPA in 1988 to have harmful effects on the ocean.

In Chapter 5, I reviewed the current literature to identify and summarize new threats that have come to the attention of researchers and regulators since the inception of the Part 503 Rule. My particular aims were to determine: (l) what approaches to sewage sludge disposal have been adopted across the world; (2) what is the history of disposing of sewage sludge in the United States; (3) and what human health and environmental risks have been quantified to this day, and which ones remain unknown or understudied. The overall objective of the following chapter was to summarize the state of knowledge and recognized data gaps in the science of assessing the risk posed by reuse of municipal sewage sludge.

CHAPTER 5

A PERSPECTIVE ON THE RISKS AND BENEFITS OF DIVERTING SEWAGE SLUDGE AWAY FROM LANDFILLS ONTO UNITED STATES SOILS

ABSTRACT

The sustainable disposal of sewage sludge has been a matter of international discussion for the past four decades. Sewage sludge contains many valuable resources as well as a variety of biological and chemical threat agents that pose a largely unknown risk to human health and the environment. Since the 1993 EPA Part 503 Biosolids Rule was established, a variety of novel threats have been detected in sewage sludge, including endocrine and neurological disruptors, prions, antibiotic resistance genes, respiratory viruses, and both nano- and microplastics. The EPA has cited a lack of biological and chemical toxicological data requisite to perform proper risk assessment of these potential threats as a reason to delay updating the Part 503 rule, but the potential risk remains regardless of whether or not it has been formalized and quantified. In addition, a series of challenges are faced in performing risk assessment, including a current inability to judiciously account for risks stemming from synergistic effects of multiple agents and from transformation byproducts. In addition, there is a notable lack of electronic record-keeping of where sewage sludge historically has been applied and of epidemiological studies to examine whether the prevalence of adverse ecosystem and human health outcomes in these locations is higher than in control locations. Following the 1988 Ocean Dumping Ban of sewage sludge, the EPA was highly incentivized to find reasonable alternative disposal methods for the 14 million tons dry weight of the substance produced

in the U.S. per year, and the term “biosolids” was created as a way to convince the public that the material was safe for usage on agricultural land. Additionally, the fact that much of sewage sludge-related research in the U.S. is funded by organization representing the owners and disposers of sewage sludge may be inhibiting the development and publication of impartial research regarding the environmental risk posed by application of treated sewage sludge on land. Since the goal of wastewater treatment is to remove toxins and hazards from the water environment, the resultant sewage sludge will always represent a complex matrix that is enriched in the content of both biological and chemical threats. As current treatment methods for sewage sludge are geared primarily on reducing biological hazards, a viable path for turning sewage sludge into a benign material free of unwanted risks currently is an illusive and potentially unattainable goal.

5.1 Introduction

Around the globe including in the United States, federal, state, and local jurisdictions and other key stakeholders are promoting the diversion of organic waste materials away from landfills to promote solid waste reduction and sustainable land use. In the state of California, for example, recently promulgated regulations call for a diversion of more organics away from landfills (Lara 2016), a goal whose attainment puts pressure on municipalities to consider the land application of treated municipal sewage sludge. Federal and state regulation governing the land application of U.S. sewage sludge are informed by the U.S. Environmental Protection Agency 1993 rule, published in the Code of Federal Regulations, Title 40 (Part 503), under Section 405 (d) of the Clean Water Act, as a guiding framework for the safe management of residuals produced during centralized municipal wastewater treatment in activated sludge treatment plants.

Adoption of land application of municipal sewage sludge shows a considerable range across the United States, with land application rates of sewage sludge ranging from 0 to 90% (North East Biosolids and Residuals Association 2007). Historically speaking, California often has set guidelines for environmental protection, sustainability and public health protection which exceeded those promulgated at the Federal level. This more restrictive California rulemaking frequently later informed further revisions of nationwide regulations to make them more stringent, with prominent examples including oil refining, agriculture, and the use of harmful chemicals such as brominated flame retardants (Berman and Bui 2001; Daub 2004; Guthman 1998; Vogel 2019).

The new Californian rules for diversion of organic waste away from landfills (Lara 2016) are a welcome change from the linear economic model of resource extraction, use and disposal (Halden and Venkatesan 2020; Venkatesan and Halden 2020). However, the commendable effort to reduce solid waste flow into landfills also may have unintended consequences by generating new ecological and human health hazards. Specifically, the application on land of treated U.S. sewage sludge meeting the requirements of the 503 Rule is not necessarily universally seen as a sound practice and good stewardship of both the soils and the planet (Oberg and Mason-Renton 2018; Pepper et al. 2019; Sidhu et al. 2019b). Specific concerns raised in the past about the safety of land application of so-called municipal sewage sludge have revolved around organic contaminants, pathogens, the development of antibiotic resistance genes and other potential health hazards (Bradley O Clarke and Stephen R Smith 2011; Gerba et al. 2002a; Zhang et al. 2018).

To inform this dialogue and evaluation, the present paper seeks to assess and summarize the state of science with respect to the safety of land application of sewage sludge on U.S. land. A specific question posed is to whether the rule book dating back to 1993 is still suitable to protect the environment and human health in the modern day, particularly in light of the many scientific advances and lessons learned over the past 30 years. Among these advances are the ability to confidently measure an ever increasing number of trace constituents in sewage sludge, new toxicological mechanisms and outcomes such as endocrine disruption, promotion of antibiotic drug resistance, epigenetic changes and transgenerational reproductive and developmental toxicity as well as synergistic effects of multi-pronged exposures.

5.2 Discussion

5.2.1 International Approaches to Use and Disposal of Sewage Sludge

There are three main disposal methods for sewage sludge implemented around the world. Sewage sludge that meet local standards for maximum levels of regulated contaminants may be mixed with traditional fertilizer and applied to agricultural soil in a process referred to as land application. The attempt to sequester sewage sludge from the rest of the environment via a physical barrier to prevent leaching is referred to as landfilling. Finally, in countries where it is permissible, sewage sludge can be incinerated with or without heat energy recovery.

Although the 1986 European Union 86/278/EEC regulates the disposal of sewage sludge across the EU, individual member countries will occasionally impose more stringent local regulations. One such example is the Netherlands, in which the requirements for landfilling and land application as fertilizer are so strict that the only

sewage sludge disposal method practiced in the Netherlands is incineration, and about half of the sewage sludge incinerated is co-incinerated with other waste products to use as a fuel source (Bauer et al. 2020). In the U.S., just under 50% of all sewage sludge produced are applied on land, and the rest are incinerated or landfilled (North East Biosolids and Residuals Association 2007), although policy varies widely between states (Table 1). Some countries, such as China, have made significant progress with regard to more responsible sewage sludge disposal over the past 20 years. Prior to 2010, over 80% of Chinese sewage sludge was estimated to be improperly dumped, but that number since has been reduced to less than 40%, as China has integrated incineration and landfilling approaches from other countries (Yang et al. 2015; Zhang et al. 2016). While countries around the world employ different combinations of these three sewage sludge disposal methods, it is not clear which methods are the most sustainable and pose the least environmental and human health risk to society.

