FATE OF NONYLPHENOL, NONYLPHENOL MONOETHOXYLATE, NONYLPHENOL DIETHOXYLATE, OCTYLPHENOL, AND BISPHENOL A IN SLUDGE, BIOSOLIDS AND BIOSOLIDS-AMENDED SOILS

by

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A Dissertation submitted to the

Graduate School-New Brunswick

Rutgers, The State University of New Jersey

in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Graduate Program in Environmental Science

written under the direction of

Daniel Giménez

and

Peter F. Strom

and approved by

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New Brunswick, New Jersey

May 2015

ABSTRACT OF THE DISSERTATION

FATE OF NONYLPHENOL, NONYLPHENOL MONOETHOXYLATES, NONYLPHENOL DIETHOXYLATE, OCTYLPHENOL AND BISPHENOL A IN SLUDGE, BIOSOLIDS, AND BIOSOLIDS-AMENDED SOILS

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Dissertation Directors:
Daniel Giménez and Peter F. Strom

Nonylphenol (NP), nonylphenol monoethoxylate (NP_1EO), nonylphenol diethoxylate (NP_2EO), octylphenol (OP), and bisphenol A (BPA) are endocrine disrupting compounds (EDCs) that are present in wastewater. Studies of fate of these compounds have primarily focused on aquatic environments but EDCs are transferred from aquatic to terrestrial ecosystems through land-based sludge and biosolids applications. Biosolids are applied to land as a source of fertilizer, liming material, and for soil conditioning. The main hypotheses of this work were that biosolids are a major source of alkylphenolic compounds and bisphenol A in soils, and that these compounds are persistent in the soil over extended period of time. The goal of this work is to study the fate of these EDCs in sludge, biosolids and soils that have been treated with biosolids. Sludge and biosolids from 14 wastewater treatment plants (WWTP) comprising of 5 sludge stabilization processes, and operating under a wide range of physical, chemical and biological parameters were studied to examine the effect of sludge stabilization on the EDCs in biosolids destined for land uses. Subsequent to that, the fate of these contaminants was

examined in 21soils of contrasting management and geomorphic characteristics 10 years after biosolids amendment. Finally, the ability of environmental model to predict the concentration of EDCs from which environmental fate can be deduced was evaluated using P*h*ATE model.

The results showed that NP, the recalcitrant end product of NPEO degradation, was detected at a range of 0.73-501mg kg^{-1} in sludge, 0.2-564 mg kg^{-1} in biosolids, and 0.01-28 µg kg^{-1} in soil. The effect of sludge stabilization process, or treatment was statistically significant ($p<0.05$) for NP and BPA, nearly significant ($p = 0.064$) for OP, but not for NP_1EO and NP_2EO. Composting produced the highest reduction followed by alkaline stabilization, lime stabilization, anaerobic and aerobic digestion processes. Thus, EDC load being transferred to the soil was minimized through sludge stabilization prior to the actions of soil and environmental processes that eventually determine their fate in soil. After 10 years of biosolids amendment, EDC concentrations in the amended soils were 0.01-28 µg kg^{-1}, and 0.01-2.3 µg kg^{-1} in control soils. EDCs were present in higher concentrations in the topsoil (2-28 µg kg^{-1}) than in the subsoil (0.03-7 µg kg^{-1}), and statistically significant difference ($p<0.05$) exists between the two sets of concentrations. However, the APEOs might have being from both sludge and biosolids, and pesticides sources as most of the sites studied were likely managed with pesticides. The EDCs studied show soil persistence at concentrations of 0.01-28 µg kg^{-1} in 3 soils that were amended with biosolids only. Soil concentration was dependent on the biosolids application rate and the concentration of EDCs in the biosolids. Modeling fate of these EDCs using PhATE model indicate that these compounds are depleted in biosolids-amended soils within 4 years of such amendment.

ACKNOWLEDGEMENTS

Many people contributed to making this work possible. First, I would like to extend my deepest appreciation to my co-advisors, Dr. Daniel Gimenez and Dr. Peter Strom for their diligent guidance, advice, insightful discussions and encouragement throughout the execution of this program. I have benefited tremendously from their wealth of knowledge and experience. I should have had more intellectual exchange with them much sooner than I did. These men know how to gently shoot down bad ideas without letting it hurt. They are gentlemen and scientists! Without them this work would not have been completed.

I would also like to thank my qualifying examination committee members, Dr. Monica Mazurek and Dr. Uta Krogman; and dissertation committee members, Dr. Mark Robson and Dr. Eileen Murphy for their contribution to fulfilling this degree. I am immensely grateful to Dr. Mark Robson for his assistance in getting this research off the ground. Dr. Robson is resourceful, frank, to the point and ever helpful. His enthusiasm is infectious. I am privileged to receive his suggestions and leads on the PhATE model. Also, my thanks to Dr. Eileen Murphy for agreeing to serve on my dissertation committee on short notice, taking the time to scrutinize my dissertation, and for her insightful observations on the study.

I will be unappreciative if I do not mention Dr. Lisa Rodenburg who not only allowed me to set up camp in her laboratory but provided valuable support with instrumental analysis in this work. She was always ready for discussion and provided leads when needed.

There are so many people to thank from various wastewater treatment plants for their assistance during the sample collection stage. They were very cooperative in obtaining the correct sludge and biosolids from correct location within their facilities.

I wish to acknowledge the generous financial support of the New Jersey Agricultural Experiment Station. When I was in the desert, as it were, seeking financial support to get this research off the ground, NJAES came through. Without their timely support this work would not have been possible.

I had the company and assistance of fellow graduate students Songyan Du, Andy Sandy, Kelly Francesco, Sarat Kannepalli, who helped to ease the strain sometimes with lighthearted chats and musings, especially Kelly whose unending day shift overlapped often with my evening/night shift. I thank you all for enriching my experience.

To many friends and family outside the University community who cheered me on: Mr. Alan Hayes, Dr. Mukaila Akinbami, Aunt Moji Agbede, Dr. Pelu & Dr. Titi Adewale, Dr. Akinwunmi & Mrs. Grace Adesina, Dr. Olumide & Dr. Bola Ogundahunsi, Mr. Oluwafemi & Mrs. Ar Ne Odediran, Dr. Kole & Mrs. Adeola Akinboboye, Mr. Michael & Dr. Jibike Itegboje, Mr. Oluranti Adewunmi, Mr. Abayomi Adewunmi, and Mr. Keith Bargmann, to name a few. Thank you all so much.

And lastly, words are not sufficient to express my gratitude to my lovely wife and great cheerleader, Abiola, who gave me the freedom of time and space to spend untold hours and years in the prosecution of this program. Thank you for your constant love, unflinching support and encouragement. And to my daughter, who without fail often asked, “Do you have to go again to the library/laboratory tonight?”

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LIST OF ABBREVIATIONS

AP	Alkylphenol(s)
AP_nEO	Alkylphenol Ethoxylates
API	Active Pharmaceutical Ingredient
ATAD	Autothermal Aerobic Digestion
BPA	Bisphenol A
BSF	Biosolids Stabilization Facility
CCE	Calcium Carbonate Equivalence
DOC	Dissolved Organic Carbon
EC	Electrical Conductivity
EDC	Endocrine Disrupting Chemical
GC-MS	Gas Chromatograph – Mass Spectrometer
HPLC/MS	High Performance Liquid Chromatograph/Mass Spectrometer
MEC	Measured Environmental Concentration
NJAES	New Jersey Agricultural Experiment Station
NP	Nonylphenol
NP_nEO	Nonyphenol Ethoxylates
OP	Octylphenol
OPEO	Octylphenol Ethoxylate
PEC	Predicted Environmental Concentration
PhATE	Pharmaceutical Assessment and Transport Evaluation
PNEC	Predicted No Effect Concentration
POP	Persistent Organic Pollutants

POTW	Publicly-Owned Treatment Works
WWTP	Wastewater Treatment Plant

CHAPTER 1

INTRODUCTION TO THE CHEMICALS IN THIS STUDY

1.1 Background

Nonylphenol (NP), nonylphenol monoethoxylate (NP_1EO), nonylphenol diethoxylate (NP_2EO), octylphenol (OP) and bisphenol A (BPA) are phenols (Figure 1.1). All but BPA belong to the group collectively known as alkylphenol ethoxylates (APEO). Their structure consists of an aliphatic chain of variable chain length and an ethoxylate chain arranged in the para position on a benzene ring. This configuration imbues them with characteristics that lend them to widespread applications. Nonyl and octyl refer to 9-carbon and 8-carbon alkyl groups respectively. The number (n) of ethoxylate units in the chain can vary from 1 to 100 (Marcomini et al., 1989; Naylor, 1995; Thiele, et al., 1997; John et al., 2000) although, for the most common polyethoxyates it is between 1 and 20.

Nonylphenol and dodecylphenol are the largest volume alkylphenol products manufactured in the United States with nonylphenol domestic consumption/production reaching 360 million lbs (1.63×10^8 kg) in 2006 and projected to reach 380 million lbs (1.72×10^8 kg) in 2010 (ICIS Chemical Market Reporter, 2007). Nonylphenol is produced from reaction of phenol with nonene (tripropylene). NP is a starting material in the production of nonylphenol ethoxylate (NPEO) surfactants. NPEO is commercially produced by base catalyzed reaction of ethylene oxide and nonylphenol in different molar ratios to yield the desired nonylphenol ethoxylate homolog. As a result of the industrial synthesis method, commercial NPEOs are a mixture of homologs and isomers. Commercial production results in a mixture of branched nonyl chain isomers, which

makes their instrumental analysis more difficult. Octylphenol, or 4-(1,1,3,3-tetramethylbutyl)-phenol is produced from the reaction of 2,2,4-trimethylpentane and phenol. The reaction yields only one OP isomer.

Bisphenol A (4,4'-dihydroxydiphenol-2,2-propane, or 4,4'-isopropylidenediphenol) belongs to the biphenol group of chemical compounds and is produced from the condensation of phenol and acetone in the presence of an acid catalyst such as hydrogen chloride and a promoter such as methyl mercaptan. In 2008, 44% (3.83 million tons) of global production of phenol was used in the production of bisphenol A and only 16% (1.41 million tons) was used in the production of alkylphenols and phenolic resins (Weber & Weber, 2010). In 2011, the United States BPA production capacity was 970,000 tonnes yr^{-1} (ICIS Chemical Business, 2011), 99.9% of which was used in the production of polycarbonates, epoxy resins, flame retardants and other specialty products (Staples et al., 1998).

1.2 Properties

APEOs are nonionic surfactants and, being amphiphilic, are capable of forming micelles. Micelles have the ability to solubilize or absorb hydrophobic organic compounds. NP is slightly soluble in water having maximum solubility of 4.9 – 6.0 mg L^{-1}. Nonylphenol and lower ethoxylate homologs are strongly hydrophobic. Reported log K_{ow} values for NP and NPEO in the literature vary, but are low, which indicates that they are readily sorbed to organic material in environmental matrices. Generally, a log K_{ow} value higher than 3 is considered to indicate accumulation. This is because log K_{ow} values above 4-5 reflect compounds that are non-polar while log K_{ow} values of 1-1.5 reflect

polar compounds. Bisphenol A is moderately soluble in water at 300 mg L^{-1} and easily migrates from packaging into foods and drinks, especially at higher than room temperatures (Krishnan et al., 1993; Fromme et al., 2002; Rykowska & Wasiak, 2006). BPA exists as a solid, in the form of crystals, prills and flakes, at ambient temperature such that release in to the environment also takes the form of particulates (Staples, et al., 1998). The properties of the studied compounds are summarized in Table 1.1.

1.3 Structure

APEOs and Bisphenol A are phenolic compounds. APEO structure consists of a hydrophobic group made up of a highly-branched alkyl chain attached to a benzene ring, and a hydrophilic group made up of a hydroxyl functional group or polyethoxylate chain. The alkyl group is predominantly positioned in the para position on the benzene ring. Bisphenol A or 2,2-bis(4-hydroxyphenyl)propane, consists of a propane molecule sandwiched between two phenol molecules. The structural configurations are presented in Figure 1.1.

1.4 Uses

Alkylphenol polyethoxylates are widely used in aqueous solutions as nonionic surfactants which accounts for their largest use. Nonylphenol ethoxylates are the largest share of APEOs, amounting to 80% of total APEO volume. Alkylphenols are extremely useful surfactants and are widely used in different household, commercial and industrial applications. Household applications are mainly cleaning products and detergents. Commercial applications include personal care products, floor and surface cleaners,

wetting agents and dispersants. They are used as adjuvants and emulsifiers in pesticide formulations. Industrial uses include: dispersive agents in paper and leather manufacturing, lube oil additives, phosphite antioxidants for rubber and plastics, auxiliary agents for drilling and floatation, degreasers, textile scouring, and almost every stage of textile manufacturing (Bennie et al., 1998). In textile manufacturing, NPEO is contained in every product formulated for fiber sizing, spinning, weaving, fiber dyeing, scouring, and washing (Naylor, 1995). Octylphenol ethoxylates are used in specialized applications such as the Triton-X series of laboratory detergents.

Bisphenol A is mainly used in the production of polycarbonates and secondarily for epoxy resins. Other uses include manufacture of unsaturated polyester-styrene resins, flame retardants, polyacrylate, polyetherimide and polysulphone resins. Polycarbonate resins are used in the manufacture of optical media (for example, eyeglass lenses and compact discs), shatterproof windows and such. These products are used as additives in thermal paper, as coatings on cans, bottle caps, packaging used for storing food products, infant feeding bottles, kitchen ware, and water supply pipes as powder paints, and as antioxidants in plastics.

1.5 Environmental Concerns

The toxic effects of AP_nEOs and BPA are due to their endocrine disruptive properties, their ability to mimic natural hormones in many organisms. NP, NP_1EO, NP_2EO, and OP have variously been identified to have impacts on trout (*Oncorhynchus mykiss*) and minnows (*Pimephales promelas*) at low concentrations (Jobling et al., 1996; Harries et al., 2000), sex development in medaka (*Oryzias latipes*) at 50 µg/L (Gray &

Metcalfe, 1997), intersexuality among wild roach (*Rutilus rutilus*; Blackburn et al., 1999), and bioaccumulation in fish tissue in Kalamazoo, MI (Keith et al., 2001) and the United Kingdom (Lye et al., 1999). They have also been found to displace 17β-estradiol from the estrogen receptor (Muller & Kim, 1978; Soto et al., 1991; Routledge & Sumpter, 1997; Cooney 2000). Low levels of NP have been reported to stimulate vitellogenin synthesis in male rainbow trout (*O. mykiss*; Jobling et al., 1996). Uptake by roaches (*R. rutilus*) (Smith & Hill, 2004), and uptake and toxicity in plants (Bokern et al., 1998) have also been reported. Although OP and its ethoxylates (OPEOs) are used in substantially smaller quantities than NP, it is considered many times more estrogenic than NP, NP_1EO, and NP_2EO (Jobling & Sumpter, 1993; White et al., 1994; Routledge & Sumpter, 1997).

Biodegradation of NPEOs occurs by sequential removal of the ethoxy molecule thus leading to accumulation of compounds with shorter ethoxylate chains and eventually nonylphenol (Ahel et al., 1994a; John & White, 1998). Hydrophobicity and biological potency of the homologs increases with the reduction in the ethoxylate chain.

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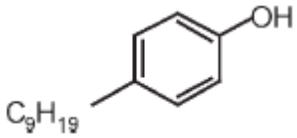
Table 1.1 Chemical properties of compounds studied

Compound (as reference standards)	CAS Number	Molecular Formula	Molecular Weight ($g\ mol^{-1}$)	Solubility (mgL^{-1})	Log K_{ow} ($atm\text{-}m^3\ mol^{-1}$)	Vapor pressure at 25°C (Pa)	Log K_{oc}	Vapor Density	Henry's Constant ($atm\text{-}m^3\ mol^{-1}$)
Nonylphenol (technical grade)	84852-15-3	$C_{15}H_{24}O$	220.36	4.9[a] 6.0[f]	4.48[b] 4.2[e]	0.3[e]	4.7-5.6[g] 5.39[h]	7.59 (air=1)	3.4×10^{-5} [a]
Nonylphenol monoethoxylate (branched)	27986-36-3	$C_{17}H_{28}O_2$	264.4	-	4.17[b]	-	5.46[h]	-	-
Nonylphenol diethoxylate (branched)	27176-93-8	$C_{19}H_{32}O_3$	308.5	-	4.21[b]	-	5.18[h]	-	-
4-*tert*-Octylphenol	140-66-9	$C_{14}H_{22}O$	206.33	12.6[j]	4.12[b] 5.28[d] 3.7[i]	8.25 mm Hg [j]	3.9[h] 3.5-4.3[h]	-	6.89×10^{-6} [j]
Bisphenol A	80-05-7	$C_{15}H_{16}O_2$	228.29	120[k]	3.3[c] 3.32[j]	4×10^{-8} mm Hg (est.)[k]	-	-	1×10^{-10} [k]

a – Brix et al., (2001); b – Ahel & Giger (1993); c – Lee & Peart (1995); d – Kinney et al. (2006); e – McLeese, et al. (1981)

f – Müller & Schlatter, (1998); g – Sekela et al., (1999); h – Ferguson et al., (2001);i – Johnson et al., (1998); j – Sigma-Aldrich MSDS;
k – Howard (1989)



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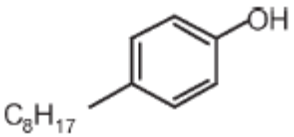

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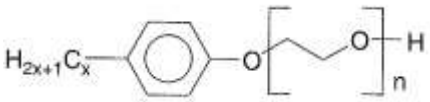

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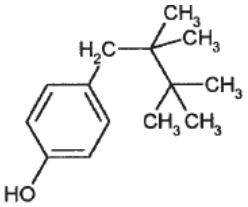

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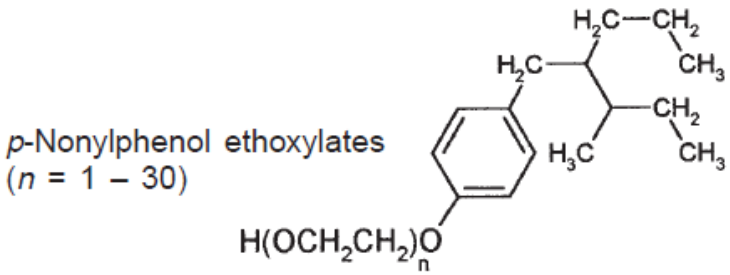
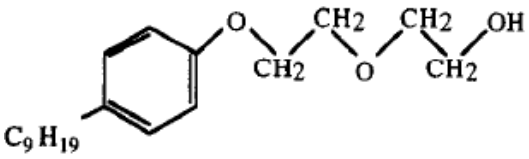
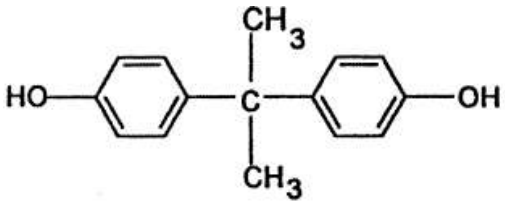




4-nonylphenol diethoxylate



Bisphenol A

Figure 1.1 Structural configurations of nonylphenol, octylphenol, their ethoxylates and bisphenol A

CHAPTER 2

EFFECT OF STABILIZATION ON ALKYLPHENOL ETHOXYLATES AND BISPHENOL A CONCENTRATIONS IN SLUDGE AND BIOSOLIDS

2.1 Introduction

Millions of tons of sludge are produced by wastewater treatment plants (WWTP) annually containing many anthropogenic organic compounds. During wastewater treatment, many organic chemicals tend to concentrate in sludge, understandably because of their affinity for the organic-rich solid phase rather than the polar liquid phase. These chemicals may not be adequately transformed in the wastewater treatment process. One reason for this is that their residence time in the wastewater treatment plant is not sufficiently long to accomplish their degradation while in the wastewater stream. For compounds with strong hydrophobic character, their fate and distribution during wastewater treatment are controlled by physico-chemical properties and the high rate of advective transport within the particular WWTP. As a result, their principal removal mechanism is not through biochemical reaction but sorption to sludge particles that settle out as sewage sludge (Byrns, 2001).