Table 5. Land Application of Sewage Sludge and Annual Sewage Sludge Production on State Basis.
Sources: (North East Biosolids and Residuals Association 2007; Seiple et al. 2017)

State	Agricultural Biosolids Disposal (2004)	Annual Total Sewage Sludge Produced (dw) (10^3 tonnes/yr)
Alabama	50-59%	150.6
Alaska	40-49%	22.0
Arizona	60-69%	155.4
Arkansas	40-49%	107.1
California	40-49%	1293.7
Colorado	60-69%	159.2
Connecticut	10-19%	141.9
Delaware	60-69%	37.9
Florida	80-89%	592.2
Georgia	10-19%	293.3

Hawaii	30-39%	50.1
Idaho	50-59%	49.9
Illinois	40-49%	841.9
Indiana	40-49%	351.9
Iowa	50-59%	135.0
Kansas	20-29%	111.4
Kentucky	10-19%	153.7
Louisiana	10-19%	188.1
Maine	80-89%	49.5
Maryland	50-59%	167.0
Massachusetts	40-49%	272.3
Michigan	20-29%	496.9
Minnesota	30-39%	182.8
Mississippi	No Data	95.0
Missouri	No Data	294.1
Montana	50-59%	29.0
Nebraska	80-89%	70.2
Nevada	0-9%	101.6
New Hampshire	60-69%	35.7
New Jersey	10-19%	435.0
New Mexico	70-79%	67.1
New York	40-49%	1006.3
North Carolina	50-59%	237.8
North Dakota	0-9%	21.8
Ohio	40-49%	683.7
Oklahoma	50-59%	134.7
Oregon	70-79%	151.5
Pennsylvania	20-29%	593.3
Rhode Island	10-19%	48.1
South Carolina	30-39%	183.7
South Dakota	60-69%	22.2
Tennessee	10-19%	270.1
Texas	20-29%	919.8
Utah	80-89%	89.7
Vermont	60-69%	16.7
Virginia	20-29%	270.1
Washington	50-59%	240.5
West Virginia	30-39%	60.1
Wisconsin	60-69%	236.5
Wyoming	80-89%	18.9

5.2.2 Contaminants Addressed and Not Addressed by the United States 503 Rule

It is important to point out that sewage sludge contain many useful rare earth metals, and this semi-solid waste has been the subject of multiple studies regarding resource recovery (Peccia and Westerhoff 2015). However, of equal importance are an ever-increasing list of persistent, potentially toxic chemicals that partition into sewage sludge and may be reintroduced into the environment depending on the sewage sludge disposal method.

5.2.3 History of Characterizing Contaminants in U.S. Sewage Sludge

One of the largest formal studies to characterize the contaminants in U.S. sewage sludge was the 1988-1989 EPA National Sewage Sludge Survey, during which samples from over 180 wastewater treatment plants were collected, with the intended goal of assessing whether any of a selection of over 400 metals and organic contaminants merited regulation in sewage sludge for application on land due to the risks posed to either the environment or human health (Environmental Protection Agency 1996). Fifteen pathways for potential exposure to humans and wildlife were considered in a wide scale risk analysis. However, due to a lack of modern risk assessment tools, a few significant assumptions were made during this study, namely, that organic contaminants that a) were not produced in the U.S., b) had less than a 5% detection rate, or c) were currently banned in the U.S., would be automatically excluded from consideration for regulation. While these conditions seem reasonable at first glance, and they likely simplified the risk assessment process, these assumptions do not ensure public health safety.

Since then, two more national surveys have been conducted in 2001 and 2006-2007, focusing on specific chemical groups including PCBs, dioxins and furans, pharmaceuticals, steroids and hormones. While the data from these surveys are publicly available, only a few risk assessments on subgroups of chemicals have been performed on these data (Sidhu et al. 2019a). As pointed out in a 2018 EPA Office of Inspector General report, research is still needed on 352 pollutants for which the EPA has determined their presence in sewage sludge, but lacks enough risk assessment data, including human health and ecological toxicity values, exposure data, and environmental fate and transport properties, to make reasonable assessments as to the need or lack of need for their regulation in sewage sludge (Environmental Protection Agency 2018c).

5.2.4 New Risks That Have Emerged After the Promulgation of the 1993 503 Rule

While the existing 503 Rule governing sewage sludge regulation in the United States attempted to address most known toxicity concerns at the time, several new environmental concerns have emerged over the past three decades that may merit further study. While endocrine disruptors such as parabens and nonylphenol ethoxylates have been detected in sewage sludge since as early as 2014 (Chen et al. 2018; Lorenzen et al. 2004), the risk they pose to the environment is largely unstudied with regard to U.S. sewage sludge disposal methods.

Microplastics (MPs) have been detected in U.S. sewage sludge as early as 2012, (Lassen et al. 2012), and since then, their presence has been detected in sewage sludge samples across the world. Not only have MPs been shown to affect the anaerobic digestion of sludge (Hatinoğlu and Sanin 2021), but MP concentrations in land-applied sewage sludge have been reported to be as high as 3500 MP particles / kg of soil

(Corradini et al. 2019). As recent as 2021, chemical groups already well characterized in sewage sludge such as phthalates have been revisited in the scientific literature due to their neurotoxicity (Hlisníková et al. 2021). Epigenetic disruptors, which can affect multiple generations of human life by altering the parents' DNA, has been discussed for its relevance in sewage sludge in the past decade (Wilkinson et al. 2016). Antibiotic resistance genes have been detected in sewage sludge as early as 2011 (Munir and Xagoraraki 2011). Prions continue to remain seen as a potential threat since 2006, since although they are only likely to be sourced from specific kinds of waste streams such as slaughterhouses, studies have concluded that modern wastewater treatment will not destroy or remove prions, and they are likely to persist actively in sewage sludge (Saunders et al. 2008). More recently, the SARS Coronavirus has been determined to partition out of the wastewater stream and into sewage sludge, and while the coronavirus is generally unstable in this environment, its potential risk is unstudied (Balboa et al. 2021; Gianico et al. 2021).

Lastly, synergistic toxicity is an extremely important component of a comprehensive risk analysis, but little research has been done in this area with regard to sewage sludge. It is still largely unknown whether the effect from multiple toxins that affect the same target species compound additively, multiplicatively, independently, or in some other way. As a result of these new developments since the 1993 503 Rule, the EPA is in a difficult position, where hundreds of pollutants have been detected in sewage sludge without a performed risk assessment, and several new classes of contaminants, including viruses and plastics, potentially contribute additional risk to the environment in the disposal of sewage sludge.

5.2.5 Studies Performed to Assess the Safety of Sewage Sludge Application on Land

Biological and chemical hazards from sewage sludge land application are largely understudied. A wide variety of pathogens such as Escherichia coli, Legionella spp., and Adenoviruses are commonly detected in sewage sludge (Jenkins et al. 2007). While there is research demonstrating that human exposure to sewage sludge land application is associated with certain illness, demonstrating causality is a difficult epidemiological task, and to our knowledge the EPA has not been able to demonstrate conclusively that exposure to sewage sludge application caused a certain viral outbreak. However, this lack of evidence is not evidence of absence, and it is reasonable for the public to have doubts about the safety of land application of sewage sludge with regard to pathogenic exposure. An even greater task exists with regard to organic contaminants, for which over 350 pollutants have been detected in U.S. sewage sludge samples without enough parameters available from literature to perform a complete risk assessment. Prions, first detected in sewage sludge in 2006 (Saunders et al. 2008), are responsible for an estimated 247 deaths in the U.S. annually (Holman et al. 2010). Phthalates, one of many classes of chemicals that act as endocrine disruptors, has been estimated to cost the U.S. 40 billion USD in lost economic productivity annually due to just under 91,000 annual deaths (Trasande et al. 2022). These novel threats that have emerged over the past two decades are having significant impacts on human health nationwide, and suggest that alternatives to land application of sewage sludge may be better for society overall. In order to fully understand if land application of sewage sludge creates disease in an agricultural community, epidemiological studies need to be performed in communities that apply sewage sludge, but whereas EPA regional sewage sludge managers keep track of where

sewage sludge is being land applied at a regional level, to our understanding that information is not made available to the general public.