Of these chemicals, there is considerable interest in alkylphenol ethoxylates (APEOs) and bisphenol A (BPA) because of their endocrine disrupting properties (Soto et al., 1991; Krishnan et al., 1993). Due to their widespread applications in household and commercial products, APEOs are discharged into sewers and thus wind up in wastewater treatment plants. As a result, wastewater treatment plants are the main discharge source into the environment (Ahel et al., 1987, 1994a and 1994b; Blackburn & Waldock, 1995;

Ferguson et al., 2001; Petrović & Barceló, 2004). Most APEOs are nonylphenol ethoxylates (NPEOs) with much of the balance made up of octylphenol ethoxylate (OPEO). NPEO oligomer distribution in wastewater, and in commercial mixture, typically centers on nine ethylene oxide units per molecule, although APEOs could possibly have as many as 50 ethoxylate units (Ahel et al., 1994a; Thiele, et al., 1997; John et al., 2000; Loyo-Rosales et al., 2007).

It has been shown that the distribution of APEO oligomers in wastewater influent takes the form of the bell shape pattern with the dominant oligomer being centered on NP_9EO (Ahel et al. 1994a, Figure 2.1a). More recently, the seasonal influence on this distribution has been demonstrated (Loyo-Rosales et al. 2007, Figure 2.1b). Both investigations show that following biological wastewater treatment, there is accumulation of the more toxic, hydrophobic and recalcitrant NP, and $NP_{1-2}EO$ while the higher oligomers have nearly disappeared. As such, this research is focused on the hydrophobic NP, AP_1EO and AP_2EO, especially as they leave the aqueous phase and partition into the solid phase.

During wastewater treatment where limited biodegradation of longer chain NPEOs occurs, and in the natural environment, degradation of longer chain NPEO results in the accumulation of more toxic, recalcitrant and hydrophobic metabolites, namely, NP, NP_1EO and NP_2EO. During the process, the ethoxylate units are readily and progressively removed leaving lower ethoxylated chain molecules that become more hydrophobic and more toxic as the chain length is reduced. Accumulation of NP is especially massive in the anaerobic sludge digestion process (Giger et al., 1984; Petrović & Barceló, 2004) and in proportion during anaerobic biodegradation in soils. However, a

different aerobic degradation pathway of APEO that involves carboxylation of the individual ethoxylate chain before shortening of the chain begins, and does not produce NP as a metabolite, has been reported (Jonkers et al., 2001). Alkylphenoxy carboxylic acids (APECs) and the longer chain APEOs are water soluble; as a result, they are found more in wastewater effluent than in sludge (Ahel et al., 1994a). Increasing ethoxy units renders the compound more soluble in water, albeit marginally (Brix et al., 2001). As with NP, OP is formed by the incomplete degradation of octylphenol polyethoxylates (OP_nEO).

Commercial NP_nEO and NP are mixtures of branched isomers (John et al., 2000), which are believed to impart some degree of environmental persistence to them (Hale et al., 2000). While NP and OP are strictly hydrophobic, the ethoxylated forms are amphiphilic in character, although, their hydrophobicity increases as the number of ethoxy units decreases. Together, these compounds tend to preferentially partition into the solid fraction while passing through the wastewater treatment process (Ahel et al., 1994a; Planas et al., 2002).

Bisphenol A (BPA) is equally an environmental contaminant that has been detected in surface waters, river sediments, wastewater effluent, sludge, manure, compost runoff and waste dump runoff (Fromme et al., 2002). BPA is widely used as in polycarbonate plastic, and is an intermediate in the production of epoxy resins (Latorre et al., 2003; Sakurai et al., 2005). BPA is readily degraded in the environment despite its ubiquitous presence or persistence, a presence that is result of continual input. Thus, a major source of environmental pollution is due to leaching from polycarbonate plastic (Krishnan et al., 1993; Latorre et al., 2003; Flint et al., 2012). Due to their massive use

and ubiquity in environmental samples, endocrine potential, and for the properties and behavior described above, these EDCs deserve close attention and methodical investigation.

The term *sludge* refers to the untreated mixture of solids and associated liquid removed from wastewater treatment before it is fed into a specific sludge stabilization process or technology. *Biosolids,* on the other hand, refers to the product of sludge treatment by any one, or combination, of many stabilization processes in order to reduce pathogens, vector attraction and nuisance characteristics, and make it suitable for safe and beneficial use and to meet regulatory standards. Sludge, being a repository for many anthropogenic organic chemicals that are present in wastewater during treatment, has the potential to transfer these pollutants to soil through soil-related uses such as manufacture of topsoil, direct application to land as fertilizer or conditioner, and in reclamation of marginal and degraded soils such as can result from mining activities. The application of sludge and biosolids to land is the United States is on the increase.

Prior to disposal or any soil-based usage, sludge recovered from wastewater treatment systems is treated or stabilized through any one, or combination, of many available treatment processes, primarily to reduce pathogens and the attraction of vectors such as rodents and insects, so as to protect people and the environment. Concerns exist about application of sludge and biosolids to land. Initial concern was focused on the presence of heavy metal and pathogens in the biosolids. The current regulations are designed to address this concern. More recently, concerns about organic pollutants have become prominent. By way of regulation, the USEPA initiated the Targeted National Sewage Sludge Survey (USEPA, 2009) program, which aims to screen WWTPs and

statistically determine the next suite of compounds to be regulated. However, pollutant (such as NP, NP_1EO, NP_2EO, OP and BPA) loads in sludge and biosolids are not uniform due to many factors including the stabilization process to which sludge is subjected before it is applied to land. In this chapter the effect of five of the most commonly used sludge stabilization processes on the concentrations of NP, NP_1EO, NP_2EO, OP and BPA in the resulting biosolids was examined. The five stabilization processes are: aerobic digestion (including one autothermal thermophilic aerobic digestion, or ATAD), anaerobic digestion, advanced alkaline stabilization, composting, and lime stabilization. These processes are defined by varying operational characteristics such as temperature, pressure, and processing duration. While some of them reduce the mass and/or volume of biosolids generated, others increase the same. Some utilize a chemical method/approach while others are biological. Processing duration varies from minutes to weeks. Also, the study compares the APEO and BPA concentrations in the raw sludge feed and the resulting biosolids.

Large variation exists in sludge APEO and BPA concentrations between aerobic and anaerobic treatments as NP is known to accumulate in anaerobic digesters (Ahel et al., 1994a, Petrović & Barceló, 2004). Such variation, though expected, has not been well documented for other sludge treatment processes. Also, it is widely believed that APEOs and BPA are biodegraded in aerobic environments. However, it is not known at what levels these target compounds exist in alkaline-stabilized, lime-stabilized and composted biosolids. APEO and BPA have been studied in various environmental media but there is insufficient data on their levels in biosolids destined for land-based uses.

2.2 Hypotheses

The hypotheses of this study are that (1) sludge treatment is an important step in reducing the concentrations of the selected organic pollutants in biosolids, that is, determines to an important extent the fate of APEO and BPA in the biosolids, (2) the ultimate concentration of APEOs and BPA in biosolids is dependent on the type of stabilization process applied to the sludge, and (3) some sludge stabilization processes are better or more efficient than others in attenuating the concentration of synthetic organic pollutants in biosolids destined for land application.

2.3 Objectives

From the foregoing, the objectives of this study are to:

(1) assess how much difference exists between the pollutant levels in sludge and biosolids and thus determine the elimination percentage during sludge treatment.

(2) establish the relative pollutant load with respect to APEOs and BPA in biosolids from different stabilization processes.

(3) examine the effect of sludge stabilization processes in attenuating the concentrations of the targeted endocrine disrupting compounds in biosolids.

2.4 MATERIALS AND METHODS

2.4.1 Sampling and Site Description

Sludge and biosolids were obtained from 13 wastewater treatment plants (WWTPs) and 1 biosolids stabilization facility (BSF) in 10 states (Figure 2.2). Of the sludge samples used in this study, 11 were a mixture of primary and activated sludge, 3 had been anaerobically-digested – a form of sludge stabilization following wastewater

treatment, while 1 was a mixture of primary, activated, and anaerobically-digested sludge (Table 2.1). These were all utilized as sludge feed for their respective sludge stabilization that followed. One WWTP produced and supplied 2 types of biosolids (AS-1 and LS-15). Another plant (CP-13) was unable to provide a sludge sample but supplied biosolids for this study. The biosolids represent 5 stabilization processes: aerobic digestion, anaerobic digestion, alkaline stabilization, lime stabilization and composting. Additional characteristics of the wastewater treatment plants are presented in Table 2.1.

2.4.2 Sample Collection and Processing

Sludge and biosolids were collected in 1.25 L wide-mouth amber borosilicate jars with Teflon-lined lids that had been cleaned to meet the EPA protocol for volatile organic compounds (VOCs), and shipped by overnight courier service. Upon receipt, liquid samples were preserved with 1% (v/v) of 37% formaldehyde solution (Fisher Scientific, Pittsburg, PA) to inhibit further biodegradation (Marcomini et al., 1989; Ahel et al., 1994a; de Voogt et al., 2000). All samples were refrigerated at 4ºC in the dark until further processing. The samples were subsequently frozen and freeze-dried using a Labconco FreeZone® 6 Freeze Dry System (Labconco Corporation, Kansas City, MO). The dry samples were kept in their respective amber bottles until further analysis.

2.4.3 Preliminary Work

A laboratory method approved for determination of APEO and bisphenol A by the USEPA Region 5, Chicago Regional Laboratory (CRL), was used in this study (USEPA, 2007). In order to determine the appropriate sample size for extraction and to adapt the cleanup step of the method, preliminary work was done to assess a variety of cleanup

techniques. Previous investigators have reported NP (Hesselsøe et al., 2001; Gibson et al., 2005) and BPA (del Olmo et al., 1997) extraction and analytical methods that do not require cleanup of the extract and with acceptable recoveries. However, standard practice in chromatography is to reduce as much interference as possible to enhance the separation, and detection of target compounds, and to prolong the useful life of the GC capillary column. In the preliminary work, biosolids were extracted and passed through gel permeation column (GPC), florisil, C18, cyanopropyl, cyclohexyl, and silica solid phase extraction (SPE) cartridges with different solvent combinations, to remove waxy high molecular weight compounds, suspended colloids and color before proceeding to instrumental analysis.

2.4.4 Extraction and Clean-up

Triplicate 5 g samples of sludge and biosolids samples were extracted by accelerated solvent extraction (ASE) (Dionex ASE 200, Sunnyvale, CA) with a 1:1 acetone-dichloromethane (DCM) (99.9% purity each) mixture. ASE provided similar extraction efficiency as Soxhlet extraction (Hale et al., 2000). Extraction conditions were: 2 extraction cycles, pressure of 1750 psi, temperature at 100 ºC, static time 5 min, 60% flush volume, purge 45 s at 150 psi, static cycle 1 min, and purge during preheat was off. These and all solvents used were high purity pesticide grade (Burdick & Jackson, Honeywell International, Inc., Muskegon, MI). Each extract was collected in 60 mL borosilicate vials with Teflon-lined septum and screw caps. The extracts were cleaned up using florisil (Restek Corporation, Bellefonte, PA) and eluted with 1:1 acetone-dichloromethane. Florisil was baked at 550℃ for at least 4 hours prior to use. Each extract was concentrated under a nitrogen stream and solvent exchanged to hexane before

acenaphthene-d_{10} (99.7% purity) and phenathrene-d_{10} (99.1% purity) (AccuStandard, New Haven, CT) were added as internal standards, and brought to 1 mL volume for analysis by GC/MS. Prior to extraction, each 5 g sample or Ottawa sand blank was fortified with 200 µL of 150 µg mL^{-1} APEO surrogate solution and allowed to dry before extraction. Employed as surrogates were p-n-nonylphenol (4-*n*-NP) (≥98% purity), p-n-nonylphenol monoethoxylate (4-*n*-NP_1EO) (≥95% purity) and p-n-nonylphenol diethoxylate (4-*n*-NP_2EO) (≥98% purity) (Cambridge Isotopes, Inc., Andover, MA). The properties of these surrogates are presented in Table 2.2.

2.4.5 GC/MS Analysis, Identification and Quantification

Concentrated extracts were separated on an Agilent 6890 gas chromatograph (GC) coupled to an Agilent 5793 mass selective detector (MSD) (Agilent Technologies, Santa Clara, CA). The target compounds were identified by matching the GC retention time and mass spectra (fragmentation pattern) of samples to known standards and quantified using their quantitation ions (Appendix A). Reference standards were nonylphenol (technical grade, 97% purity) (Sigma-Aldrich Corp., St. Louis, MO), nonylphenol monoethoxylate (branched isomers, ≥98% purity), nonylphenol diethoxylate (branched isomers, ≥98% purity) (custom-synthesized by Cambridge Isotopes, Inc., Andover, MA), 4-tert-octylphenol (97% purity) (Sigma-Aldrich Corp., St. Louis, MO) and bisphenol A (99% purity) (Sigma-Aldrich Corp., St. Louis, MO). 2 µL injection of each sample was made by automated liquid sampler and analyzed in splitless mode under the following GC conditions: injector port set at 290ºC, helium was the carrier gas at pressure of 11.16 psi, purge flow 30 mL/min, purge time 0.75 min and total flow of 34.2

mL/min. Separation was carried out on J & W HP-5MS 30 m x 0.25 mm internal diameter capillary column with 0.25 µm film thickness (J&W Scientific Inc., Folsom, CA). Temperature programming was 50ºC held for 2 min, the ramp rate was 10ºC/min to 320ºC and the final temperature was held for 5 min. The MSD was operated in electron ionization (EI) mode at 70 eV with source temperature of 230ºC and quadropole temperature of 150ºC. The instrument was tuned with perfluorotributylamine (PFTBA) and performance checks were done with difluorotriphenylphosphine (DFTPP).

2.4.6 Quality Assurance

Reference standards and working solutions were prepared at 5 concentration levels from stock solutions prepared as outlined in CRL method (USEPA 2007). The range for each compound was:

Nonylphenol (branched isomer)	25-400 ug mL^{-1}
Nonylphenol monoethoxylate (branched isomer)	50-800 ug mL^{-1}
Nonylphenol diethoxylate (branched isomer)	100-1600 ug mL^{-1}
4-tert-octylphenol	5-80 ug mL^{-1}
Bisphenol A	5-80 ug mL^{-1}
p-n-nonylphenol	5-80 ug mL^{-1}
p-n-nonylphenol monoethoxylate	5-80 ug mL^{-1}
p-n-nonylphenol diethoxylate	5-80 ug mL^{-1}

Surrogate spiking solution consisted of the 3 surrogates at a concentration of 150 µg L^{-1}. Laboratory blanks consisting of Ottawa sand, spiked in the same manner as the samples, were run with every batch of 10 subsamples from extraction to instrumental analysis. Samples were run in triplicates and the data was corrected for blanks. The instrument detection limit was determined by sequential dilution of the lowest standard. This limit was taken as the lowest detection where a signal to noise ratio of 3:1 was obtained.

2.4.7 Statistical Analysis

SPSS (SPSS Inc., Chicago, IL) was used for P-P plots, ANOVA, GLM and Pearson correlation. Student's t-test was done in Microsoft Excel. Logarithmic transformation was applied to the data because it did not conform to the normal distribution assumption. Normal distributions were obtained following the data transformation (Figure 2.3). Comparison of means was carried out on the sludge and biosolids data using SPSS.

2.5 RESULTS AN DISCUSSION

Successful separation, identification and quantification of the target compounds were obtained using GC/MS (Figure 2.4). As shown in the chromatogram, NP, NP_1EO and NP_2EO appear as clusters of peaks and are reported as the sum of the clusters because the industrial production of NP and NP_nEO usually results in a mixture of branched chain isomers rather than individual straight chain isomers. For this reason, straight chain 4-n-nonylphenol (4-n-NP), 4-n-nonylphenol monoethoxylate (4-n-NP_1EO) and 4-n-nonylphenol diethoxylate (4-n-NP_2EO) were custom-synthesized and used as surrogates as they are not found in environmental samples (Vikelsøe et al., 2002). OP and BPA were separated as single peaks. Alkylphenols have been previously analyzed by GC/MS (Topp & Starratt, 2000; LaGuardia et al., 2001; Vikelsøe et al., 2002; Planas et al., 2002; Jacobsen et al., 2004; Petrović & Barceló, 2004; Gibson et al, 2005) and GC-FID (Brix et al, 2001). While GC/MS satisfactorily and quantitatively separate the lower AP_nEOs, the less volatile AP_nEOs with longer ethoxy group units are better separated by HPLC/MS (Castillo et al., 2000; John et al., 2000; Ferguson et al., 2001; Petrović et al., 2002; Loyo-Rosales et al., 2007). However, analysis by gas chromatograph has an

advantage over HPLC in that it has the ability to separate branched from linear isomers (Jacobsen et al., 2004).

Trace concentrations of NP, NP_1EO, NP_2EO, OP and BPA were detected in the sludge (Tables 2.3) and biosolids (Tables 2.4) samples. Sludge and biosolids samples from all the wastewater treatment plants (WWTPs) used in this study contain detectable concentrations of all of these target compounds. In all cases, NP is the most abundant of these pollutants in sludge for each WWTP, which is a reflection of its greater proportion in applications relative to OP. The higher concentration of NP is also indicative of the fact that biological degradation of NP_nEO often leads to the accumulation of NP. Comparatively, BPA had the lowest concentration of the 5 compounds in 11 out of the 14 WWTPs. Mean and median biosolids concentrations were lower compared to sludge concentrations. Lower and higher concentrations of BPA (0.004 – 1.363 mg kg^{-1}) have been measured by other investigators (Fromme et al., 2002). Previous studies have reported different background concentrations of NP in sludge (Castillo et al., 2000; Hesselsøe et al., 2001). Concentrations of NP in sediment are typically higher (12.4 mg kg^{-1}) than in effluent discharge (33 μg L^{-1}) in samples collected from the same wastewater treatment plant outfall (Hale et al., 2000).

The higher concentrations of NP compared to NP_1EO and NP_2EO are consistent with the degradation pattern of NPEO in which the longer ethoxy chains are progressively reduced, as the molecule is metabolized, to produce short chain ethoxylates or NP. Therefore, the relative higher concentration of NP observed in this study may reflect an accumulation product of NPEO degradation. Unlike the higher NP level, NP_1EO and NP_2EO are present in much lower amounts and there is no evidence of

NP_1EO accumulation from the degradation of NP_2EO.

OP concentrations in both sludge and biosolids samples are 1 to 2 orders of magnitude lower than those of NP and actually less than or comparable to NP_1EO and NP_2EO concentrations. OP does not have as widespread applications as NP, accounting for about 20% of total APEO usage; as such, the lower concentrations measured relative to the NPEO reflect its relative level of consumption. Overall, pollutant concentrations are higher in sludge than in biosolids, which suggests that the stabilization processes have managed to reduce the concentrations either through degradation or dilution with additives. Thus a reduction percentage can be calculated for each and/or all pollutants combined during stabilization from raw sludge to biosolids.

The concentrations of pollutants in sludge and biosolids were compared by independent t-test for each target compound. There were significant ($p<0.05$) statistical difference between sludge and biosolids concentrations for all 5 pollutants (Table 2.5). The difference lies in the lower pollutant concentrations measured in the biosolids relative to sludge; which suggests that sludge stabilization processes or treatments were influential in reducing pollutant concentrations. Most (12 out of 14) of the WWTPs sampled for this study were known to have employed activated sludge wastewater treatment, which would have produced sludge with similar characteristics. However, factors such as mode of operation of the wastewater treatment process, influent pollutant concentration, the demographics of the WWTP service area, presence and nature of industrial discharge into the WWTP (for example, textile industry), may account for the differences in the pollutant concentrations measured in the various sludge samples. In addition, a few (3 out of 14) of the sludge samples were further treated following

separation from the wastewater treatment process by anaerobic digestion prior to the final biosolids production process. Alkylphenols have been reported to accumulate in anaerobically-digested sludge (Ahel et al., 1994a; Bennie, 1999; Petrović & Barceló, 2004) and this is consistent with observations made for samples CP-9 and CP-10. Sample AS-2, a mixture of activated sludge and anaerobically-digested sludge, is lower in concentration than the other two.

Sludge recovered from wastewater treatment systems is required to be treated or stabilized, primarily to protect public health and prevent adverse effects on the environment, specifically by reducing pathogens and the sludge's attraction for vectors such as rodents and insects. To produce biosolids, variables such as temperature (application of heat in different forms), presence or absence of oxygen, pH control, addition of chemicals, time (duration of the treatment) and moisture content are varied in each treatment technology to produce biosolids of different characteristics. Biosolids, a sludge treatment product, is much different in physical, chemical and biological characteristics from sludge itself. For the 5 treatment systems included in this study, the elapsed time ranges from 30 minutes in a pressurized vessel (alkaline stabilization) to 23 hours in ATAD to 90 days in composting. The change in pollutant concentration before and after sludge stabilization for all five pollutants is graphically presented in Figures 2.5 to 2.9.

Since NP accumulates in environmental samples as a product of NP_nEO degradation, the magnitude of the reduction might be the most pronounced simply because of its high initial concentration (i.e. in sludge, prior to treatment). Its reduction may be due to the oxidation of NP when sludge is treated by a process that exposes it to

aeration leading to the production of nonylphenol carboxylated derivatives (NP_nEC), which could explain why there is no corresponding increase or accumulation of NP_1EO and NP_2EO. The implication is that NP concentration in biosolids to be placed in soil is significantly reduced as a result of sludge stabilization processes. Although other pollutants likewise showed decreases in concentrations, the magnitude of change is less pronounced compared to NP because their concentration level is 1 to 3 orders of magnitude lower than NP in the sludge prior to stabilization. From Tables 2.3 and 2.4, mean percent reduction can be determined for each contaminant by,

$$Mean\ \%\ Reduction\ = \left(\frac{Mean_{sludge} - Mean_{biosolids}}{Mean_{sludge}}\right)100 \qquad 2.1$$

The mean in Table 2.4 is re-calculated to exclude CP-13 as it does not have a corresponding sludge component in Table 2.3 against which to measure increase or decrease in concentration. Thus, mean reduction percentages of 5.3 for NP, 58 for NP_1EO, 31 for NP_2EO, 82 for OP, and 43 for BPA were determined. NP reduction percentage improved from 5.3 to 48 when the change in NP concentration due to anaerobic digestion is removed as an outlier, in which case, the NP biosolids mean changes from 76 to 41. While reduction percentage demonstrates the effect of sludge stabilization on the contaminants, it does not reflect the numerical change in concentration, which is more pronounced for NP than the other contaminants. Percent change in contaminant concentration as a result of individual stabilization process is presented in Table 2.6. While most showed reduction (negative values) in contaminant concentration, some showed the opposite (positive values). The increase is due, in part, to the effect of aerobic and anaerobic digestion where biomass is destroyed without a corresponding magnitude of pollutant biodegradation, resulting in higher pollutant

concentration. Accumulation may also suggest that NP, NP_1EO and NP_2EO being formed from degradation of higher oligomers than they are being degraded. For alkaline stabilized biosolids, increases are calculated on minute changes in numeric concentrations of <1 mg kg^{-1}.

The effect of the sludge stabilization process on the residual concentration of pollutants in biosolids was tested by one-way analysis of variance (ANOVA). Due to the difference in magnitude between concentrations measured among the pollutants, the data was normalized by dividing each value (measurement) by the mean for that pollutant. The normalized data was then logarithmically-transformed to obtain normal distribution before statistical analysis was done. A statistically significant difference ($p<0.05$) was found between the stabilization processes (Table 2.7a). Post hoc analysis was carried out using Tukey's HSD, Scheffe, and LSD tests to determine which processes are different. Most statisticians recommend Tukey's HSD because it reduces Type 1 error at the expense of power and is more conservative than LSD. Scheffe is the most conservative of post hoc tests while LSD is the most liberal. While Sheffe is suitable for making complex comparisons, LSD is more appropriate for making few comparisons. Between the three post hoc tests, differences were mainly between alkaline stabilization and composting, anaerobic digestion and lime stabilization, composting and lime stabilization, alkaline stabilization and anaerobic digestion, and aerobic and anaerobic digestion processes. This suggests that each treatment or stabilization process is uniquely different from the others and has attributes that causes reduction in the concentration of these pollutant to occur when it was being used to treat sludge. A further closer look at the data suggested that, to different degrees, each treatment yielded a reduction in the pollutant concentrations. One

way to look at the effectiveness of each stabilization process is to look at the percentage of cases in which the 5 pollutants were at lower concentration in the biosolids compared to the sludge from which they were produced (rather than the amount of the reduction). Based on the results in Table 2.6, this type of effectiveness ranked in the order:

Composting > Alkaline > Lime Stabilization > Anaerobic > Aerobic
(90%) (84%) (80%) (60%) (53%)

In addition, the effect that the five stabilization processes had in reducing the concentration of each individual pollutant in the biosolids was tested using one-way ANOVA (Table 2.7b). There was a statistically significant difference ($p<0.05$) among the treatments for nonylphenol and bisphenol A. However, there were no statistically significant differences ($p<0.05$) among treatment means for NP_1EO, and NP_2EO, while the differences for OP was almost significant ($p=0.064$). These data thus show that some stabilization processes appear to be effective more often than the others in attenuating the concentrations of these pollutants during sludge treatment. As shown above, in 9 out of 10 measurements, or 90% of the time, composting produced reductions in the concentration of all the pollutants. Similarly, alkaline stabilization showed reduction 21 out of 25 occasions, lime stabilization in 8 out of 10, anaerobic digestion 6 out of 10 and aerobic digestion produced reductions on 8 out of 15 occasions or 53% of the time (Figures 2.4 to 2.8).

Comparatively high pollutant concentrations were measured in biosolids composted *without* bulking agents. This reflects both sludge and operational characteristics of the WWTP CP-11 (Table 2.1). The sludge was produced from activated sludge wastewater treatment followed by anaerobic digestion before being composted. The concentration of NP in the sludge is compatible with the initial treatment method.

The extent of NP reduction during composting was minimal (12.8%). At this facility (CP-11), the anaerobically digested sludge is laid out in windrows, in the sun to allow evaporation, and mechanically turned daily until the moisture content is 50%, after which it is placed in static piles to begin composting. In this composting approach, the stockpile received no additional fibrous material to absorb moisture and create pore space for the purpose of aerating the compost pile, and no biota external to the sludge was introduced to the stockpile to diversify the microbial populations during the composting process. As air was not forced (pushed or pulled) through the static pile, it appears that pollutant concentrations contained in the sludge were preserved except from the limited aerobic biodegradation that likely took place within the first few centimeters into the pile. The sludge essentially went from wet anaerobically-digested sludge through a drying process to dry composted biosolids. It is plausible that more pollutants would have been biologically-degraded if the composting material had been better aerated.

A conventional composting process is an aerobic biological decomposition where the conditions for microbial growth and metabolism are controlled and optimized to breakdown organic matter. In sludge composting, microorganisms biologically oxidize the sludge when adequate air and moisture are provided and in the process release heat, which is distributed through the compost pile to kill pathogenic organisms. Composting accelerates degradation of organic pollutants by exposing them to high microbial diversity and activity, changing pH and successive aerobic-anaerobic microenvironments within the composting process. Composting has been shown to be effective in removing 80% of NP within 2 weeks (Das & Xia, 2008) and composted biosolids have been reported to have lower total AP_nEO than either limed or aerobically- or anaerobically-

digested biosolids (La Guardia et al., 2001). These studies referred to biosolids composting with bulking agents where the dilution effect of the bulking agents, such as leaves, wood chips and yard waste, will undoubtedly result in reduced concentrations compared to the sludge. However, sludge composting without bulking agent, allows the effect of bulking agent and composting as a treatment to be evaluated.

The sludge from the three composting facilities (CP11, CP12, and CP13) had been initially digested anaerobically, which accounts for the very high concentration of sludge NP before it was fed into the composting process. The sample from facility CP-12 was bulked with wood chips and the sample from CP-13 was bulked with wood chips and paper sludge for composting. Raw sludge and matured compost could not be compared in facility CP-13. The facility had no sludge sample available but provided finished compost. While it cannot be deduced whether or not there are reductions in target compounds, it can be compared to a similar process in CP-12 as both used similar sludge types (information supplied by the facility) and composting processes to achieve the finished product. Pollutant concentrations in CP-13 are comparable to those of CP-12 except for lower concentrations of NP_1EO, NP_2EO and BPA in CP-13.

Apparent accumulation of nonylphenol was observed in one anaerobically-digested biosolids (AN-7) but not in the other (AN-6). The reason for this anomaly is not clear. Previous works have reported nonylphenol build up in sludge in anaerobic digesters due to release from NP_nEOs and the lack of oxygen for further degradation (Ahel et al., 1994a; Bennie, 1999; Petrović & Barceló, 2004). Although, biosolids AN-6 was sampled from the centrifuge, it is unlikely to have had sufficient residence time to be oxygenated and biodegraded.

Sludge stabilization processes such as aerobic digestion, anaerobic digestion and composting without bulking additives, result in reduction of sludge dry mass and/or volume. Other stabilization processes require additives to the sludge and result in increases in dry mass and/or volume of biosolids. Alkaline stabilization processes add alkaline materials such as quicklime, hydrated lime, fly ash, cement kiln dust or lime kiln dust to generate heat, raise the pH, and adjust the wetness or dryness of the resultant biosolids. Composted biosolids can be bulked with additives such as wood chips, wood shavings, dry leaves or paper mill sludge. Lime stabilization requires addition of lime. It follows that the pollutant concentrations in the sludge feed going into these processes will be diluted upon stabilization of the sludge. For the purpose of comparing the two groups of treatment outcomes, mass balance calculations were undertaken to estimate what the expected concentrations of the pollutants would be in the biosolids for each of the 5 stabilization processes, assuming no factor other than dilution is acting on the sludge during treatment to affect its concentration in the final biosolids product (i.e., no loss of dry solids or pollutant). Therefore, the calculation assumed the conservation of mass and utilized percent dry weight solids of the sludge and biosolids and the sludge pollutant concentration to predict the pollutant concentration in the biosolids. In digestion processes where no bulking additives were added, the mass balance is calculated using equation 2.2 below. In stabilization processes where additives were added to the sludge, the mass balance follows equation 2.3:

$$C_{p,biosolids} = \frac{C_{p,sludge}}{\%\ M_{dry\ sludge}} \times \%\ M_{dry\ biosolids} \qquad 2.2$$

$$C_{p,biosolids} = \frac{C_{p,sludge}}{\%\ M_{dry\ sludge}} \times \left[\frac{\%\ M_{dry\ biosolids}}{100+\%\ BA}\right] 100 \qquad 2.3$$

where,

$C_{p,\ biosolids}$ = expected pollutant concentration in biosolids (mg kg^{-1} wet mass)
$C_{p,\ sludge}$ = measured pollutant concentration in sludge (mg kg^{-1} wet mass)
% $M_{dry\ sludge}$ = percent dry mass of sludge
% $M_{dry\ biosolids}$ = percent dry mass in biosolids
% $BA_{\ dry}$ = percent bulking agents or additives (100 x kg bulking agent x kg^{-1} wet sludge

Most of the calculated (expected) concentrations were higher than measured (observed) concentrations (Table 2.8). This is understandable since the calculated concentrations did not take into consideration any chemical and biological transformations that may be going on in the system. The fact that laboratory-measured concentrations are lower than the predicted concentrations point to disappearance of pollutants to a greater extent than loss of dry solids due to mechanisms inherent in the sludge stabilization processes. Additionally, the loss of sludge dry mass during treatment would tend to increase the pollutant concentration. This further supports the notion that important mechanisms were taking place during each of these treatment processes that leads to lower pollutant concentrations. Thus, the stabilization processes were effective tools in reducing the pollutant concentrations, and transformation of the target pollutants took place during the stabilization process. The transformation could be microbial metabolism or due to physicochemical processes that do not lead to biodegradation (Ahel et al., 1994a), such as sorption to the organic matter residue thus becoming recalcitrant to extraction or formation of large chemical complexes.

Five of the biosolids in this study (AS-1 to AS-5) are alkaline-stabilized, but were produced using 3 different technologies -- N-Viro (N-Viro International Corporation, Toledo, OH), Bioset (SchwingBioset, WI) and RDP *En-Vessel* (RDP Technologies, Inc., Conshohocken, PA). Though the 3 technologies are different, the biosolids that they

produced are similar in characteristics and have comparable pollutant concentrations (Table 2.4). The key features of the 3 technologies are that they produce high temperature and raise the pH of treated sludge to the highly alkaline range. The Bioset process blends dewatered sludge with lime and sulfamic acid. The exothermic reaction takes place in a pressurized vessel to achieve the required time and temperature to produce alkaline-stabilized product. The RDP *En Vessel* process similarly mixes dewatered sludge with lime sufficiently to raise the pH but in a quantity not sufficient to produce the required temperature. Thus RDP process provides supplemental heat to the mixer and pasteurization vessel from electrical sources. N-Viro's Advanced Alkaline Stabilization with Subsequent Accelerated Drying (AASSAD) process employs different alkaline materials, including lime, to raise the sludge pH and generate the required heat to sterilize the sludge without increased pressure. The three technologies operate in the thermophilic temperature range for duration varying from 30 min. to 3 days.

Biosolids AN-6 and AN-7 were products of anaerobic digestion from two big cities, each with a WWTP serving a population of >1 million. They have industrial contributions of 7.5 and <10 % respectively, to their wastewater stream. Consistent with published knowledge, substantial NP accumulation was found in one sample, but not in the other. NP concentration was low in AN-6 sludge prior to digestion and much lower following digestion. Similarly, the remaining pollutants in this sample also showed reduction following digestion.

Three of the studied biosolids (AE-8, AE-9 and AE-10) were products of aerobic digestion. Samples AE-9 and AE-10 were produced under mesophilic temperatures while AE-8 was operated under thermophilic conditions. While AE-9 and AE-10 used

conventional aerobic digestion performed at ≈ 26℃ for about 35 days, WWTP AE-8 used Advanced Thermophilic Aerobic Digestion (ATAD) and operated at 60℃ for only 23 hours. Although, AE-8 and AE10 have 2.5% and 60% industrial contribution to their respective wastewater streams, the strength of these industrial contributions and their impact on the contaminants of concern are not known. APEOs are readily biodegraded in the aerobic terrestrial environment; however, it is not clear if the same applies to sludge treatment under aerobic environments. The pollutant concentrations from these three samples are not discernibly lower than other stabilization processes.

Two biosolids samples (LS-14 and LS-15) were from lime stabilization processes, which are similar to but less stringent to alkaline stabilization. Enough lime is added to raise the pH of the sludge to ≥12, but not as much as needed to produce pasteurizing heat. As a result, the biosolids are more like sludge in consistency. Nevertheless, a reduction in concentration was observed for some of the pollutants.

The characteristics of sludge and biosolids that make them attractive agricultural inputs include nutrients such as nitrogen (measured as total Kjedahl nitrogen, TKN) calcium, magnesium, potassium, organic matter (OM), and acid neutralizing value (calcium carbonate equivalence, CCE). Sludge and biosolids samples were analyzed for these and additional common parameters such as pH, percent total solids, and electrical conductivity (Table 2.9), to characterize each sample so as to understand the effect these properties may have on the behavior of the pollutants in the sludge matrix. In facilities and processes that used alkaline additives, (AS-1 to AS-5, LS-14 and LS-15), there is an increase in pH and reduced wetness (increased % total solids) from sludge to biosolids as a result of the alkaline additive. Salt content, measured as electrical conductivity, also

increased markedly, while organic matter (OM) decreased, showing (in part) the dilution effect of the sludge OM by alkaline materials. In the digested samples (AN-6 to AE-10), there is, in general, a smaller decrease (from destruction) in organic material and a minimal increase in pH, salts (electrical conductivity) and total nitrogen (TKN) – all resulting from the thickening effect of digestion. Both composting methods showed a slight decrease in pH and total nitrogen. However, the effects of the respective composting techniques were reflected in the other parameters. Composting without bulking agent showed a small destruction of OM but an increase in salt concentration – a concentrating effect from drying of the sludge before and during composting. In contrast, composting with bulking agent showed both an increase in OM and a decrease in salt content due to bulking material.