This being said, it is important to remember that sewage management will never be a completely risk-free process. Regulators can only strive to take an approach that poses as little risk as possible to the stakeholders involved, based on available data. It is imperative that further research be performed to better characterize the biological and chemical hazards

5.2.6 Challenges in Risk Assessment.

One of the biggest criticisms by the EPA Office of Inspector General regarding the EPA's approach to sewage sludge is that hundreds of contaminants have been detected in sewage sludge, but have not had risk assessment performed with regard to disposal methods. As the EPA pointed out in their response, there are several challenges impeding a broad risk assessment of these contaminants, including synergistic effects (Roccaro and Vagliasindi 2014; Urasa and Mwebi 2011) and newly understood transformation byproducts (Chen et al. 2020; Wu et al. 2015).

A lack of many toxicological parameters necessary to perform a thorough risk assessment was pointed out as early as the 1987 EPA risk assessment performed on the data from the second National Sewage Sludge Survey. In this study, one of the fifteen pathways, Pathway 8, was focused on the risk to plants due to the land application of sewage sludge. While noted as a pathway, the authors directly stated that there was not enough data on the phytotoxicity effects of the pollutants in question. Several decades later, the exposure of wildlife continues to be an understudied aspect of sewage sludge direct application as a soil amendment, and while phytotoxicity data is more readily

available than it was three decades ago, phytotoxicity risk assessments have only been performed for a few chemicals in specific studies, such as ciprofloxacin and azithromycin in 2019 (Sidhu et al. 2019a). As an example, during the EPA's 2016/17 biennial review on sewage sludge, the EPA noted that 28 new organic contaminants had been detected in sewage sludge during the two years prior, but human health toxicity parameters were only available for three of those new contaminants, and toxicity parameters for wildlife were available for 17 of them (EPA 2016/17 biennial review). This delay in toxicity data makes it difficult for researchers to swiftly respond to new threats. While it may be unreasonable to assume that risk assessments can be performed for every single analyte detected in sewage sludge, there are many groups of chemicals for which little to no risk assessment has been performed at all.

In addition, the lack of standardization in terms of data formatting, lack of CAS numbers for the targeted analytes, and lack of consistency across the EPA's multiple National Sewage Sludge Surveys were not conducive to combining data from multiple studies, and these factors inhibit the EPA's ability to perform risk assessment on their data (Environmental Protection Agency 2018c). As shown in Table 1, the most recent publicly available data on state-level sewage sludge disposal methods are from the year 2004. These factors have and continue to impede researchers' ability to perform proper risk assessment and characterize the hazards disposal methods of sewage sludge pose to greater society.

5.2.7 Alternatives to Land Application

While land application of sewage sludge is the most common disposal method in the U.S., there are alternatives that may be more environmentally responsible. One of the

core principles of treating toxic chemicals is to treat them in as concentrated a state as possible, as you usually get higher treatment efficiency in concentrated states. When sewage sludge were dumped in the ocean prior to the 1988 Ocean Dumping Ban, any persistent organic contaminants were diluted into the ocean, making any treatment nearly impossible, and laying the groundwork for slow accumulation of these chemicals overtime. One possible strategy would be to use dedicated landfills for sewage sludge only, so that as further sewage sludge treatment technologies are invented, the sewage sludge material remains concentrated for easy treatment.

Researchers continue to study pretreatment techniques to enhance anaerobic digestion and reduce the volume of sewage sludge, although many of these technologies do not remove the persistent organic contaminants present. Countries in Europe have taken a wide variety of other approaches, such as the Netherlands, where all sewage sludge are incinerated, and about half of the incinerated sewage sludge serves as energy for fuel production or is used to make cement. Other countries, such as Germany and Sweden, enacted local legislation placing much lower limits for toxic metal element concentrations in sewage sludge, and requiring phosphorus recovery technologies to be implemented in phosphorus-rich sewage sludge.

5.2.8 Balancing Waste Minimization Goals with Public Health Protection

While source reduction of persistent chemicals, microplastics, and other potentially harmful pollutants in sewage sludge is the ultimate solution, this is a longer-term solution. The reality that the wastewater treatment community faces is that these harmful chemicals are already in our environment. With this in mind, the topic of this

literature review is to support the need to update the State's sewage sludge land application standards.

5.2.9 Risk-benefit Analysis

In 2016, SB 1383 passed the California legislature, and carried significant modifications for the state's sewage sludge disposal program. In order to reduce methane emissions, a total of 75% of organic waste, including sewage sludge, are to be diverted away from landfills by 2025. Since California does not incinerate their sewage sludge, land application on agricultural land as a fertilizer amendment has become a reality.

5.2.10 Public Trust

Environmentally responsible management of sewage sludge in the U.S. has been a contentious topic since as early as the 1988 Ocean Dumping Ban. While this legislation was a good step in the right direction toward environmentally responsible waste management, it created an immediate challenge to wastewater treatment plant operators across the country – how should the U.S. dispose of its sewage sludge now that ocean dumping was no longer deemed safe to ocean wildlife? The EPA took an economical and creative approach to this problem by coining the term "biosolids" to refer to treated sewage sludge, and at the same time suggested that any contaminants present in sewage sludge were at low enough concentrations to pose little threat to the public.

While this approach improved public sentiment toward the land application of sewage sludge, especially for people who were not familiar with the history of the terminology, calling a hazardous waste material a positive word is not being honest towards the many known unknowns and unknown unknowns regarding sustainable disposal of sewage sludge. Other events such as the sudden rebuilding of the EPA

website during 2016 as well as the 2018 OIG report shed light on the size of the tasks that must be undertaken before sewage sludge applications on land can be truly understood and the public can fully trust in the disposal methods utilized in the U.S.

5.3 Conclusions

The issue of environmentally responsible sewage sludge disposal is not going to go away. While in theory, the most efficient method of reducing human and environmental risk is to research new source reduction treatment technologies, stakeholders and government agencies must use the available data and tools to practice responsible disposal given the present limitations. In 1988, the U.S. President signed into law the Ocean Dumping Ban Act, officially stating that sewage sludge are unsafe for dumping into the ocean. Land application of sewage sludge is in theory the most sustainable approach when compared to alternatives such as landfilling and incineration, but since the Part 503 rule, many new potential threats were not considered in development of the Part 503 rule have emerged, including endocrine disruptors, neurological disruptors, prions, antibiotic resistance genes, and both micro- and nanoplastics. While the EPA has conducted multiple National Sewage Sludge Surveys to quantify the presence of some of these new threats, these surveys have focused mostly on metals and a selection of organic contaminants, and the older surveys suffer from a lack of consistency in analyte identification that make it difficult to utilize older data. Additionally, whether collected at the state or federal level, information about where sewage sludge are currently being applied is not accessible to the public, and the most recent survey estimate of such data is 15 years old. While best practices, such as only applying biosolids on agricultural land for non-edible crops, are useful methods to reduce

the risk posed to human health and the environment, there is an urgent need for environmental and toxicological research to better understand these novel threats in biosolids, and a need for the federal biosolids standards to be revisited and potentially updated in accordance with the findings of these studies.

CHAPTER 6

RESEARCH IMPLICATIONS AND RECOMMENDATIONS

This work has analyzed the fate of plastic waste and sewage sludge from both an environmental and human health perspective, providing insight into the risks present in their respective current management strategies, as well as exploring the potential impact of alternative management strategies. In Chapter 2, an inventory of all organic chemical concentrations from a total of 105 studies. The raw concentrations and corresponding metadata were compiled into a database of 795 organic contaminants, 269 of which had previously been studied in China as well. This allowed for chemical-by-chemical comparisons for highly studied analytes, during which it was found that concentrations on average were four times higher in the U.S. than in China. Whether this is due to the U.S. having more sophisticated sewage sludge treatment, higher input concentrations of the organic chemicals, or some other factor, the finding was unexpected and highlights the lack of knowledge with regard to the complex nature of sewage sludge. Given these known unknowns and unknown unknowns in sewage sludge, understanding and quantifying the human health and environmental risks present in the various disposal methods is critical to responsible disposal of sewage sludge, and Chapter 3 takes previously unanalyzed metal concentration data and applies modern human health risk assessment to sewage sludge for the first time. Instead of a single point-value risk for each metal, Monte Carlo simulations provide a range of potential risks to better characterize the impact of agricultural land application. Additionally, synergistic effects were accounted for by incorporating toxicity data into the simulations, to understand if

metals that affect the same bodily systems, when combined, pose a risk. This study demonstrated that given the current concentrations of metals, the risks come close for some metals, but do not ultimately appear to pose a threat to humans who involuntarily consume farm soil that has been treated with sewage sludge, but at the same time, there continue to be hundreds of organic contaminants and metals that have been detected in sewage sludge, but for which no risk analysis has been performed. In chapter 4, results from fragmentation and degradation studies were combined with plastic transport models to understand the potential impact of plastic production policy on plastic pollution in the ocean ecosystem. Given a scenario of unlimited continued plastic production growth, the total mass of MPs and NPs were predicted to reach 74.2 ± 14.8 and 38.9 ± 7.8 M tonnes by 2100, and in a scenario of plastic production phase-out by 2100, MP and NP masses showed a peak at 23.6 ± 4.7 and 12.2 ± 2.4 M in 2063, demonstrating that even with active policy changes to minimize future plastic production, plastic waste already in existence will continue to feed into the ocean ecosystem, potentially harming aquatic wildlife, and by extension, humankind as well in the coming decades. Lastly, in Chapter 5, a broad perspective on current sewage sludge disposal methods was given, overviewing the history, the logic behind the current choices for disposal methods, the recently discovered threats in sewage sludge, and the next steps to fully characterizing the risks posed to humans and the environment by the different disposal methods possible.

6.1 Recommendations for Future Research

It may be easy to point out that the EPA has lagged behind in performing follow-up analyses on threats discovered both in their own studies as well as external studies, but their task is one that takes a significant amount of resources. New chemicals are

developed every day that have properties and behaviors that may cause risk when partitioned into sewage sludge destined for land application. Additionally, several new threats have been discovered in the past 20 years as discussed in Chapter 5. Ideally, a more comprehensive monitoring system for sewage sludge would include (i) conducting national sewage sludge surveys at regular intervals, and not only analyzing these samples for a set of known potential threats, but freezing these samples and storing them as a window into the past as new threats will inevitably be discovered, (ii) supporting and conducting toxicology studies and risk assessments on the most persistent chemicals to better understand the risks they pose, (iii) being more transparent about where sewage sludge is being disposed of in the United States by making that information public, and (iv) conducting epidemiological studies on these areas to have a deeper understanding of the way in which recently discovered threats in sewage sludge might be adversely affecting people in the area.

With regard to plastic pollution, one of the biggest challenges facing the research community is finding ways to calibrate and validate small-scale models in a world ocean system that is full of varied geography, with many unknown interactions with plastic. One of the biggest challenges in studying plastics in the ocean is that net mesh sizes are not small enough to capture nanoplastics reliably. In fact, some studies have suggested that the smallest net mesh sizes are not even reliably capturing microplastics in their entirety (Lindeque et al. 2020). While mechanical fragmentation and photodegradation, two of the more well-studied processes affecting plastic waste, were incorporated into this model, other processes such as chemical degradation and biodegradation were excluded from the model, largely because researchers have published wildly different

findings, some suggesting that these are insignificant contributors to plastic breakdown, and others suggesting that they are the most significant contributors (Wayman and Niemann 2021).

The problems confronted in this dissertation have no simple solutions. If they did, those solutions would have been adopted decades ago. Sewage sludge is an inevitable byproduct of modern society that is likely to continue to contain multiple potential health threats. Even if drastic plastic production efforts took place on a global scale, the amount of plastic waste on land will continue to affect ocean masses of high-risk micro- and nanoplastics, affecting aquatic wildlife and potentially humans as well. Only by taking great effort to characterize these threats and understand their impact on humans and the greater environment, can stakeholders and decision makers create responsible policy with regard to the disposal of sewage sludge and plastic.