In addition, concentration of the organic pollutants in sludge and biosolids is influenced by the organic content of the solids in wastewater. Although, the organic matter content of the sludge samples is high, no correlation was found between the pollutant concentrations and OM. It could be that OM is not the most suitable organic property for the correlation. Other forms, such as dissolved organic carbon (DOC), particulate organic carbon (POC) or total organic carbon (TOC) may yet present a better correlation. There is however, positive correlation between OM and total nitrogen (TKN) ($p < 0.05$, $r = 0.65$) as most of the nitrogen in sludge is in organic form. Among the remaining sludge and biosolids properties, there is positive correlation between biosolids EC and CCE ($r = 0.77$), but negative correlation between EC and TKN ($r = -0.59$) and EC and OM ($r = -0.68$) at the $p<0.05$ level. Similarly, biosolids OM is negatively correlated

with CCE ($r = -0.9$) and with pH ($r = -0.7$) at $p<0.01$ level, undoubtedly as a result of the large addition of liming materials in alkaline and lime stabilization processes.

Few relationships are found between the properties above and pollutant concentrations measured in the biosolids (Table 2.10). There is positive correlation between biosolids TKN and NP ($r = 0.62$) and between TKN and OP ($r = 0.67$), while CCE is negatively correlated with NP_1EO ($r = -0.81$) at $p <0.05$ level. Similarly, there is negative correlation between sludge TKN and NP_1EO ($r = -0.61$) at $p<0.05$ level.

The relationships between the sludge and biosolids pollutant concentrations were examined (Table 2.11). Positive correlation ($p<0.05$) exists between sludge NP and biosolids NP ($r = 0.57$), sludge NP and biosolids NP_1EO ($r = 0.65$), and biosolids NP_2EO ($r = 0.65$). Similarly, there is positive correlation ($p<0.05$) between sludge NP_1EO and biosolids NP_2EO ($r = 0.6$), and sludge NP_1EO and sludge OP ($r = 0.61$). Sludge NP_2EO is positively correlated ($p<0.05$) to sludge BPA ($r = 0.58$), and sludge OP is positively correlated to biosolids NP_1EO ($r = 0.55$) and NP_2EO ($r = 0.65$).

2.6 CONCLUSIONS

Portions of the synthetic organic pollutants nonylphenol (NP), nonylphenol monoethoxylate (NP_1EO), nonylphenol diethoxylate (NP_2EO), octylphenol (OP) and bisphenol A (BPA) in wastewater are transferred into the sludge during wastewater treatment. Sludge treatment or stabilization provides a depletion mechanism for pollutants in the sludge, and seeks to render it safe for environmental management. If these biosolids are applied to the land, the potential pollutant load has been substantially reduced and the pollutants can be expected to be further depleted in a biologically rich

environment such as the soil. Thus, it is possible to reduce the amount of organic chemicals in sludge before it is transferred into the public domain for use on garden, recreational, agricultural, horticultural and reclamation lands. The results of this study have shown that sludge stabilization processes represent important removal mechanisms and produce substantial reduction in the concentrations of these chemicals. Aerobic digestion, anaerobic digestion, composting, lime- and alkaline stabilization methods prove to be satisfactory mechanisms for further eliminating pollutants from biosolids. The extent of the reduction depends on the stabilization process. Among the five stabilization processes examined, composting showed the strongest performance in causing a decrease in pollutant concentration, followed by alkaline and lime stabilization.

Nonylphenol accumulates more in sludge than the other pollutants in this study, and it is also the pollutant that showed the greatest amount of reduction. The observed reduction in NP concentration could have been from it being metabolized, or is likely to have produced NP_nEC and perhaps other breakdown products, none of which are not the subject of this study. Sludge and biosolids may be similar in matrix but are different in their chemical constituents. A statistically-significant ($p<0.05$) difference was found in concentrations of pollutants between sludge and biosolids, which shows that sludge stabilization is important. As shown in anaerobically-digested sludge and composting of anaerobically-digested sludge, exposure of NP to aerobic environments may be the key to substantially lower the burden of this pollutant before it is placed in the soil. Currently, there are no government regulatory standards in the USA for NP, NP_1EO, NP_2EO, OP, or BPA in sludge and biosolids but growing public and environmental concerns continue to exist. In future, WWTPs may have to consider reductions in organic chemicals as sludge

quality criteria or goals when selecting sludge processing technologies. Risk is a function of exposure and toxicity, neither of which this study addressed; however, the results from this study show that the potential concentration of pollutants can be reduced before exposure is triggered. This study does not examine the fate of carboxylated alkylphenols (AP_nEC), which would have provided a comprehensive assessment of the fate of lower ethoxylated AP_nEOs in sludge and biosolids; this is a subject for future research.

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Table 2.1 Characteristics of the wastewater treatment plants that participated in this study

Facility Identification	Sludge Type	Population served (x1000)	Design Capacity (10^6 day^{-1})	Industrial Contribution (%)	Sludge Stabilization Method	Sludge Processing Temperature (°C)	Additive (as a % of wet wt.)	Sludge Processing Duration	Biosolids Classification
AS-1	Primary + Activated	790	147	15	Alkaline Stabilization	90	65	3 days	A
AS-2	Primary + Activated + anaerobically digested	270	80	-	Alkaline Stabilization	53	125	3 days	A
AS-3	Primary + Activated	23	4	10	Alkaline Stabilization	70	17.5	30 min	B
AS-4	Primary + Activated	12	4.5	3.5	Alkaline Stabilization (Bioset)	66	Varies	>40 min	B
AS-5	Primary + Activated	350	45	12.5	Alkaline Stabilization	87.5	220	3 days	A
AN-6	Primary + Activated	1025	354	7.5	Anaerobic Digestion	≥35	Not appl.	>21 days	B
AN-7	Primary + Activated	1300	130	<10	Anaerobic Digestion	36.1	Not appl.	18 days	B
AE-8[a]	Primary + Activated	31	3	2.5	Aerobic Digestion	60	Not appl.	23 hours	A
AE-9	Primary + Activated	6.2	2.5		Aerobic Digestion	28	Not appl.	15 days	B
AE-10	Primary + Activated	0.25	0.45	60	Aerobic Digestion	26	Not appl.	35 days	B
CP-11	Primary + Activated followed by anaerobic digestion	70	8.9	10	Composting	55	0	15 days	A
CP-12	Primary + Activated followed by anaerobic digestion	1000	200	-	Composting	55	100	45 days	A
CP-13	Primary followed by anaerobic digestion	132	35	<10	Composting	55	100	90 days	A
LS-14	Primary + Activated		10	8	Lime Stabilization	Not appl.[b]	6	24 hours	B
LS-15	Primary + Activated	790	147	15	Lime stabilization	Not appl.[c]	6	24 hours	B

a – Autothermal Thermophilic Aerobic Digestion (ATAD).
b – Not a process requirement for this stabilization method.
c – Not required for this stabilization method but 40 °C was measured during processing.

Table 2.2 Surrogate compounds used in this study

Compound	CAS Number	Molecular Formula	Molecular Weight ($g\ mol^{-1}$)	Vapor pressure at 20°C (Pa)	K_{ow}	Specific Gravity/Density (g/cm^3)
4-n-Nonylphenol (unbranched)	104-40-5[a]	$C_{15}H_{24}O$	220.36	8.175×10^{-4} mm Hg[a]	5.76[a]	0.937[a]
p-n-Nonylphenol monoethoxylate	104-35-8	$C_{17}H_{28}O_2$	264.4	-	-	-
p-n-Nonylphenol diethoxylate	Sigma 20427-84-3	$C_{19}H_{32}O_3$	308.47	-	-	-

a-Aldrich MSDS

Table 2.3 Pollutant concentrations in the sludge

Facility	Sludge Type	NP	NP_1EO	NP_2EO	OP	BPA
		------mg kg^{-1} dry wt.---------				
AS-1	Primary + Activated	6.73	0.20	0.44	0.10	0.14
AS-2	Primary + Activated + AnD†	45.5	1.27	0.60	0.99	0.12
AS-3	Primary + Activated	36.3	0.60	0.87	0.15	0.01
AS-4	Primary + Activated	1.15	0.63	0.50	0.01	0.01
AS-5	Primary + Activated	1.92	0.48	0.62	0.01	0.01
AN-6	Primary + Activated	24.4	0.58	0.66	0.94	0.14
AN-7	Primary + Activated	139	0.54	0.18	2.06	0.03
AE-8	Primary + Activated	16.4	0.44	1.09	0.52	0.42
AE-9	Primary + Activated	43.8	2.38	1.17	3.18	0.15
AE-10	Primary + Activated	0.73	0.09	0.19	0.08	0.01
CP-11	AnD	501	1.04	1.10	10.48	0.08
CP-12	AnD	296	2.38	1.42	25.14	0.03
LS-14	Primary + Activated	2.58	0.24	0.36	0.04	0.01
LS-15	Primary + Activated	6.73	0.20	0.44	0.10	0.14
Min		0.73	0.09	0.18	0.01	0.01
Max		501	2.38	1.42	25.14	0.42
Mean		80.1	0.79	0.69	3.13	0.09
Median		20.4	0.56	0.61	0.33	0.05
SD		145	0.75	0.38	6.91	0.11

† AnD -- Anaerobically-digested sludge

Table 2.4 Pollutant concentrations in biosolids

Facility	Sludge Treatment	NP	NP_1EO	NP_2EO	OP	BPA
		----- mg kg^{-1} (dry weight basis) -----				
AS-1	Alkaline (N-Viro)	0.71	0.06	0.19	0.03	0.04
AS-2	Alkaline (N-Viro)	0.56	0.42	0.52	0.02	0.02
AS-3	Alkaline (RDP En-Vessel)	13.0	0.67	0.71	0.08	0.01
AS-4	Alkaline (Bioset)	1.11	0.18	0.19	0.01	0.01
AS-5	Alkaline (N-Viro)	0.20	0.08	0.19	0.01	0.01
AN-6	Anaerobic	0.78	0.43	0.23	0.04	<0.01
AN-7	Anaerobic	564	0.15	0.41	3.04	0.03
AE-8	Aerobic (ATAD*)	42.0	0.28	1.13	1.29	0.09
AE-9	Aerobic	0.36	0.09	1.03	0.04	0.01
AE-10	Aerobic	0.78	0.12	0.19	0.11	<0.01
CP-11	Composted (w/o bulk)	437	1.02	0.60	3.00	0.01
CP-12	Composted	1.09	0.74	0.72	0.05	0.48
CP-13	Composted	1.22	0.19	0.27	0.22	<0.01
LS-14	Lime	0.32	0.21	0.27	0.02	<0.01
LS-15	Lime	0.49	0.24	0.27	0.01	0.01
Min		0.20	0.06	0.19	0.01	0.01
Max		564	1.02	1.13	3.04	0.48
Mean		70.9	0.32	0.46	0.53	0.05
Median		0.78	0.21	0.27	0.04	0.01
SD		176	0.28	0.31	1.06	0.12

*ATAD -- Autothermal Thermophilic Aerobic Digestion

Table 2.5. Summary of Independent *t-test* analysis performed on logarithmically-transformed data*

Pollutant	Sludge		Biosolids		p value	Outcome
	Mean	n	Mean	n		
Nonylphenol	9.33	40	1.12	42	0.0008	Significant
Nonylphenol monoethoxylate	0.41	40	0.17	42	0.0026	Significant
Nonylphenol diethoxylate	0.46	40	0.15	42	0.0034	Significant
Octylphenol	0.13	40	0.04	42	0.0313	Significant
Bisphenol A	0.03	40	0.16	42	0.0423	Significant
*						

*Mean is geometric mean (mean of log concentration values, converted back to concentration); units are mg kg^{-1} dry weight.
n = number of observations

Table 2.6 Percent change in contaminant concentration during sludge treatment*

Sludge Treatment	Facility	NP	NP_1EO	NP_2EO	OP	BPA	Overall change (grouped by treatment)**	Reduction likelihood (grouped by treatment type)†
Alkaline	AS-1	-89.5	-69.6	-57.3	-72.5	-71.9		
Alkaline	AS-2	-98.8	-66.8	-13.8	-98.5	-86.4		
Alkaline	AS-3	-64.2	11.1	-18.1	-44.5	-40.5	-47.7	84
Alkaline	AS-4	-3.4	-71.1	-67.3	52.1	-33.3		
Alkaline	AS-5	-89.4	-84.0	-69.4	49.4	0.0		
	Mean	**-69.1**	**-56.1**	**-45.3**	**-22.8**	**-29.1**		
Anaerobic	AN-6	-96.8	-25.7	-65.2	-95.3	-93.1	4.82	60
Anaerobic	AN-7	306.7	-71.4	126.2	47.4	15.5		
	Mean	**105.0**	**-48.6**	**30.5**	**-23.9**	**-38.6**		
Aerobic (ATAD)	AE-8	156.8	-36.7	3.3	148.3	-78.6		
Aerobic	AE-9	-99.2	-96.1	-12.1	-98.8	-93.0	9.05	53
Aerobic	AE-10	5.6	26.3	-0.33	33.5	5.22		
	Mean	**21.1**	**-35.5**	**-3.03**	**27.7**	**-55.4**		
Composted (w/o bulking)	CP-11	-12.8	-2.7	-45.3	-71.4	-80.2	-58.9 (without 1359.7)	90
Composted	CP-12	-99.6	-69.0	-49.1	-99.8	1359.7		
	Mean	**-56.2**	**-35.9**	**-47.2**	**-85.6**	**639.8**		
Lime	LS-14	-87.7	-10.7	-24.6	-35.6	5.2	-45.1	80
Lime	LS-15	-92.8	18.1	-38.5	-90.6	-93.5		
	Mean	**-90.2**	**3.7**	**-31.6**	**-63.1**	**-46.2**		

*

Ne* Negative -- net loss

Positive -- net formation; accumulation is faster than degradation

**Overall change is the average of the 5 means for the individual chemicals

† Reduction likelihood is calculated from number of samples showing net loss as a percentage of total number of samples within each treatment.

Table 2.7a One-way ANOVA testing the effect of stabilization on the pollutant concentrations†

One-way ANOVA Summary

	N	df	p-value
Stabilization processes	5	4	<0.001
Pollutant concentrations	215	210	

†Data was normalized by dividing each value (individual measurement) by the mean for that pollutant, and due to non-normality, was log-transformed before statistical tests.

Post hoc tests

	Mean Difference	Std. Error	p-value
Alkaline stabilization - Composting	0.014	0.441	<0.001*
Aerobic digestion - Composting	0.037	0.487	0.031*
Composting - Lime stabilization	0.009	0.545	0.002*

* Tukey's Honestly Significant Difference and LSD indicate significant at p<00.05

Descriptive Statistics

	N	Mean	SD	Std. Error
Alkaline stabilization	70	0.42	0.908	0.109
Anaerobic digestion	25	1.41	3.169	0.634
Aerobic digestion	45	0.84	1.276	0.190
Composting	45	2.26	4.128	0.615
Lime stabilization	30	0.21	0.256	0.047
Total	215	0.98	2.408	0.164

Table 2.7b One-way ANOVA of treatment means for pollutant concentrations

Pollutant	N	p-value	Interpretation
Nonylphenol	42	0.043	Significant
Nonylphenol monoethoxylate	42	0.572	Not significant
Nonylphenol diethoxylate	42	0.113	Not significant
Octylphenol	42	0.064	Not significant
Bisphenol A	42	0.048	Significant

Table 2.8 Expected (calculated) values based on mass balance assuming no pollutant or dry mass loss and observed (measured) concentrations of target compounds in biosolids

Facility ID	NP		NP_1EO		NP_2EO		OP		BPA	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
	---------- mg kg^{-1} ----------									
AS-1	4.08	0.71	0.12	0.06	0.27	0.19	0.06	0.03	0.08	0.04
AS-2	20.21	0.56	0.56	0.42	0.27	0.52	0.44	0.02	0.05	0.02
AS-3	31.28	12.98	0.52	0.67	0.75	0.71	0.13	0.08	0.01	0.01
AS-4	0.77	1.11	0.42	0.18	0.34	0.19	0.01	0.01	0.01	0.01
AS-5	0.60	0.20	0.15	0.08	0.19	0.19	<0.01	0.01	<0.01	0.01
AN-6	195.1	0.78	4.66	0.43	5.31	0.23	7.51	0.04	1.10	<0.01
AN-7	1011.6	563.6	3.95	0.15	1.33	0.41	15.03	3.04	0.20	0.03
AE-8	16.37	42.03	0.44	0.28	1.09	1.13	0.52	1.29	0.42	0.09
AE-9	184.0	0.36	10.01	0.09	4.92	1.03	13.36	0.04	0.63	0.01
AE-10	2.42	0.78	0.24	0.12	0.16	0.19	0.26	0.11	0.01	<0.01
CP-11	1302.4	436.9	2.72	1.02	2.87	0.60	27.24	3.00	0.20	0.01
CP-12	148.1	1.09	1.19	0.74	0.71	0.72	12.57	0.05	0.02	0.48
CP-13*	-	1.22	-	0.19	-	0.27	-	0.22	-	<0.01
LS-14	2.44	0.32	0.22	0.21	0.34	0.27	0.04	0.02	0.00	<0.01
LS-15	6.35	0.49	0.19	0.24	0.42	0.27	0.09	0.01	0.13	0.01

* No sludge sample available for calculation

Table 2.9. Selected sludge and biosolids characteristics from various treatment processes

	Sludge						Biosolids					
WWTP	pH	TKN	Organic Matter	Electrical Conductivity	Total Solids	Sludge Processing Method	$CaCO_3$ Equiv.	pH	TKN	Organic Matter	Electrical Conductivity	Total Solids
		mg kg^{-1}	%	mS cm^{-1}	%		%		mg kg^{-1}	%	mS cm^{-1}	%
AS-1	6.48	67500	84.0	7.83	18.9	Alkaline	69.64	12.5	14600	13.12	11.39	59.6
AS-2	7.78	38700	46.1	5.93	34.4	Alkaline	30.8	12.3	17400	30.78	7.05	55.4
AS-3	6.09	59200	88.3	6.32	-	Alkaline	37.8	12.4	25700	38.0	7.49	-
AS-4	7.16	41500	52.4	1.13	15.7	Alkaline	58.1	12.5	20600	13.1	6.56	31.7
AS-5	5.43	59000	60.8	3.49	4.41	Alkaline	72.4	12.5	13900	13.53	11.1	55.0
AN-6	5.71	47100	65.9	3.1	4.95	Anaerobic	NA	7.83	43300	62.53	7.3	24.0
AN-7	5.14	60300	85.4	3.47	-	Anaerobic	NA	6.38	63800	75.75	5.84	-
AE-8	5.14	70600	72.6	2.51	8.03	Aerobic (ATAD)	NA	6.52	87000	61.8	3.98	3.7
AE-9	6.71	57500	65.1	1.66	2.92	Aerobic	NA	-	-	-	-	-
AE-10	6.27	-	-	-	-	Aerobic	NA	6.34	-	-	-	-
CP-11	6.84	50500	60.0	6.72	21.0	Composting (w/o bulking)	NA	6.02	45500	52.6	8.7	-
CP-12	7.03	39700	51.2	5.81	-	Composting	NA	6.07	23500	78.7	4.9	-
CP-13	-	-	-	-	-	Composting	NA	5.5	18900	34.4	9.98	-
LS-14	7.6	60400	64.6	4.24	15.9	Lime	29.5	12.5	46700	43.6	7.8	20.7
LS-15	6.48	67500	84.0	7.83	18.9	Lime	31.7	12.3	38800	51.5	4.37	33.5
MIN	5.14	38700	46.1	1.13	2.92		29.5	5.5	13900	13.1	3.98	3.69
MAX	7.78	70600	88.3	7.83	95.6		72.4	12.5	87000	78.7	11.4	96.3
MEAN	6.42	55346	67.7	4.62	32.6		47.1	9.4	35362	43.8	7.42	57.4
MEDIAN	6.48	59000	65.1	4.24	18.9		37.8	10.1	25700	43.6	7.30	55.4

- No sample available for this analysis NA – Not Applicable

Table 2.10 Correlation ($p<0.05$) between pollutants and selected chemical properties of sludge and biosolids

	TKN_{sludge}	$TKN_{biosolids}$	$CCE_{biosolids}$	$pH_{biosolids}$	$EC_{biosolids}$
NP_{sludge}					
NP_1EO_{sludge}	-0.61				
NP_2EO_{sludge}					
OM_{sludge}	0.77*				
$NP_{biosolids}$		0.62			
$NP_1EO_{biosolids}$			-0.81		
$OP_{biosolids}$		0.67		-0.76*	
$OM_{biosolids}$		0.65	-0.90*	-0.70*	-0.68
$EC_{biosolids}$		-0.59	0.77		

*Correlation at $p<0.01$

Table 2.11 Significant correlations ($p<0.05$) between pollutants in sludge and biosolids

	NP_b	NP_1EO_b	NP_2EO_b	NP_s	NP_1EO_s	NP_2EO_s
NP_b	1					
NP_1EO_b		1				
NP_2EO_b			1			
OP_b	0.91*					
BPA_b			0.62			
NP_s	0.57	0.65	0.65	1		
NP_1EO_s			0.60	0.70*	1	
NP_2EO_s			0.66		0.77*	1
OP_s		0.55	0.65	0.91*	0.61	
BPA_s						0.58

b -- biosolids
s -- sludge
*Correlation at $p<0.01$

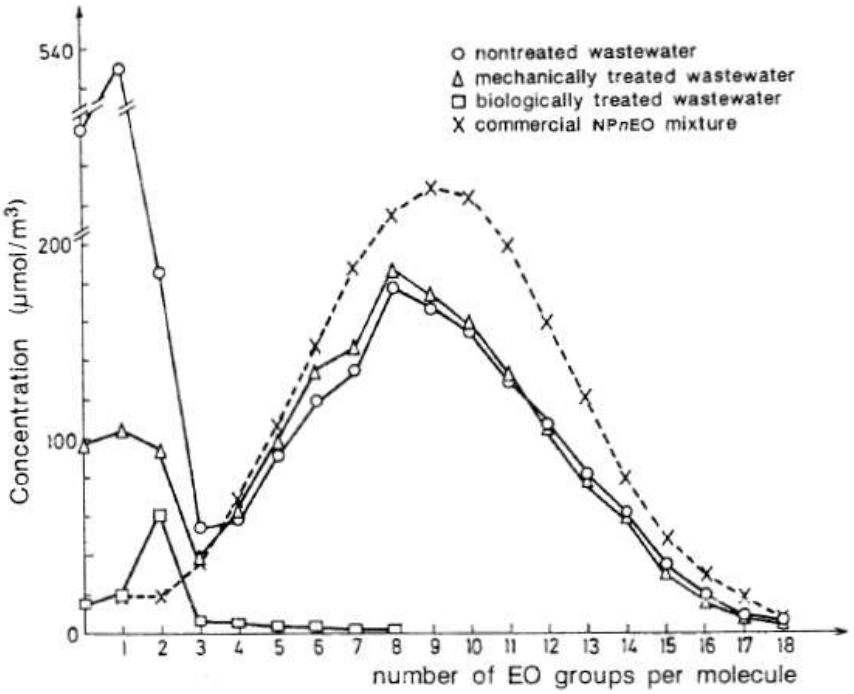


Figure 2.1a Distribution of NP_nEO oligomers in Ulster, Switzerland wastewater influent, effluent and in a commercial mixture Marlophen 810 (Source: Ahel et al. 1994a)

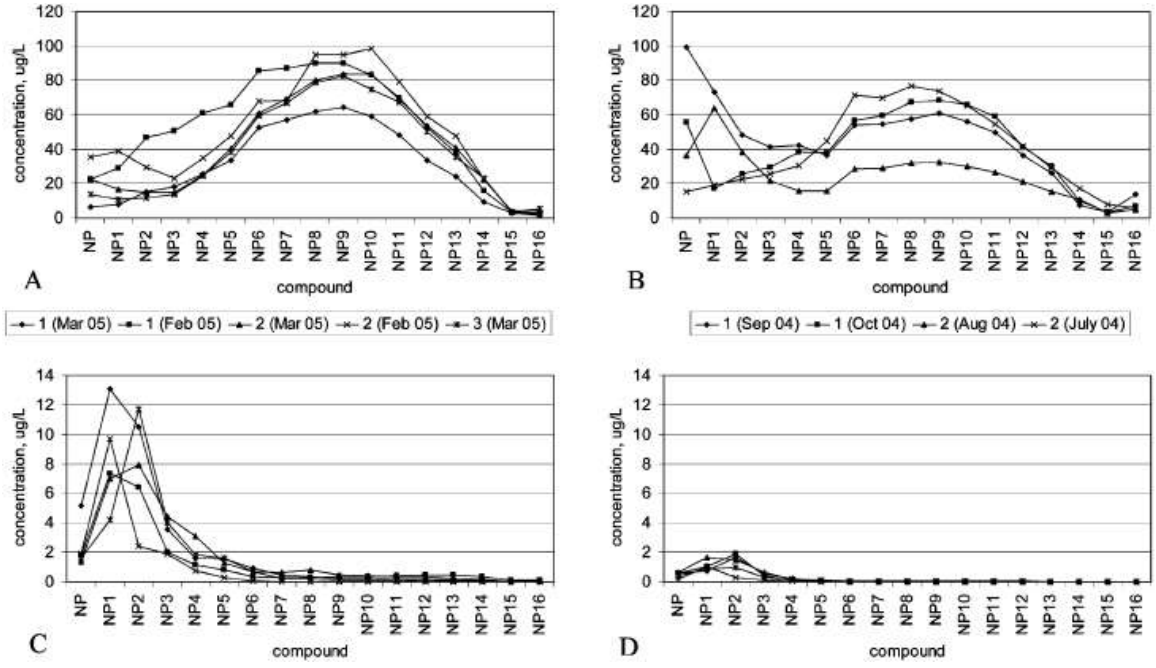


Figure 2.1b Seasonal distribution of NP_nEO oligomers in municipal wastewater influent in winter (A) and summer (B), and effluent in winter (C) and summer (D) in three municipal WWTP in the United States (Source: Loyo-Rosales et al. 2007)

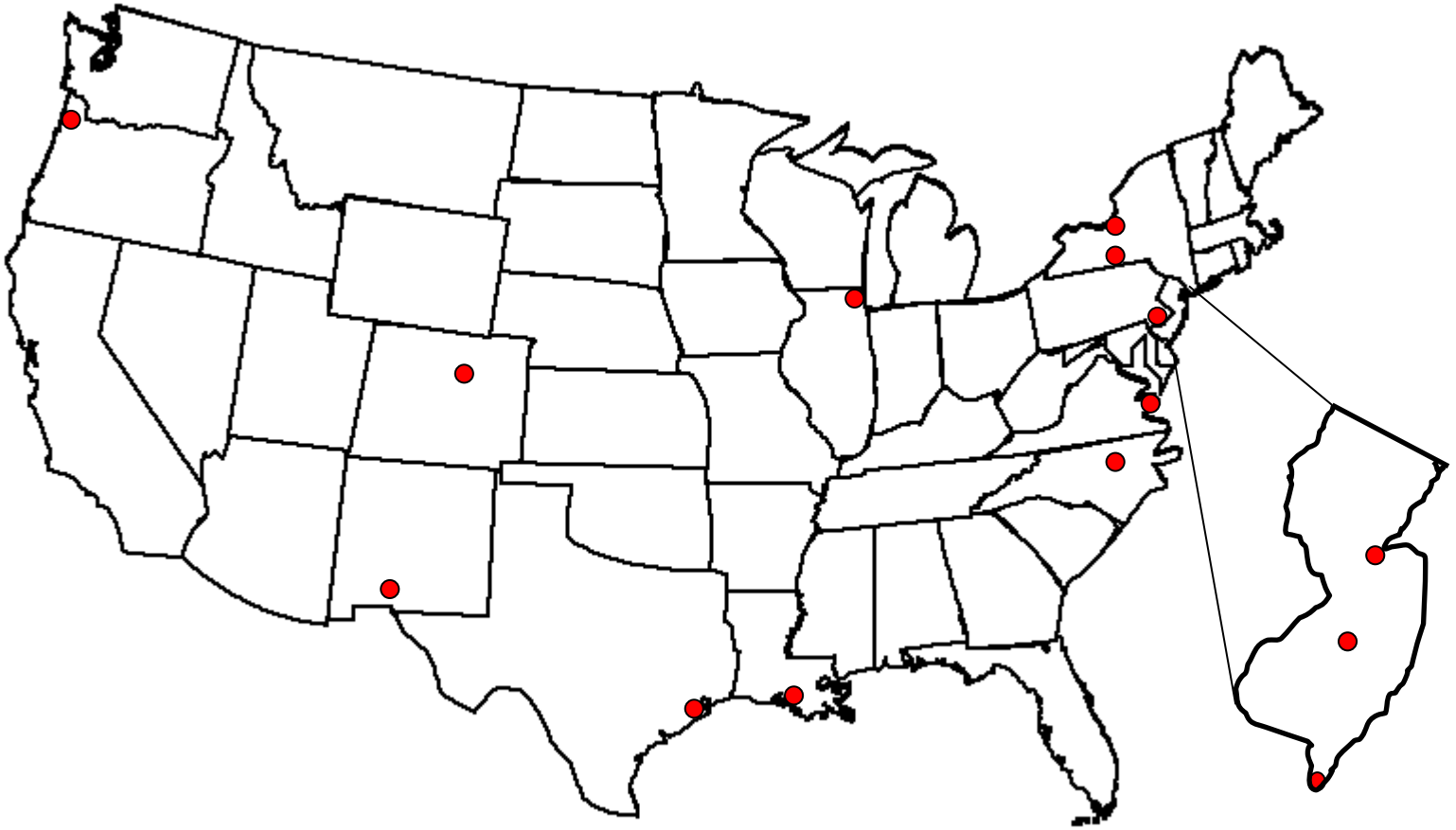


Figure 2.2 Sludge and Biosolids Sampling Locations

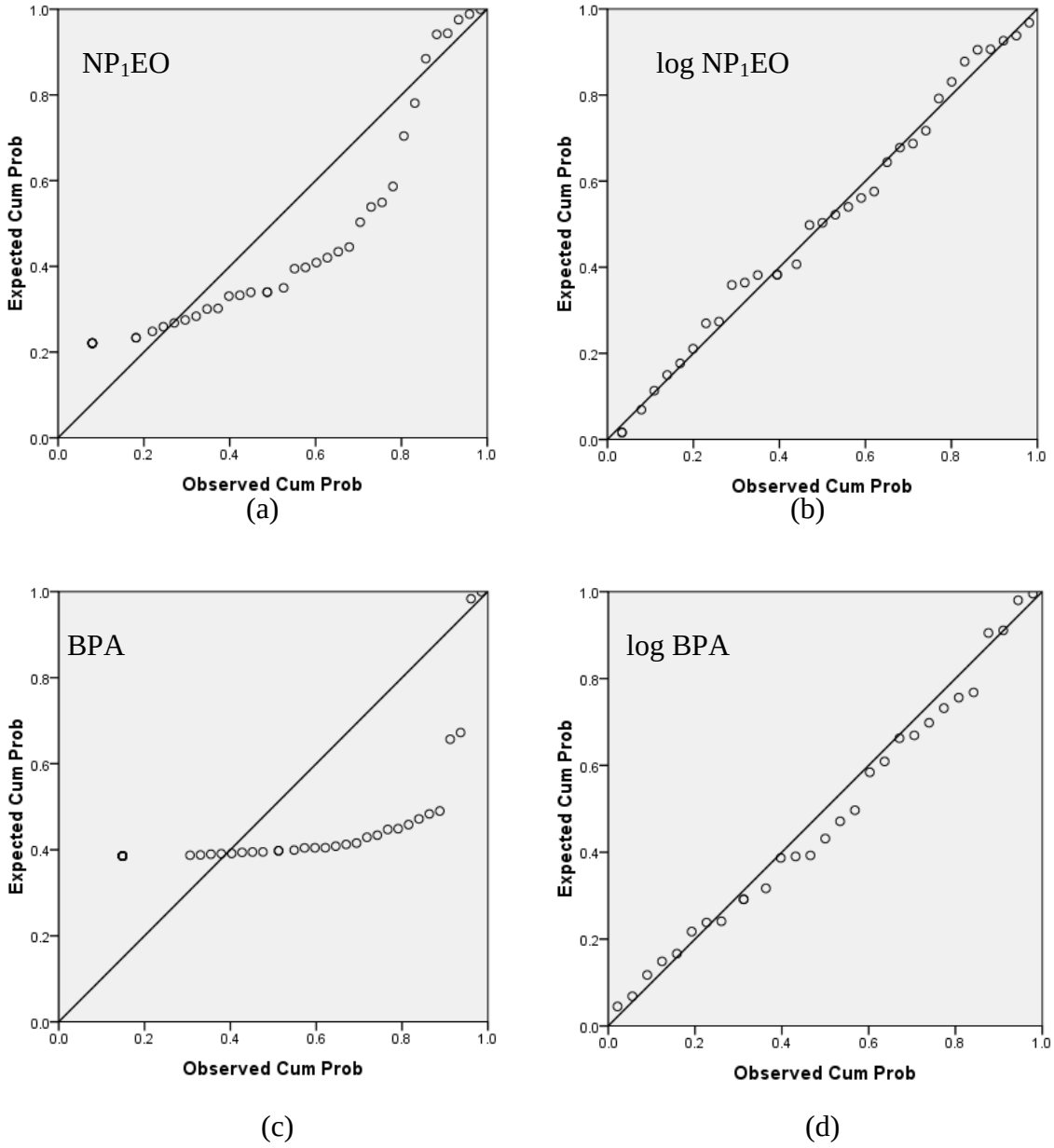


Figure 2.3 Distribution of sludge NP_1EO (a) before and (b) after logarithmic transformation and, distribution of biosolids BPA (c) before and (d) after logarithmic transformation. The before images indicates nonconformity to the normal distribution assumption and the after images shows that normal distribution was approximated after transformation.

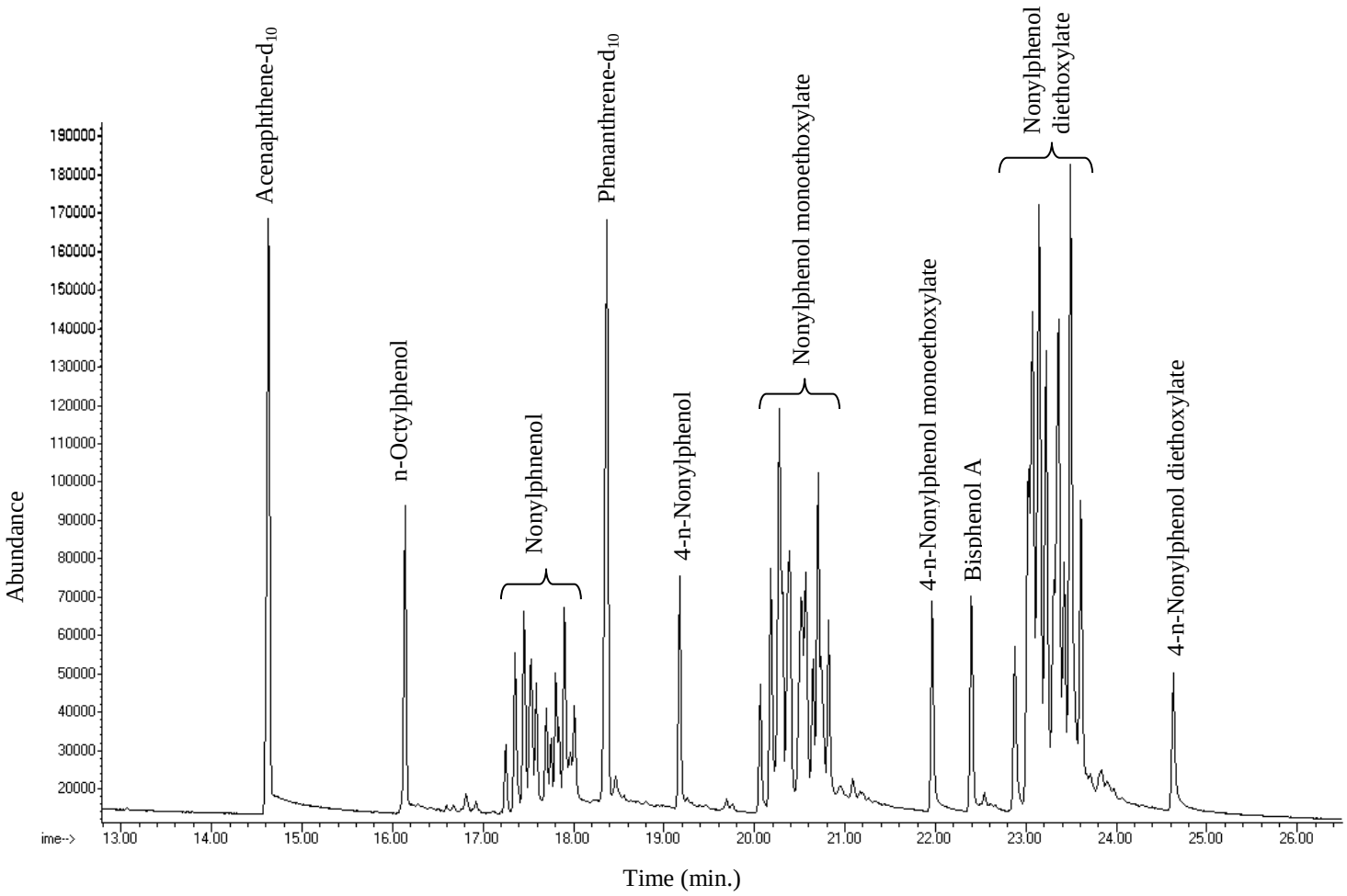
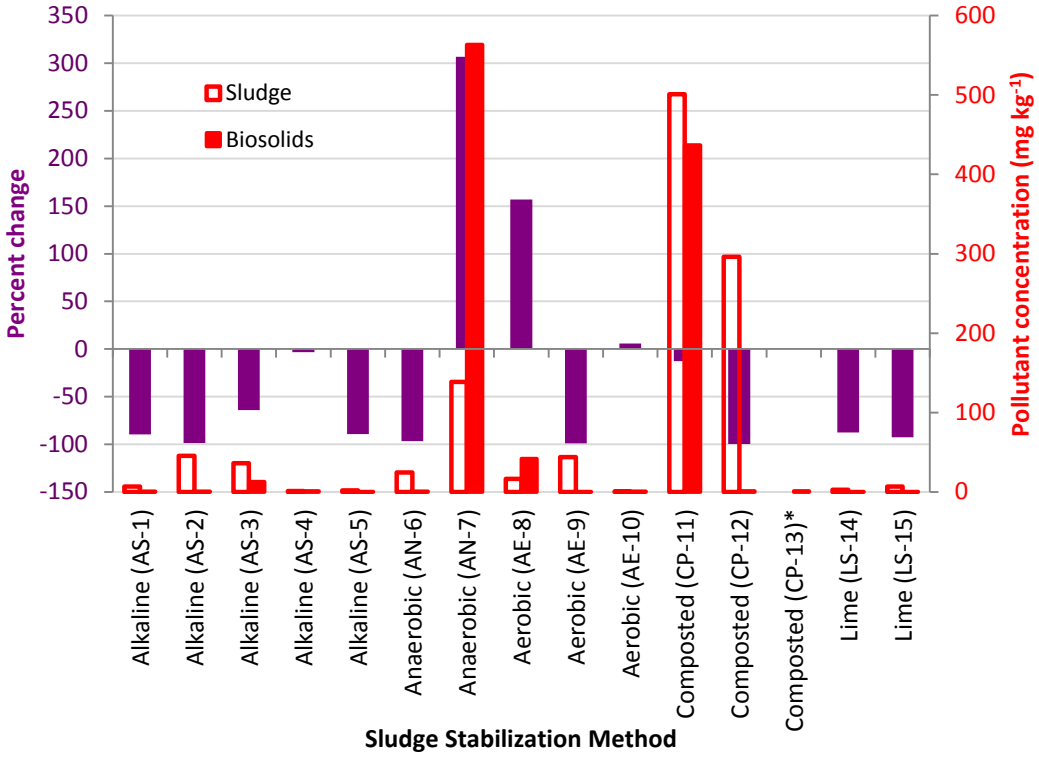