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APPENDIX A

SUPPLEMENTAL MATERIAL FOR CHAPTER 2

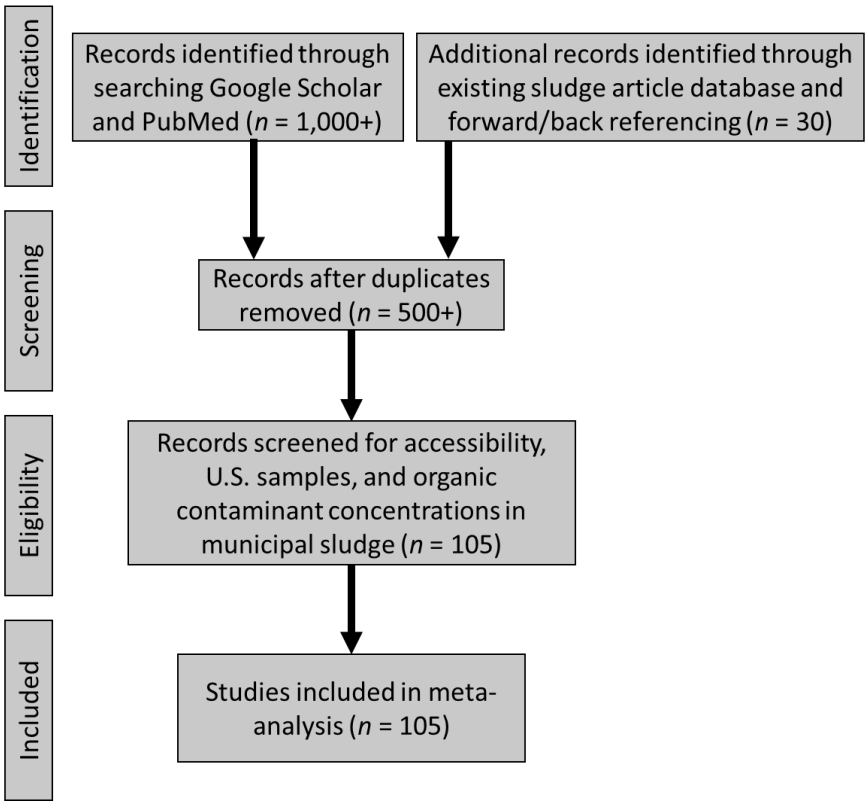

Figure 13. PRISMA Flow Diagram Showing Search Engine Results and Screening

Table 6. China to U.S. Comparison Summary Data Used in Figure 4

Class	Chemical Name	United States				
		Mean (µg/kg dw)	Standard Error (µg/kg dw)	Number Studies	Number Samples	References
Aromatic Amines	2,6-Dinitrotoluene	1235	0	1	176	(Environmental Protection Agency 1996, 2009c)
	4-Chloroaniline	1296	0	1	84	
Antibiotics	Tetracycline	1119	26	8	397	(Ding et al. 2011; Environmental Protection Agency 2009c; Gao et al. 2012a; Gao et al. 2012b; McClellan and Halden 2010; Spongberg and Witter 2008; Venkatesan and Halden 2014a; C Wu et al. 2010a; C Wu et al. 2010c; CX Wu et al. 2010)
	Chlortetracycline	423	34	5	208	
Alkylphenol Ethyl Oxylates (APEOs)	Nonylphenol	502843	57585	8	79	(Buyuksonmez and Sekeroglu 2005; Chalaux et al. 1994; Keller et al. 2003; Kinney et al. 2006; Kinney et al. 2008; La Guardia et al. 2001; La Guardia et al. 2004; Pryor et al. 2002; Ross et al. 2016; Xia et al. 2010; Yu and Wu 2012; Yu et al. 2013)
	NP1EO	35418	3350	4	26	

Bisphenols	Bisphenol A	827	115	5	102	(Bradley O. Clarke and Stephen R. Smith 2011; Kinney et al. 2006; Yu et al. 2015; Yu and Wu 2012)
	Bisphenol AF	6	0	1	76	
Steroids and Hormones	Estrone	61	4	6	189	(Bevacqua et al. 2011; Environmental Protection Agency 2009c; Kinney et al. 2006; Kinney et al. 2008; Lozano et al. 2010; Venkatesan and Halden 2014a; Yang et al. 2012; Yu and Wu 2012; Yu et al. 2013)
	Testosterone	131	24	3	38	
Organochloride Pesticides	Hexachlorobenzene	3883	23	2	479	(Environmental Protection Agency 1982; Furr et al. 1976; Heidler and Halden 2009; Sadaria et al. 2016; Sadaria et al. 2017; U.S. Environmental Protection Agency 1996)
	Endosulfan-II	8	0	1	175	
Phthalate acid esters/plasticizers	DEHP	163938	3309	7	770	(Buyuksonmez and Sekeroglu 2005; Environmental Protection Agency 1982, 1996, 2009c; Kinney et al. 2006; Kinney et al. 2008)
	DnBP	24063	561	4	674	
Polycyclic Aromatic Hydrocarbons	Fluoranthene	39522	1544	6	751	(Environmental Protection Agency 1982, 1996, 2009c; Kinney et al. 2006; Kinney et al. 2008)
	Pyrene	14494	1346	6	751	
Polybrominated Diphenyl Ethers	BDE-47	610	15	20	292	(Anderson and MacRae 2006; Andrade et al. 2010; Andrade et al. 2015; Arnold et al. 2008; Ciparis and Hale 2005; Davis et al. 2012; Davis et al. 2015; Environmental Protection Agency 2009c; Gaylor et al. 2014; Hale et al. 2001; Hale et al. 2002; La Guardia et al. 2004; La Guardia et al. 2006; North 2004; Petreas and Oros 2009; Ricklund et al. 2008; Rocha-Gutierrez and Lee 2013; Venkatesan and Halden 2014b; Vonderheide et al. 2002; Xia et al. 2010)
	BDE-209	3424	209	20	331	
Phenolic Compounds	2-chlorophenol	383	5	2	475	(DeWalle et al. 1982; Environmental Protection Agency 1982, 1996; Kinney et al. 2006; Kinney et al. 2008)
	2,4-dichlorophenol	2999	232	3	518	
Polychlorinated Biphenyls	PCB-52	10	0	1	94	(Environmental Protection Agency 2002b; Furr et al. 1976; Gutenmann et al. 1994; Mumma et al. 1983; Mumma et al. 1984; Mumma et al. 1988; Richards et al. 2004)
	PCB-209	1	0	1	94	
PCDDs and PCDFs	2,3,7,8-TCDD	0	0	5	302	(Environmental Protection Agency 1996, 2002b; Lamparski et al. 1984; Litten et al. 2003; Rappe et al. 1998; Weerasinghe et al. 1985)
	2,3,7,8-TCDF	0	0	4	299	
Perfluoroalkyl and	PFOS	247	13	9	192	(Armstrong et al. 2016; Bradley O. Clarke and Stephen R. Smith 2011; Higgins et al. 2005;
	PFDA	26	1	7	136	

polyfluoroalkyl substances						Loganathan et al. 2007; Schultz et al. 2006; Sepulvado et al. 2011; Sinclair and Kannan 2006; Venkatesan and Halden 2013)
Pharmaceuticals	Carbamazepine	127	2	14	427	(Buyuksonmez and Sekeroglu 2005; Chari and Halden 2012; Chenxi et al. 2008; Ding et al. 2011; Environmental Protection Agency 2009c; Gao et al. 2012a; Kinney et al. 2006; Kinney et al. 2008; McClellan and Halden 2010; Spongberg and Witter 2008; Subedi and Kannan 2015; Venkatesan and Halden 2014a; C Wu et al. 2010a; CX Wu et al. 2010; Yu and Wu 2012; Yu et al. 2013)
	Caffeine	215	5	8	397	
Synthetic Musks	Galaxolide	25296	1859	10	115	(Buyuksonmez and Sekeroglu 2005; DiFrancesco et al. 2004; Environmental Protection Agency 1996; Horii et al. 2007; Kinney et al. 2006; Kinney et al. 2008; La Guardia et al. 2004; Osemwengie 2006; Reiner et al. 2007; Sun et al. 2014)
	Tonalide	20333	4613	9	96	
Triclosan, Triclocarban, and Derivatives	Triclosan	11596	172	28	554	(Agyin-Birikorang et al. 2010; Ahn et al. 2016; Andrade et al. 2015; Armstrong et al. 2016; Cha and Cupples 2009; Chari and Halden 2012; Chenxi et al. 2008; Davis et al. 2012; Davis et al. 2015; Environmental Protection Agency 2009c; Heidler et al. 2006; Heidler and Halden 2007; Heidler and Halden 2009; Higgins et al. 2011; Kinney et al. 2006; Kinney et al. 2008; La Guardia et al. 2004; Lozano et al. 2010; Lozano et al. 2012; Lozano et al. 2013; McAvoy et al. 2002; McClellan and Halden 2010; Pannu et al. 2012; Pycke et al. 2014; Ross et al. 2016; Sapkota et al. 2007; Snyder et al. 2010; Venkatesan and Halden 2014a; Waria et al. 2011; C Wu et al. 2010a; Xia et al. 2010; Yu and Wu 2012; Yu et al. 2013)
	Triclocarban	29303	328	15	504	