Figure 2.4 Typical GC-MS chromatogram showing separation of all the chemicals



* No sludge sample available

Figure 2.5 Percent change in NP concentration from sludge to biosolids with various sludge stabilization processes

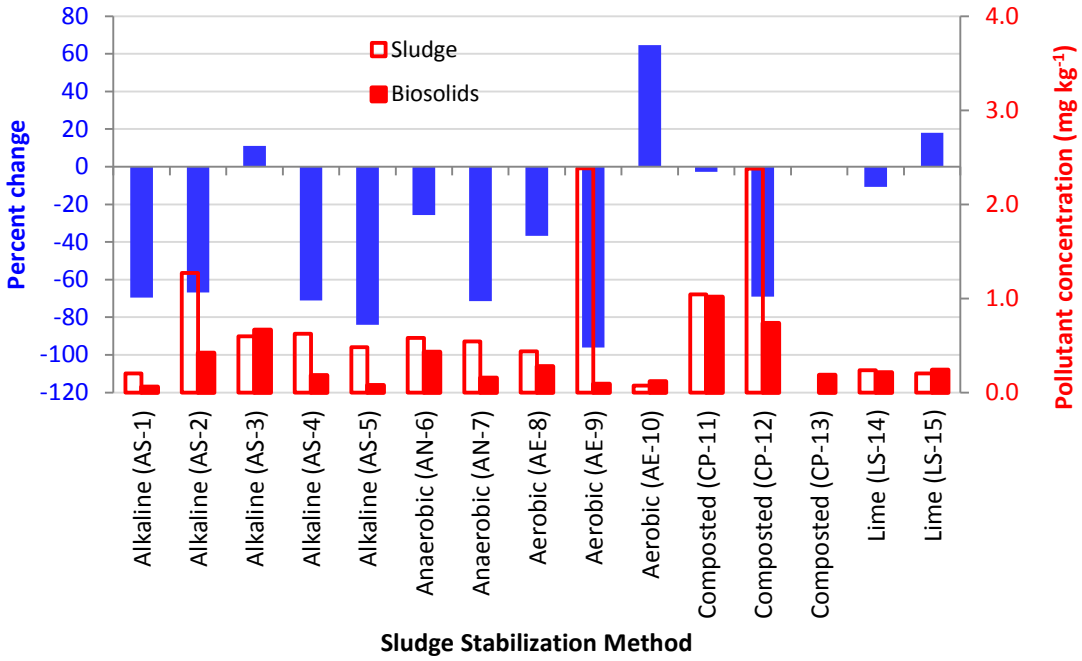


Figure 2.6 Percent change in NP_1EO concentration from sludge to biosolids with various sludge stabilization processes

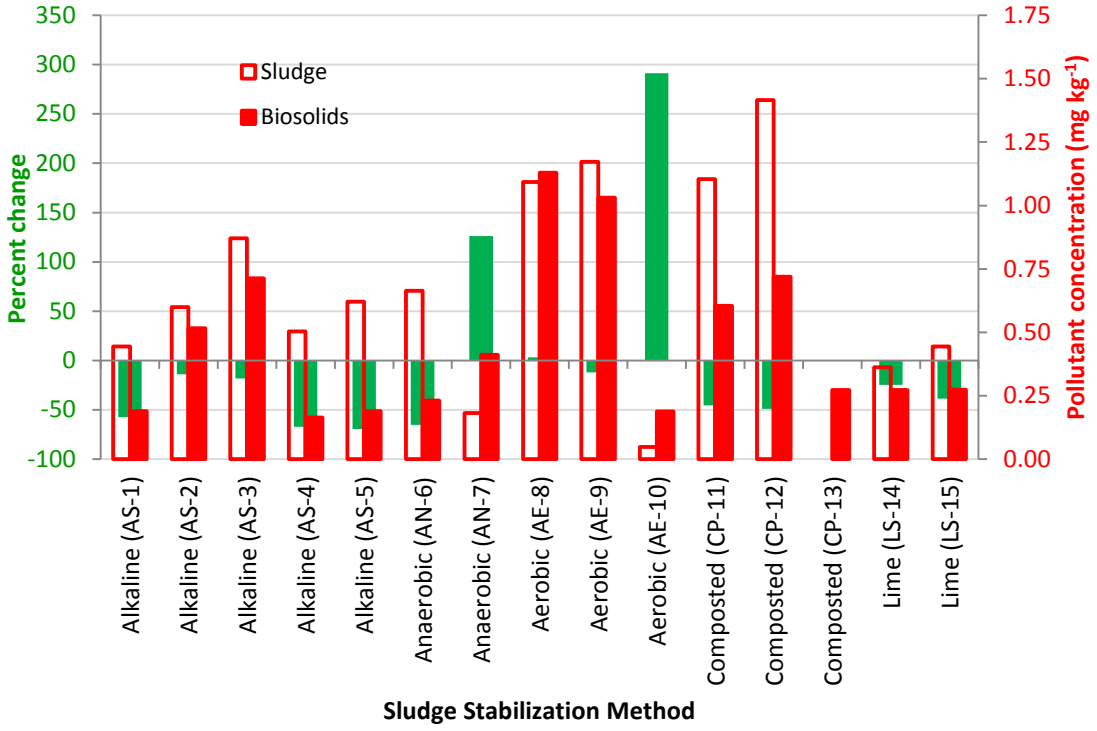


Figure 2.7 Percent change in NP_2EO concentration from sludge to biosolids with various sludge stabilization processes

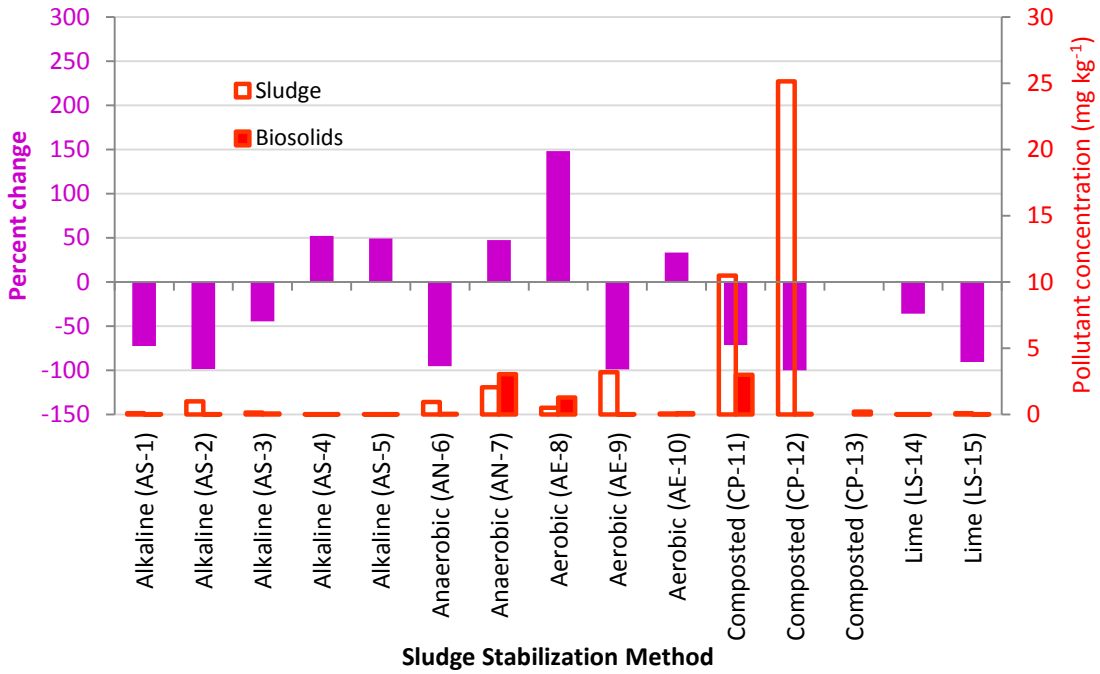


Figure 2.8 Percent change in OP concentration from sludge to biosolids with various sludge stabilization processes

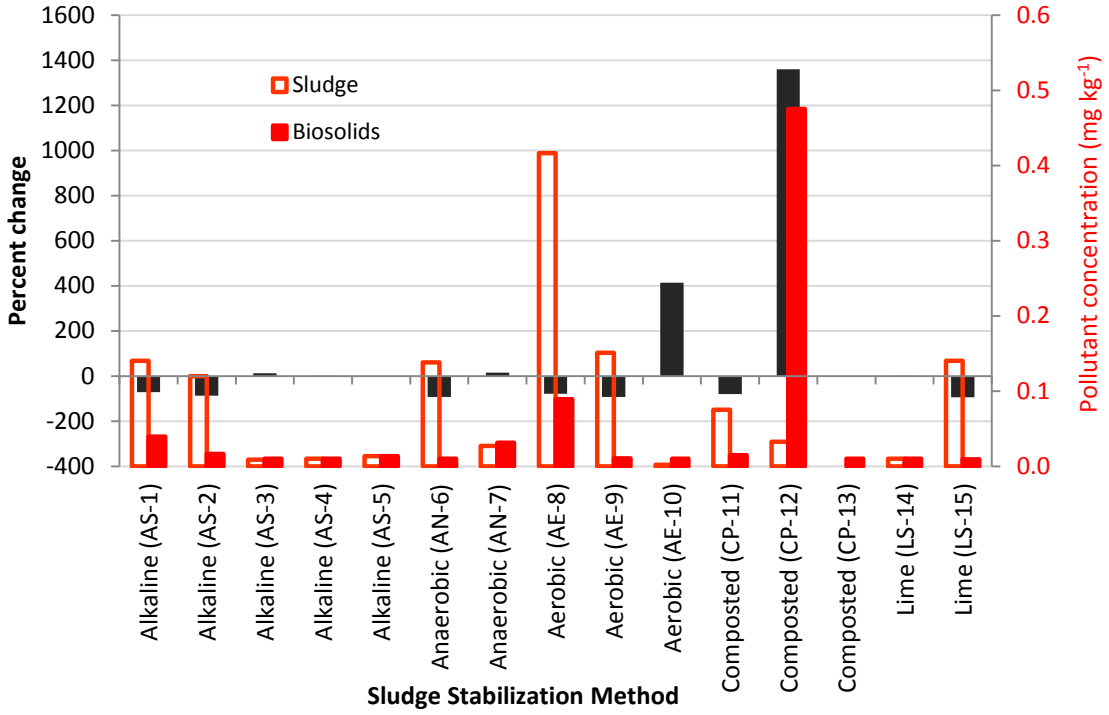


Figure 2.9 Percent change in BPA concentration from sludge to biosolids with various sludge stabilization processes

CHAPTER 3

PERSISTENCE OF AP_nEO AND BISPHENOL A IN SOILS AMENDED WITH ALKALINE-STABILIZED BIOSOLIDS UNDER LONG-TERM FIELD CONDITIONS

3.1 Introduction

Land application is a sludge management option for wastewater treatment facilities. It is a widespread practice in the United States and on the increase. In 1996, an estimated 5.3 million metric tons of sludge/biosolids were produced by publicly-owned treatment works (POTW) in the United States of which 36% was applied to land in support of agricultural, recreational, horticultural and reclamation lands (National Research Council, 1996). USEPA estimated that 6.9 million dry tons of biosolids were generated in the United States in 1998, 60% of which were land-applied, composted or used as landfill cover (USEPA, 1999). The report projected 8.2 million tons in production and 70% in beneficial uses by 2010. In 2003, USEPA estimated that over half of all sludge produced each year was beneficially-used on soil-based activities, that is, out of 8 million dry metric tons (DMT) of sludge produced annually 54% or 4.32 million DMT was applied to agricultural, horticultural, forested and reclamation lands around the country (USEPA, 2003).

Sludge is the direct byproduct of wastewater treatment aimed at protecting people from diseases that can result from untreated wastewater, and the environment from the destructive potential of the oxygen demand that untreated waste can exert on surface waters. Biosolids refer to sludge that has been further treated by one or more stabilization processes. Biosolids and sludge, irrespective of the treatment process, have been and continue to be land-applied as a means of replenishing soil nutrients, as a soil conditioner

to improve soil tilth due to its high organic matter content, and as a low cost source of liming, if the material is lime or alkaline-stabilized. The practice of land-application also serves as a conduit for transferring natural and synthetic organic compounds from biosolids to soil. Application rates vary considerably as they may be determined by either the nutrient requirement of the crop, lime requirement of the soil, or other considerations. In addition, an application site may receive repeated biosolids application as determined by soil testing, thus leading to the accumulation of unintended pollutants that may be present in the biosolids.

Rules governing the application of biosolids to agricultural, recreational and rangeland are codified in Title 40 Code of Federal Regulations, Part 503, *Standards for the Use and Disposal of Sewage Sludge* (USEPA 1993). There rules do not address organic compounds that may be present in the sludge and biosolids. This is because in the early days of land-application of biosolids, most of the concern was about heavy metals. However, biosolids also contain organic pollutants, many of which have estrogenic potential and are referred to as endocrine disrupting compounds (EDCs) because they possess the ability to mimic hormonal compounds in living organisms in such a manner as to interfere with normal physiological functioning of the system. Their fate in the soil has neither been fully determined nor explained.

Though land application of sludge and biosolids is commonplace, the concentration of pollutants in them varies in part due to the stabilization method applied to the sludge, industrial contribution to a wastewater treatment plant (WWTP) and, the degree of urbanization within the WWTP service area. Some processes reduce the concentration of pollutants in the course of the treatment, but in anaerobic digestion

nonylphenol (NP) accumulates. Alkylphenols (APs), their ethoxylates (APEOs) and bisphenol A (BPA) are common aquatic environmental pollutants because of their aqueous applications which are largely discharged into the wastewater systems. However, land application of wastewater residuals, such as biosolids, have been a mechanism for transferring these pollutants from the aquatic compartment into terrestrial environments. Research has shown the advantages of amending soils with biosolids but much work needs to be done to ascertain the ultimate fate of the organic compounds contained in them once they reach the soil.

The fate of pollutants in soil amended with biosolids may be controlled by a variety of mechanisms, which includes microbial degradation, sorption to soil constituents, plant uptake, photodegradation, transport into deeper soil horizons and/or groundwater, and soil erosion into surface water. Field and laboratory-scale studies of aerobically- and anaerobically-digested sludges have shown that alkylphenols are readily biodegradable at different rates in well aerated soils, sludge or soil-sludge mixtures (Marcomini et al., 1989; Topp and Starratt, 2000; Hesselsøe et al., 2001; Jacobsen et al., 2004).

Nonylphenol biodegradation has been reported to be accomplished at low concentrations (Topp & Starratt, 2000; Roberts et al., 2006). However, only a fraction of the total concentration in soil is microbially mineralized (Roberts et al., 2006). Thus varying proportions of NP products applied to land are unaccounted for by biodegradation. The persistent fraction is thought to be sequestered in soil residues as aging takes effect, thus reducing its availability (Marcomini et al., 1989; Cousins et al., 2002; Flint et al., 2003; Sjöström et al., 2008), or become bound to microbial biomass (Topp & Starratt, 2000). Nonylphenol biodegradation and/or disappearance in soil in

laboratory studies is measured in days (Topp & Starratt, 2000; Hesselsøe et al., 2001; Roberts et al., 2006) while in field studies it can take as long as 4-16 weeks (Marcomini et al., 1989; Jacobsen et al., 2004). This is due to the fact that laboratory studies are small and the mixture is well controlled unlike field conditions which are much slower and contents may not be well mixed.

The fate of organic pollutants in soil is heavily influenced by sorption characteristics of the soil, and in turn, by the organic matter component of soil. In sorption studies of NPEO homologs to a variety of adsorbents, John et al. (2000) reported that the adsorption partition coefficient, K_d, is closely correlated with organic content of the adsorbent. This study found strong sorption to sewage sludge (K_d=12,000-33,000 L kg^{-1}) but weak adsorption to silica (K_d=25-90 L kg^{-1}) and alumina (undetectable at 25 g L^{-1}). The study also found that native river sediment possessed higher sorptive capacity (K_d=450-1460 L kg^{-1}) than organic-free sediment (K_d=230-450 L kg^{-1}) and kaolinite (K_d=190-490 L kg^{-1}). Roberts et al. (2006) found that 85% of NP added to soil was sorbed to the solid phase in 2.5 hours. Similarly, Johnson et al. (1998) reported K_d values ranging from 6 to 707 L kg^{-1} for OP in sediments collected from three UK rivers. The distribution of partition coefficients is correlated to the TOC and particle size of the sediments.