APPENDIX B

SUPPLEMENTAL MATERIAL FOR CHAPTER 3

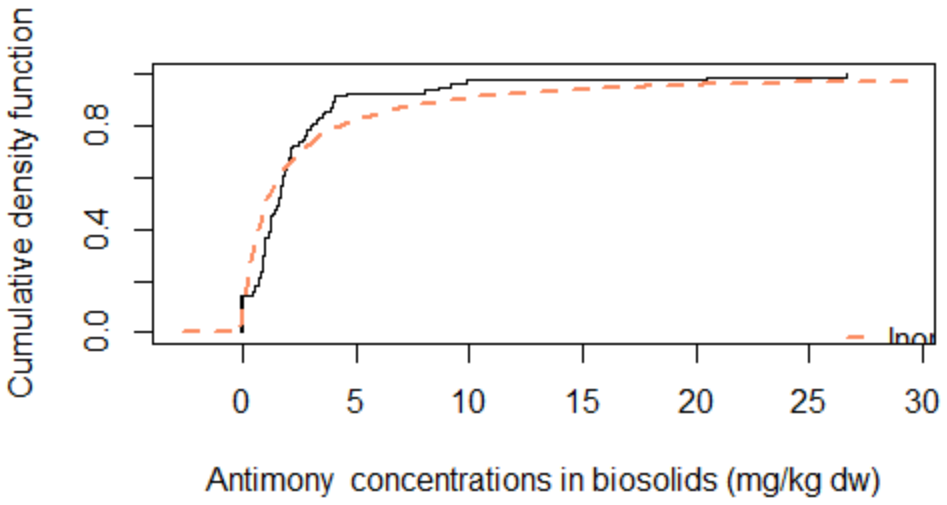

Figure 14. Lognormal Model for Antimony Concentration in Biosolids

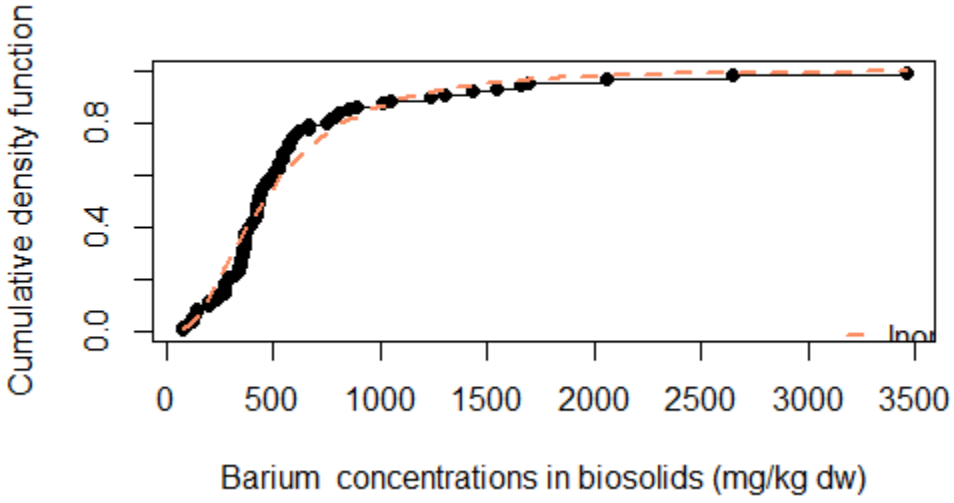

Figure 15. Lognormal Model for Barium Concentration in Biosolids

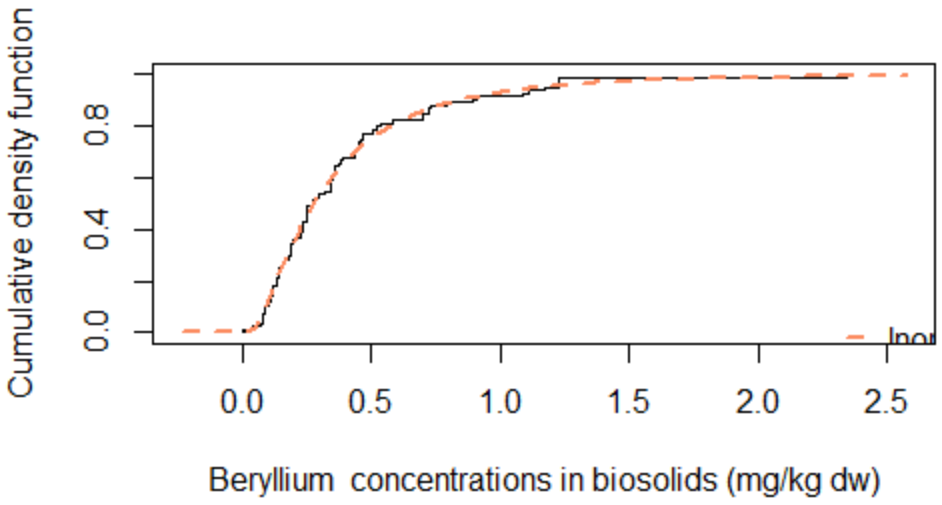

Figure 16. Lognormal Model for Beryllium Concentration in Biosolids

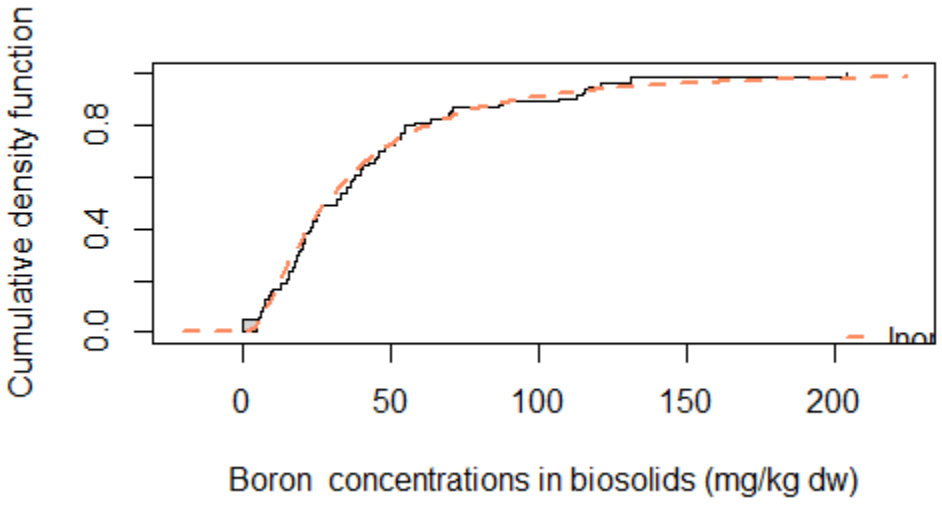

Figure 17. Lognormal Model for Boron Concentration in Biosolids

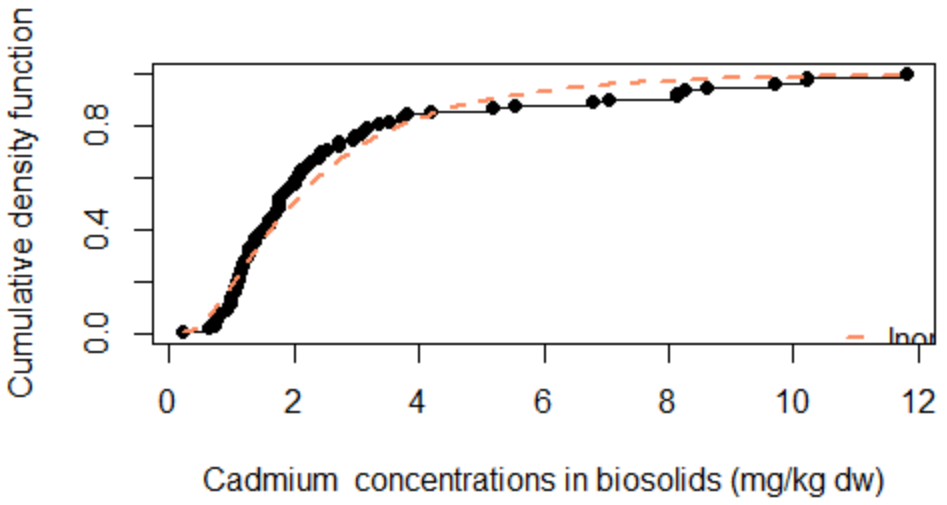