Photodegradation can also take place in surface-applied biosolids with a half-life of approximately 30 days (Xia and Jeong, 2004). Metabolism of long-chain alkylphenol ethoxylates takes the form of progressive reduction of the ethoxyl chain resulting in accumulation of short-chain APEO.

Biosolids contain as much as 65% organic matter and this is one of the benefits successfully promoted in favor ofland-application (Sánchez-Monedero et al., 2004) as biosolids applied to soils have the potential to raise the soil organic matter content substantially. Structurally, soil organic matter (SOM) is massive, complex and acts as a sink for organic additions into the soil (Simpson, 2006). Thus, a great portion of organic compounds introduced into the soil has affinity for and partitions into the soil organic matter fraction. Therefore, discussing fate and behavior of organic compounds in soil will be incomplete without considering the role of SOM.

Nonylphenol ethoxylates and octylphenol ethoxylates (OPEOs) are nonionic surfactants and are used as adjuvants in pesticides formulations (Krogh et al., 2003), although NPEOs constitute the greater share of this application than OPEOs. The dual surfactant property of being simultaneously hydrophilic and hydrophobic make them suitable for pesticide delivery in that they are able to form micelle in solution of water. Pesticides in the form of insecticides, herbicides, fungicides, algicides, nematicides, biocides, and the like are routinely used in agricultural and non-agricultural management, and though they are chemically potent and specific in their action, their delivery on the field is not so effective as both the target crop and non-target surrounding soil are sprayed with the pesticide. The exact amount of surfactant in these pesticides is not disclosed (Green 1999).

Persistence of NP has been reported in river sediments at a wastewater outfall with last known discharge having occurred 20 years earlier (Hale et al., 2000). Similarly, Ferguson et al. (2001) found short-chain APEOs in estuarine sediments and indicates that the fate of APEOs is strongly influenced by both biodegradation and sorption processes.

These workers further found that NPEO in estuarine sediment was present at concentrations that nearly correlate to the organic carbon content of the sediment.

While most studies have focused on the occurrence, degradation and toxicology of APEOs in sludge and water, there have been comparatively fewer studies on the occurrence, behavior and fate in soil environments. Marcomini et al. (1989) found that about 10%, was resistant to degradation and was left in the soil after 210 days, perhaps due to strong sorption to soil. In a lysimeter study, Jacobsen et al. (2004) found a 55% reduction in the initial concentration of NP within 10 days of incorporation into the soil, and this was reduced further to below detection level at 110 days. Furthermore, in a study of soil profiles of eight soils that have been treated with and without sludge, Vikelsøe et al. (2002) found the contaminants in horizon(s) below the plow layer 8 years after application ceased and concluded both persistence and mobility of the pollutants exists below the plow layer although the soils are sandy in character and have been amended with sludge for 3 to 25 years. However, in a laboratory study, Hesselsøe et al. (2001) reported that 4-n-NP was completely degraded as no detectable concentration of NP was found after 38 days, thus implying no short-term persistence in sludge-amended soils. These workers suggested that a low risk of leaching to groundwater exists. Uncertainty still remains about the fate and behavior of APEOs and BPA following their application or transfer from sludge and biosolids to soil. In fact, data on BPA levels in soils are sparse. Few studies have looked at the persistence of APEO and BPA in soil save those extrapolations and deductions from short term sorption and biodegradation studies. Thus persistence in soils is usually inferred from degradation studies carried out for short periods of time. Substantive data is lacking on long-term fate and behavior in soils to

which sludge and biosolids have been applied. Long-term assessment of fields that have been previously subjected to biosolids application for many years provides a means to evaluate the persistence of the contaminants after many years of exposure to environmental processes and having been subjected to repeated biodegradation cycles. In addition, because land-application of biosolids has been widely practiced for two decades since the ban on dumping of sewage sludge in the ocean, it is appropriate to conduct long-term assessment of the chemical and physical impacts of this practice on soils so amended. In addition, with the use of pesticides in agriculture being a common practice, it is appropriate to obtain an estimate of this contribution to the APEO load in agricultural soils so that adequate assessment of APEO loading due to land-application of biosolids can be made leading to providing answers to the sludge-biosolids theory of this research. This could be achieved by obtaining samples from agricultural fields that do not utilize sludge or biosolids but routinely apply pesticides as a standard practice in crop production.

3.2 Hypotheses

The hypotheses of this chapter are that (1) sludge and biosolids represent an important source of APEOs and BPA in soil as a result of land-application, and (2) APEOs and BPA in soils amended with alkaline-stabilized biosolids are immobilized within the soil as a result of organic matter content presumably due to adsorption and may not be a pollution threat to groundwater.

3.3 Goals

The goals of this study are to assess/determine the persistence of NP, NP_1EO, NP_2EO, OP and BPA in soils that have been amended with alkaline-stabilized biosolids, and presumably pesticides, and identify the likely process(es) that influence the fate of alkylphenol ethoxylates and bisphenol A in these soils.

3.4 Objectives

Since NP, NP_1EO, NP_2EO, OP and BPA are not naturally present in the soil, this study intends to:

- obtain long-term environmental or residual concentrations of the selected contaminants in soils many years following biosolids application;
- obtain an estimate of NP, NP_1EO, NP_2EO and OP residual concentrations in agricultural soils due to pesticide use;
- assess the persistence of the contaminants from analysis of long-term biosolids-amended soils; and
- determine from the observations the processes that are likely to have influenced the persistence and fate of NP, NP_1EO, NP_2EO, OP and BPA in these soils.

3.5 MATERIALS AND METHODS

3.5.1 Sample Collection and Handling

The study sites consist of 21 locations spread across 3 physiographic regions of New Jersey. There were 15 agricultural soils that were managed with alkaline-stabilized biosolids and, presumably pesticides; 1 recreational and 2 reclamation lands that were not managed with pesticides, and 3 research facilities that were treated with pesticides only

(Figure 3.1). Sludge and biosolids application rates to the agricultural sites were from 9.9-17.7 Mg ha^{-1}, and both recreation and reclamation fields were 47.5-147.5 Mg ha^{-1}. The For each of the 21 locations, a corresponding control site was sampled which consisted of wooded land and/or overgrown vegetation adjacent to the treated fields where neither biosolids nor pesticides have been used, and were sampled many meters inside, away from the edge and direct influence of the treatments, that is, from stray biosolids or pesticide broadcast. The sites were selected to represent most of the range of soils presented by the physiographic regions of New Jersey. The sites also represent the different land use practices to which the soils are subjected following biosolids application. The sites were identified and selected from historical records that were maintained by the biosolids producer, who also had oversight of the application. During the sampling period, most of the sites were functioning cultivated farms while some were fallow, recreation fields, and reclaimed lands. Surface (0-17cm) and subsoil (18-50) were collected with a 4-inch core sampler. Composites from each site were made up of 3 core samples from the respective depth were well mixed and transferred into 32 oz. paper cups. Samples were air-dried, ground and sieved to pass USA standard sieve No. 10 and stored at room temperature.

3.5.2 Extraction and Clean-up of Soil Samples

Duplicate samples were extracted as described in Chapter 2. Ten (10) grams of soil were subjected to accelerated solvent extraction (ASE), concentrated, cleaned up and analyzed as described earlier. Prior to extraction, each sample was fortified with 200 µL of surrogate solution consisting of 150 µg μL^{-1} 4-n-nonylphenol, 4-n-nonylphenol monoethoxylate and 4-n-nonylphenol diethoxylate (Cambridge Isotopes, Inc., Andover,

MA) in ethyl acetate. Each batch of extractions included a blank that was treated exactly as the samples except that it contained oven-baked Ottawa sand.

3.5.3 GC/MS Analysis, Identification and Quantification

Concentrated extracts were separated on an Agilent 6890 gas chromatograph coupled to an Agilent 5793 mass selective detector (Agilent Technologies, Santa Clara, CA). Target analytes were identified by matching retention time and mass spectra with reference standards and quantified using their quantitation ions and internal standards. Acenaphthene-d_{10} (99.7% purity) and phenanthrene-d_{10} (99.1% purity) (AccuStandard, New Haven, CT) were used as internal standards. The surrogates were p-n-nonylphenol, p-n-nonylphenol monoethoxylate, p-n-nonylphenol diethoxylate (Cambridge Isotopes, Inc., Andover, MA). Reference standards were nonylphenol (technical grade, 97% purity) (Sigma-Aldrich Corp., St. Louis, MO), nonylphenol monoethoxylate (branched isomers), nonylphenol diethoxylate (branched isomers), 4-tert-octylphenol and bisphenol A (Sigma-Aldrich Corp.). A 2 µL injection of each sample was analyzed in splitless mode under the following GC conditions: injector port 290 ºC, constant Helium carrier gas at pressure of 11.16 psi, purge flow 30 mL min^{-}1, purge time 0.75 min and total flow of 34.2 mL min^{-}1. Separation was carried out on J & W DB-5MS column 30 m x 0.25 mm i.d. and 0.25 µm film thickness (J&W Scientific Inc., Folsom, CA). Temperature programming was 50 ºC hold for 2 min, ramp rate of 10 ºC/min to 320 ºC and hold time of 5 min. The MSD was operated in EI mode at 70eV, source temperature 230 ºC and quadropole temperature of 150 ºC. The instrument was tuned with perfluorotributylamine (PFTBA) and performance check was done with difluorotriphenylphosphine (DFTPP).

The target compounds were identified by comparing the mass spectra (fragmentation pattern) of samples to known standards and quantified using their quantitation ions.

3.5.4 Quality Assurance

Quality assurance steps were as outlined in Section 2.4.6.

3.5.5 Statistical Analysis

SPSS (SPSS Inc., Chicago, IL) was used for P-P plots, ANOVA, GLM and Pearson correlation. Student's *t*-test was done in Microsoft Excel. Statistical tests were performed on log-transformed values.

3.5.6 Calculation of Projected Pollutant Concentrations in Soil

The soils were amended with alkaline-stabilized biosolids from a WWTP, labeled as AS-1, in Chapter 2. Concentration of each pollutant in the soil following land application of biosolids was determined by equation 3.1.

$$C_{pollutant} = AR_{biosolids} \times CF_1 \times CF_2 \times C_{biosolids} \qquad 3.1$$

where,

$C_{pollutant}$ = Concentration of APEO or BPA (mg kg^{-1})
$AR_{biosolids}$ = Biosolids application rate, Mg ha^{-1}
CF_1 = Conversion Factor, ha/2.5acre
CF_2 = Conversion factor 2, mass of 1 acre furrow slice, acre/907.3 Mg
$C_{biosolids}$ = Pollutant concentration in biosolids, mg kg^{-1}

3.6 RESULTS AND DISCUSSION

The 21 soil sampling locations in this study were distributed over 3 out of 4 New Jersey's physiographic provinces (Figure 3.1). The soils represented a broad range of physico-chemical properties. Their diverse characteristics (Tables 3.1 – 3.4), were the

product of the geology, geography and ecology of the respective physiographic regions. Soils of sites 1-3 were developed from sedimentary rocks consisting of sandstone, shale and limestone in the Valley and Ridge physiographic province of the State. The landscape consists of steep ridges and flat valleys. Soil characterization data (Tables 3.1, 3.3 and 3.4) showed that the 3 biosolids-amended soils from this region were loamy in texture with higher organic matter than other soils in the study. The 3 sites were high in basic cations and the pH was in the neutral to alkaline range. Soils of sites 4-9, 20 and 21 were developed in red sandstone, conglomerate, shale, basalt and diabase on gentle rolling landscape of the Piedmont physiographic province, a region in transition between the mountainous topography to the north and flatter terrain to the south. Soil analysis data showed that the soils from this region were more silty in texture but contain less organic matter than their northern counterparts. The remaining sites (10-19) consist of soils developed in the sediments of the Coastal Plains physiographic region where deposits from oceans and seas overlay older metamorphosed rocks. The sediments are dominated by sand but could also consist of layers of silt and clay deposited alternately in river deltas and marine environments as the sea level fluctuated. As a result, soil particle size is dominated more by sand than clay or silt, thus the soil texture was mostly sandy loam or loamy sand. The soils are low in organic matter and rather acidic.

Trace concentrations ($\mu g\ kg^{-1}$) of APEOs and bisphenol A were detected in the18 biosolids-amended soils designated as Treatment 1 (Table 3.5). In addition to biosolids amendment, many of these sites are presumed to have also been managed with pesticides during farming operations, although this study had no access to the management records. Adjuvants and tank mix in spray delivery systems used in pesticide applications may

contain APEOs, and the records would have provided the type of pesticide, application rates, and frequency of application. In general, higher contaminant concentrations were measured in the topsoil than in the subsoil. In both soil depths, NP concentration is multiple times that of NP_1EO and NP_2EO, which are similar, and which average about twice the OP concentration. BPA was the least detected with median concentrations almost 2 orders of magnitude lower than NP. Plow layer NP concentrations were especially higher in the three reclamation sites (14, 16 and 17), which are non-cultivated soils where biosolids were applied at rates of 48, 75 and 148 Mg ha^{-1}, respectively – rates that are substantially greater than what is used on cultivated farms (9.9 -17.7 Mg ha^{-1}). Also, relatively high NP was found at sites 1, 3, 4 and 6, which were sampled from staging areas of the field, where biosolids were stockpiled prior to spreading on the fields. Thus NP concentration at these spots were probably greater than in the rest of the field. Together, these seven sites, and especially the three reclamation sites, suggest that residual concentration of these contaminants increases with application rate. Similarly, NP_1EO, NP_2EO and OP show increased concentrations at site 17 where biosolids application rate was at the highest. It is noteworthy that over a time period of 10 years biodegradation and other removal mechanisms have not reduced the contaminant concentration to a lower and perhaps common baseline as other sites with lower application rates. This observation suggests that while biodegradation is important, there are other processes also acting to determine the fate of these contaminants in soils. Furthermore, it seemed that degradation may be a function of both the amount of applied sludge or biosolids and the concentration of NP products in the sludge or biosolids. Thus, the pollutants may be removed faster when soils are amended with biosolids at

agronomic rates and remain longer in soil when biosolids are applied to land at higher (non-agronomic) rates. In studies that compared low (0.7 t ha^{-1}), medium (4.3 t ha^{-1}) and high (17 t ha^{-1}) sludge amendment to soils, Vikelsøe et al. (2002) found the highest concentration of NP (2430 μg kg^{-1}) and NP_2EO (2240 μg kg^{-1}) in the high sludge-amended soil despite cessation of sludge amendment 8 years earlier, and showed that persistence of organic pollutants is related to the sludge application rate. The soil in the study sites is sandy in character, and the field with high application rate has been with sludge for 25 years, while the fields with low and medium application rates were amended with sludge for 3 years.

Comparison of means between the topsoil and subsoil concentrations was performed using paired Student's *t*-test and was statistically significant ($p<0.05$) for the five contaminants (Table 3.6a). With pollutant concentrations higher in the topsoil than in the subsoil, and 1.4 to 3.2 as much soil organic matter in the cultivated topsoils as in the subsoils, it is likely that greater retention of the pollutants is taking place in the topsoil that in the subsoil. In many soils, organic matter is typically higher in the topsoil than subsoil. SOM content of cultivated soils varies depending on agricultural practice, soil type, climate and other factors. Values range from 0.58 – 5.3% for cultivated topsoil (Vikelsøe et al., 2002; Kumar & Philip, 2006) and 2.7 -4.4% for farms with tree crops (Loewy et al., 2011). Soil characterization data (Tables 3.3 and 3.4) suggest that organic matter may have influenced the immobilization of these chemicals, as organic pollutants have the tendency for sorption to soil organic matter (Alexander 2000; Drori et al., 2006). Binding of hydrophobic compounds to soil organic constituents may be likened to partitioning between polar and nonpolar phases which is described by the octanol-water

partition coefficient (K_{ow}). Having lost their hydrophilic moiety during biological transformation, NP and OP are strictly hydrophobic as any synthetic organic compounds, and with K_{ow} of 4.48 and 4.12 respectively, they readily partition through hydrophobic sorption reactions into soil organic constituents. Similarly, NP_1EO and NP_2EO which are metabolic products of the hydrophilic higher-substituted oligomers, such as NP_9EO, and are hydrophobic in character and behaves in like manner as NP and OP, The distribution of soil organic matter reflects the ecoregions, physiographic influence on the formation of the soils, and soil management. The 3 locations within the Valley and Ridge have SOM between 4.4 and 5.4% in the topsoil. The locations within the Piedmont have between 2.9 and 4.0% while the remaining locations within the Coastal Plains have between 1.5 and 2.2% excluding the reclamation sites. A similar break in SOM is measured in the subsoil. In all the samples, the topsoil (0-17 cm) contains higher soil organic matter (SOM) content than the subsoil (18-50 cm) with the exception of reclamation sites 16 and 17. In the topsoil, weak correlations (r^2=0.22 for NP, 0.41 for NP_1EO, 0.09 for NP_2EO, 0.34 for OP and 0.41 for BPA) were found between the individual contaminant concentrations and soil organic matter. SOM decreases in these soils along the physiographic groupings in the north-south direction of the State, and this reflects both the effects of moisture and temperature in the decomposition of organic additions to the soil, and the reduced ability of sandy soils to retain finer soil constituents as a result of increased porosity. In the upper physiographic province, fine soil particles (clay and silt) are higher while sand is lower than in the Coastal where the reverse is the case. This parallel is similar to the findings of Johnson et al. (1998) in which regression analysis showed that sediments with greater total organic carbon and fine particle fractions sorbed greater quantities of OP in

river sediments, though they thought the total organic carbon was controlling sorption of the chemical. In the current study, there is no evidence to suggest incremental accumulation of NP due to sequential breakdown of higher substituted NPEO into lower substituted NPEO, but that NP is present in the soils at 4 to11 times more than NP_1EO, 3 to 38 times more than NP_2EO; it is also 4 to16 times higher than OP and 13 to 949 times more than BPA.

Since the 18 fields comprising treatment 1 (Table 3.5) were treated with alkaline-stabilized biosolids of known APEO concentrations, the expected contaminant concentration in the soil was determined from the biosolids application rates and contaminant concentration in the biosolids using equation 3.1. This calculation assumed that no losses from biodegradation and other processes occurred. Based on this calculation, the measured contaminant concentrations were sometimes less than projected, as expected, but also were higher than projected in many cases (Figures 3.2 to 3.6). However, in sites 14, 16 and 17, where biosolids were applied at reclamation rates (much higher than typical agronomic rates), measured concentrations were below projected concentrations by 39 to 71%. While contaminant concentration is a function of biosolids loading, measured concentrations in sites 1 to 8 were not commensurate with the application rates, at least, when compared to sites 14, 16 and 17. This suggests that there is possibly an additional source of these contaminants to these farms beside biosolids, which supports the assumption that pesticides were applied to these fields at some time in the past. As a result, they received more AP_nEOs than the recorded biosolids application rates suggests.