Figure 18. Lognormal Model for Cadmium Concentration in Biosolids

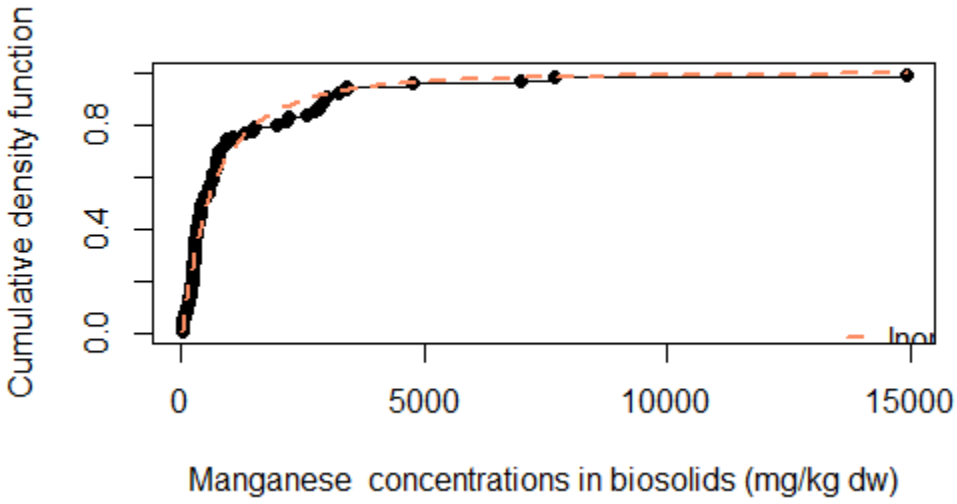

Figure 19. Lognormal Model for Manganese Concentration in Biosolids

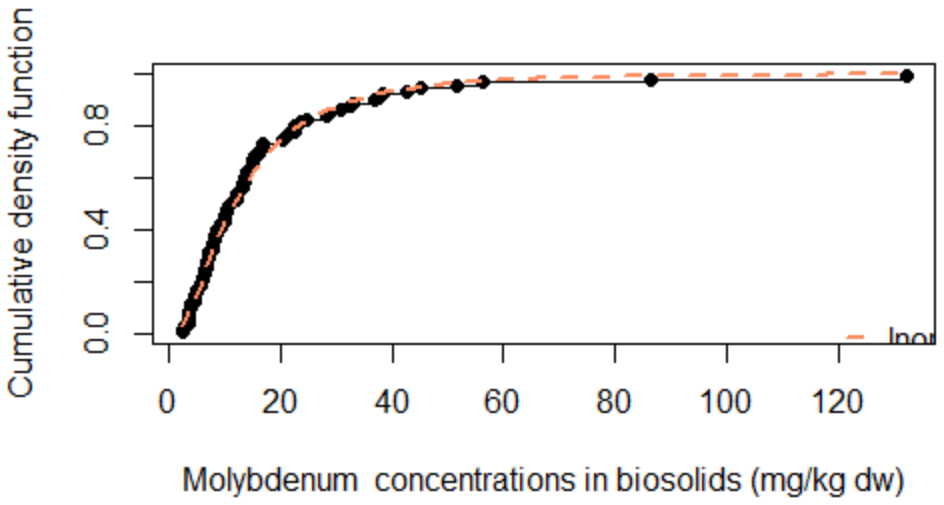

Figure 20. Lognormal Model for Molybdenum Concentration in Biosolids

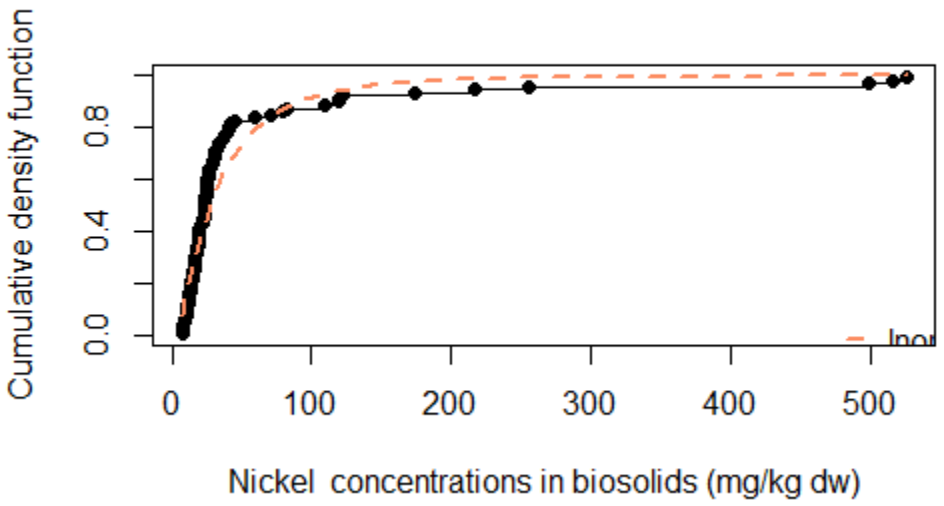

Figure 21. Lognormal Model for Nickel Concentration in Biosolids

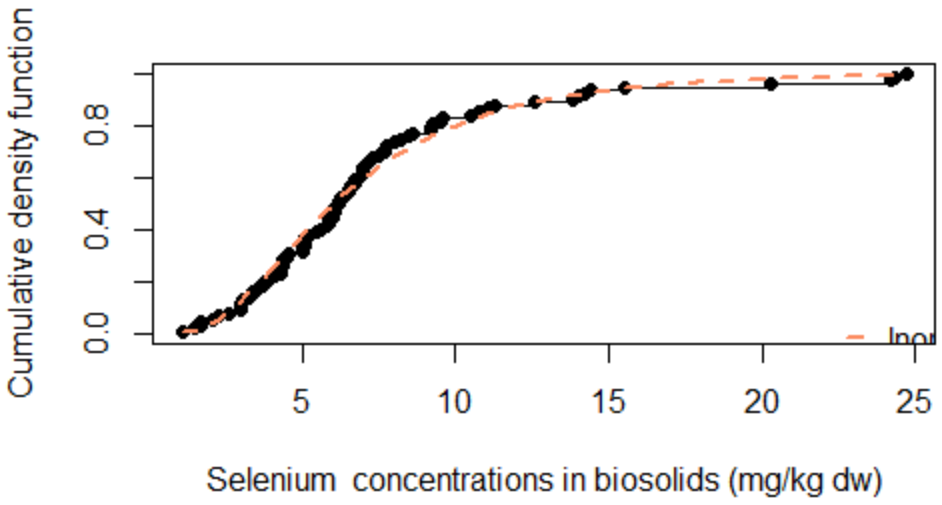

Figure 22. Lognormal Model for Selenium Concentration in Biosolids

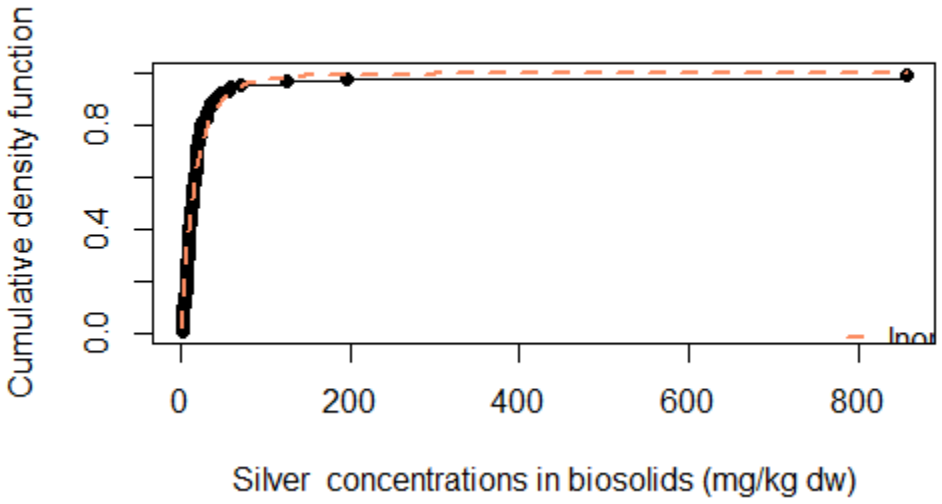

Figure 23. Lognormal Model for Silver Concentration in Biosolids

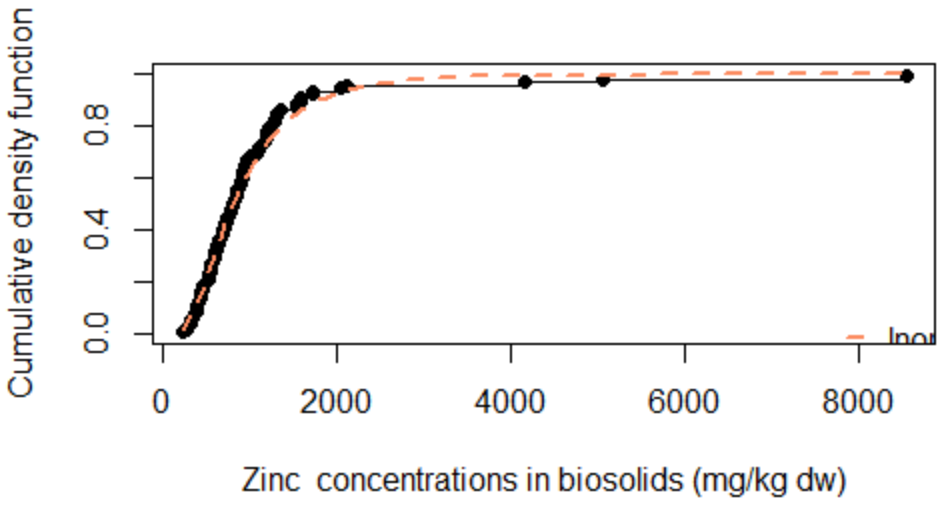

Figure 24. Lognormal Model for Zinc Concentration in Biosolids

APPENDIX C

SUPPLEMENTAL MATERIAL FOR CHAPTER 4

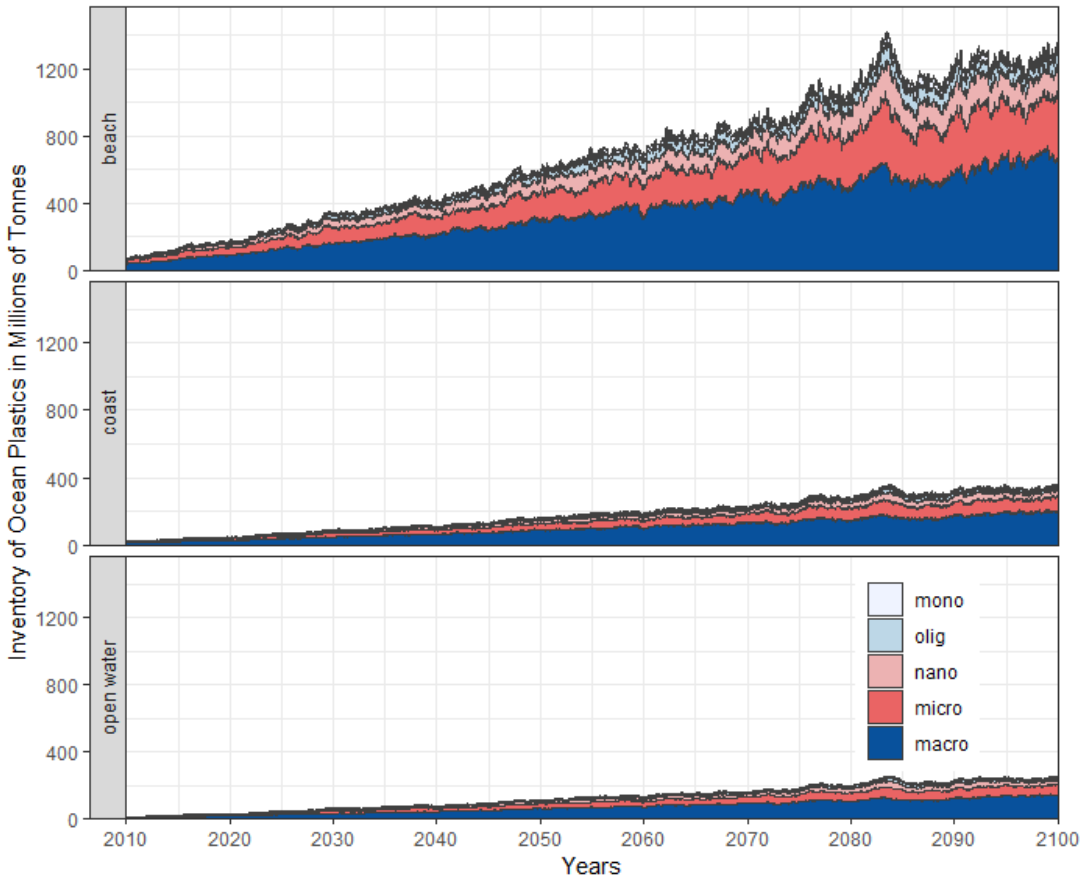

Figure 25. Inventory of Plastic in Ocean Compartments Illustrating Relative Magnitude of Plastic Waste in Beach, Coast, and Ocean Compartments for Scenario 1 (Unlimited Continuous Growth Plastic Production).