Contribution due to pesticide use on the cultivated soils in Treatment 1is difficult to assess since the application records were not available, and information regarding which pesticides contain APEOs and the concentrations of surfactants in the pesticide formulations are not readily available (Green 1999). Nevertheless, an attempt was made to estimate what the likely surfactant concentration in the soil would be using pesticide application rates from 3 New Jersey Agricultural Experiment Stations (NJAES) sites, and assuming 0.25% surfactant in the spray volume (Green 1999). In the calculations (Appendix C) which were made for 20 herbicides, insecticides, and fungicides and over wide-ranging application rates, soil surfactant concentration resulting from a single pesticide application is estimated to be from 0.09 to 14 μg kg^{-1}. These values compare very well with the range of concentrations (0.03 – 28.3 μg kg^{-1}) measured in Treatment 1 from combined biosolids and assumed pesticide application, except for site 17 where a large quantity of biosolids was applied. Conversely, the calculated values were less than the range (0.08 – 67.9 μg kg^{-1}) of residual APEO in Treatment 2 which received annual pesticide treatment. It can be deduced from these calculations that, in addition to sludge and biosolids, pesticide use was a contributing source to the residual APEO observed in the farms included in this study. In addition, field observations showed that 5 of the agricultural sites were fallow and was under pasture at the time of sampling for this study, indicating that pesticide use may not have been consistent for 15 of the 18 sites, however concentrations of pollutants in the 6 sites were not lower than the ones that might have been managed with pesticide. While persistence of APEOs in the 15 sites would be hard to establish without accurate data on pesticide usage during the period covered by this study, at the 3 reclamation sites where pesticides were not used, there is

adequate data to establish persistence of these pollutants as there were relatively higher contaminant concentrations to suggest that the source of the contaminants was the biosolids applied more than 10 years prior to sampling for the study. Nonylphenol and bisphenol A are among many synthetic chemicals that are described as persistent organic pollutants (Laws et al., 2000; Lalah et al., 2003). They are characterized as persistent organic pollutants because they show detectable concentration in the environment after being subjected to biological and chemical degradation, repeated biogeochemical processes, and are not completely eliminated but rather still remain in the environment for a long time.

OP and NP are hydrophobic compounds with octanol-water partition coefficients (log K_{ow}) of 4.12 and 4.48, respectively, which suggest the tendency for them to sorb to organic materials in the soil (Kohl et al., 2000). Soil organic matter (SOM) is made up of plant residues, microbial tissues, humic substances, and lipids, and participates in sorption reactions with pesticides and organic pollutants in soil (Ahmad et al., 2006; Drori et al., 2006). Since these contaminants are nonionic and are less likely to dissociate in the soil environment, they are likely to be largely contained within the topsoil, which has greater organic matter content than the subsoil; this reduces the likelihood of the pollutants entering the groundwater. However, Kuhnt (1993) expressed the notion that the presence of nonionic surfactants in the soil influences the solubilization of other xenobiotics thereby rendering them prone to either faster or slower biodegradation.

APEOs are used in some pesticide formulations, and pesticides are an essential part of pest management in agriculture. To evaluate the potential contributions of NPEOs from pesticides, five plots from the New Jersey Agricultural Experiment Station that have

received annual pesticide application but not received biosolids were included in the study (Table 3.2) and designated as Treatment 2. The target compounds were detected in these soils in greater concentrations than in Treatment 1 (Table 3.7). The average topsoil NP concentration is 29.7 μg kg^{-1}, four times the topsoil concentration found in Treatment 1. The average subsoil NP is 16.9 μg kg^{-1}, which is five times the average subsoil NP concentration in Treatment 1. Although, OP and BPA are 1 to 2 orders of magnitude lower than NP, they are similarly observed 1.4 to 7 times the concentrations in Treatment 1. In contrast, NP_1EO and NP_2EO concentrations are lower, on the average, in Treatment 2 than in Treatment 1. In the subsoil, contaminant concentrations are generally lower than in the topsoil for all contaminants studied. Nevertheless, there is no statistically significant difference ($p< 0.05$) between the topsoil and subsoil concentrations for these 5 plots (Table 3.6a). Since biosolids were not applied to these 5 plots, the higher contaminant concentrations found in them likely reflects the cumulative residual effect of repeated pesticide application. Hale et al. (2000) concluded that most of the NP in the environment is a result of degradation of NPEO and from NP production. A list of pesticides that were applied to crops planted on these sites is presented in Appendix B. Although, the ingredients in these pesticide formulations are not available to enable identification of the ones containing NP or NPEO, the comparatively greater concentration in Treatment 2 (pesticide-only sites) suggests that annual pesticide application activity on these sites results in APEO accumulation in soils. In pesticide formulation, typically 5-7% is actual surfactant, which is further diluted by the user for field application (Mueninghoff et al., 2000) but specifically, NPEO and other nonionic surfactants (such as alcohol ethoxylates, AEOs, and alkylamine ethoxylates, ANEOs)

application in the U.S. constitute only 0.25% of the tank spray volume (Green 1999), a value that was used in subsequent calculation below.

Each treated site has a complementary control site. These control sites are grouped as Treatment 3. They consisted of wooded lands adjacent to the treated fields where neither biosolids nor pesticides have been used, and were sampled many meters inside, away from the edge and direct influence of the treatments, that is, from stray biosolids or pesticide broadcast. These sampling locations provide soil background concentrations of the target contaminants within the different locales against which to evaluate the other treatments. Most of the contaminant concentrations in the control samples are <1 $\mu g\ kg^{-1}$ with the exception of NP in 11 sites where concentrations in the range of 1.07 to 2.27 $\mu g\ kg^{-1}$ were measured (Table 3.8). The calculated surfactant concentrations (0.09 to 14 $\mu g\ kg^{-1}$) in Appendix C are much higher and do not account for the concentrations found in the control. As the control concentrations are very small, they are likely to have resulted from pesticide drift, post-application volatilization, surface runoff, particulate matter associate with wind erosion or soil tillage, and atmospheric deposition. Atmospheric deposition has been previously suggested as source when NP and NP_2EO were detected in uncultivated control soil and the concentrations were not lower than treated soils (Vikelsøe et al., 2002). Dachs et al. (1999) were the first to document the occurrence of NP in the atmosphere around the Lower Hudson River Estuary. The pollutants, measured over a range of 0.2 to 69 $ng\ m^{-3}$ in air and 0.21 to 51 $ng\ m^{-3}$ in aerosol, enter the atmosphere through volatilization from wastewater effluent discharge into rivers and the estuary, the same source that produced the sludge and biosolids that are placed in the terrestrial environment. Since then, atmospheric

transport and deposition of persistent organic pollutants, which includes NP_nEO, OP and BPA, have been well established (LeNoir et al., 1999; Van Ry et al., 2000; Lyons et al., 2014). Subsequent study of atmospheric concentration of APEO within the New Jersey Atmospheric Deposition Network (NJADN) by Van Ry et al., (2000) detected higher concentrations (0.13 - 81 ng m^{-3}) in air of "a suburban site located in an agricultural and botanical research area" than the coastal sites, a fact that the authors attributed to land-applied sources of APEO. The pollutants, which are volatilized or associated with particulate matter, are carried by prevailing winds to be deposited far beyond the originating source. Wania & Dugani (2003) suggested that persistent organic pollutants with octanol-air partition coefficient (log K_{OA}) values between 6.5 and 10 have the potential for long-range air transportation and deposition. In addition, it has been reported that nonylphenol's relatively high vapor pressure and K_{OA} enabled it to be carried over long distances in aerosol or droplet form (Wania & Mackay, 1996; Lalah et al., 2003). The estimated log K_{OA} and vapor pressure for NP are approximately 7.9 and 0.2 Pa respectively (Lyons et al, 2014; Seinfeld & Pandis, 1998).

Pesticide spray drift is a common occurrence and have been detected near and far from the application source. Dicamba herbicide vapor drift has been detected at 0.56 g acid equiv. ha^{-1} as far as 21 meters from the application source, and the severity of the drift was found to be significantly correlated to the air temperature (Egan & Mortensen, 2012) while endosulfan and propargite were detected 46 km from the source (Bradford et al., 2010). Spray drift is more often measured in air than in soil (Jensen et al., 2014) and is intertwined with atmospheric transport and deposition. Atmospheric deposition of pesticides from the agricultural activity in California's San Joaquin Valley has been well

documented in air, lakes, rain and snow in the Sierra Nevada Mountains (LeNoir et al., 1999; Bradford et al., 2010, 2013; Lyons et al., 2014). Nonetheless, Loewy et al., (2011), in a drift experiment, reported soil concentrations up to 19 μg kg^{-1} for Azinphos-methyl, 26 μg kg^{-1} for Carbaryl, 60.5 μg kg^{-1} for Chlorpyrifos, and 1.1 μg kg^{-1} for Methidathion in soil samples taken 5 m from sprayed plots. From the discussion above, the observed concentrations in the control sites of this study can be considered background concentrations for the treated sites. Bisphenol A, although a persistent organic pollutant, is mostly non-detected in this environment as it does not have application in the agricultural environment. Independent *t*-test of Treatment 1 (biosolids and pesticides) and Treatment 3 (control), and Treatment 2 (pesticides only) and Treatment 3 (control), indicate that there is no significant statistical difference ($p < 0.05$) between the means of both treatments and controls for BPA (Table 3.6b). This indicates that BPA is at background levels in both treatment sites and control sites. BPA is readily degraded but its detection in soils and other environmental compartments is due to continual introduction (Flint et al., 2012).

The results of this study suggest that perennial pesticide application is a major source of NPEO in soils under active cultivation. The higher contaminant concentrations found in Treatment 2 relative to Treatment 1 suggests that pesticide application to crops is a continual source of NP, NP_1EO, NP_2EO and OP in the NJAES soils studied. Mean concentrations of NP, NP_1EO, NP_2EO and OP of Treatments 2 (pesticides only sites) and 3 (control) are significantly different at $p<0.05$ (Table 3.6b). Though the concentrations are at trace levels, the probability is small that the differences between the two sets of data could have been random. A similar significant outcome was obtained in independent

t-test analysis of treatments 1 and 3. However, in comparing Treatments 1 and 2 it should be remembered that in one set of observations, pesticides were applied almost every cropping season and the potential for residual accumulation exists, whereas in the other set of observations, biosolids, whose effect is being studied, were applied once over 10 years ago but presumably pesticides were also applied during the same period.

There is insufficient data from this study to determine which soil mechanism(s) accounts for the persistence of the 5 target contaminants, in the reclamation soils treated with biosolids (Treatment 1). Annual APEO input through pesticide application refreshes the APEO concentrations in the 5 sites, treated with pesticides only (Treatment 2) therefore persistence is not an issue. However, it could be hypothesized from the data that sorption strongly influences the fate of these contaminants, perhaps limiting biodegradation, thus leading to detectable concentrations even after a decade following their introduction to the soils in this study.

3.9 CONCLUSIONS

The five contaminants in this study were detected in trace concentrations in the tested soils but at higher concentrations in the topsoil than in the subsoil. Greater concentrations in the topsoil than the subsoil corresponds to greater soil organic matter in the topsoil and indicative of the interaction between the pollutants and SOM as a result of the hydrophobic character of the pollutants which predisposes them to have greater affinity for soil organic matter constituents. Therefore, sorption to soil organic constituents is presumed to be the process involved in immobilizing the contaminants predominantly in the topsoil. This finding proves one hypothesis of this research that the

4 APEOs in this study are retained to a greater extent in the 0-17 cm layer and to a lesser extent in the 18-50 cm layer of soil.

This study further shows that sludge and biosolids application to soil is a major source of APEO and BPA in the absence of pesticide usage as demonstrated in 3 sites where biosolids were applied at a high rate and resulted in sustained pollutant concentrations 10 years after the application. However, this result would have been strengthened if more than 3 reclaimed sites were studied where only biosolids were applied. Nevertheless, it proves the hypothesis that sludge and biosolids are an important source of APEOs to soils whether they are used for agricultural or other soil management purposes. The study equally demonstrated that annual pesticide application is likely the major source of APEO in soils without biosolids amendment and produced higher residual APEO in soil. Measured contaminant concentrations in the soils studied are at the same level or greater than projected (calculated) concentrations introduced to the soils through biosolids, and increased with biosolids application rate, a fact that may be due in part to pesticide usage. As a result, much larger residual concentration were found in reclaimed soils where larger quantities of biosolids were applied compared to agricultural soils where biosolids were applied at agronomic rates. Use of pesticide formulations containing nonylphenol and/or octylphenol likely contributed to the residual contaminant concentrations on the agricultural fields. Despite biodegradation, higher contaminant concentrations were observed with large biosolids application suggesting that additional processes other than biodegradation may determine the fate of these contaminants in the soil. The fact that both biosolids and pesticides are equally important sources of APEOs in soil does not disprove the other but shows that applying both to the same soil raises the

concern of potential APEO pollution. What is not known is the magnitude of the pollution unless a systematic study pairing both sources is conducted. Persistence of APEOs and BPA in the soils studied cannot be generalized; however, the study confirms the persistence at μg kg^{-1} levels of NP, NP_1EO, NP_2EO and OP in soils amended with alkaline-stabilized biosolids in 3 reclaimed fields 10 years after a one-time soils-amendment with biosolids. BPA was essentially not present in the control sites because it has no application as an agricultural input or in soil management, but was higher in the active agricultural sites without biosolids application than biosolids-amended sites. As have been shown statistically, the hypothesis that sludge and biosolids are a major source of bisphenol A in the soil does not hold.

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Table 3.1 Characteristics of the soil sample locations where biosolids and pesticides were applied.

Site No.	Location	Land Use	Geographic Coordinates Latitude (N), Longitude (W)	Current or last Crop	% Sand	% Silt	% Clay	Textural Class	Comment/ Observation
1	Oxford	Agriculture	40° 49' 22.68", -75° 0' 25.89"	Fallow	30	48	22	Loam	
2	Bilyck	Agriculture	40° 49' 29.52", -75° 2' 9.17"	Corn	32	46	22	Loam	Gentle slope
3	Hope	Agriculture	40° 52' 57.60", -74° 59' 10.98"	Pasture	34	46	20	Loam	
4	Readington	Agriculture	40° 32' 21.36", -74° 46' 29.72"	Fallow	32	46	22	Loam	
5	Flemington	Agriculture	40° 28' 36.34", -74° 52' 47.23"	Corn	20	52	28	Sandy Clay Loam	Red triassic shale
6	West Trenton	Agriculture	40° 16' 38.06", -74° 49' 18.72"	Fallow	10	64	26	Silt Loam	
7	Blawenburg	Agriculture	40° 24' 10.29", -74° 43' 30.47"	Soybeans	24	52	24	Silt Loam	
8	Belle Meade	Agriculture	40° 28' 9.33", -74° 41' 11.89"	Corn	14	54	32	Silty Clay Loam	Red triassic shale
9	Skillmans	Agriculture	40° 28' 18.18", -74° 31' 52.36"	Corn	20	52	28	Silty Clay Loam	
10	Leone-Harrison	Agriculture	39° 45' 22.95", -75° 15' 52.88"	Peppers	70	20	10	Sandy Loam	Sandy. Loose
11	Coles-Elk	Agriculture	39° 40' 35.90", -75° 12' 12.55"	Fallow	78	14	8	Loamy Sand	Loose sand/Stony
12	Wood-Quinton	Agriculture	39° 33' 8.91", -75° 25' 40.95"	Soybeans	42	42	16	Loam	
13	Gershal Avenue	Agriculture	39° 28' 57.42", -75° 5' 17.37"	Wheat	82	10	8	Loamy Sand	Staging pad has caked biosolids w/ no plant life
14	Linden Pit	Reclamation	40° 28' 14.67", -74° 19' 35.67"	Native Grasses	80	6	14	Sandy Loam	Clay interspersed with sand.
15	Rustin-Groveville	Agriculture	40° 10' 12.99", -74° 37' 54.02"	Fallow	59	14	27	Sandy Clay Loam	About 3% slope
16	Shore	Recreation	39° 46' 17.93", -74° 13' 1.48"	Turfgrass	38	43	19	Loam	Pesticide flag in place. Loose sand.
17	Route 33, Freehold	Reclamation	40° 14' 8.07", -74° 15' 10.13"	Turfgrass	92	3	5	Sand	Fe_2S-rich soil
18	Airport Farm	Agriculture	39° 56' 56.15", -74° 48' 57.63"	Soybeans	70	17	13	Sandy Loam	Sandy. Loose

Table 3.2 Characteristics of the soil sample locations where only pesticides were applied.

Site No.	Location	Land Use	Geographic Coordinates Latitude (N), Longitude (W)	Current or last Crop	% Sand	% Silt	% Clay	Textural Class	Comment/ Observation
19	NJAES Rutgers Agricultural Research and Extension Center, Upper Deerfield	Agriculture	39° 31' 8.01", -75° 12' 17.56"	Soybeans	50	33	17	Loam	
19		Agriculture	39° 30' 58.57", -75° 12' 16.24"	Grapes	68	23	9	Sandy Loam	Orchard
20	Horticulture Farm III, Rutgers	Agriculture	40° 27' 43.16", -74° 25' 32.38"	Corn	32	46	22	Loam	Plowed
21	NJAES Snyder Research and Extension Farm, Pittstown	Agriculture	40° 33' 36.94", -74° 57' 5.21"	Soybeans	26	48	26	Loam	
21		Agriculture	40° 33' 36.94", -74° 57' 5.21"	Asparagus	28	48	24	Loam	Crop standing

Table 3.3 Selected chemical properties of the soil plow (0-17 cm) layer

Site No.	Location	P	K	Ca	Mg	Na	pH	CEC	SOM	EC
		---------- mg kg^{-1} ----------						meq/100g	%	S m^{-1}
1	Oxford	120	89	6400	130	20	7.9	33.4	4.4	0.3
2	Bilyck	64	161	1200	130	21	6.6	8.8	4.6	0.5
3	Hope	225	113	2400	130	23	7.2	13.5	5.4	0.3
4	Readington	63	57	5350	120	24	7.7	28.0	3.7	0.3
5	Flemington	73	63	1400	115	21	7.2	8.2	2.9	0.2
6	West Trenton	96	82	2600	110	23	7.8	14.2	3.6	0.3
7	Blawenburg	61	87	950	195	25	6.3	7.9	3.6	0.2
8	Belle Meade	14	79	1750	200	23	7.2	10.7	4.0	0.2
9	Skillmans	50	80	100	135	19	6.2	7.6	3.3	0.2
10	Leone-Harrison	501	250	650	70	17	5.3	8.1	2.0	0.4
11	Coles-Elk	284	60	750	35	16	6.7	4.3	1.9	0.2
12	Wood-Quinton	90	84	600	80	19	5.6	6.4	1.9	0.1
13	Gershal Avenue	255	31	450	55	15	5.6	4.1	1.8	0.1
14	Linden Pit	14	24	1150	40	22	7.2	6.2	1.9	0.4
15	Rustin-Groveville	30	32	5956	65	18	7.2	30.5	2.2	1.9
16	Shore	72	42	1482	158	19	6.5	10.1	2.7	0.1
17	Route 33, Freehold	17	24	260	41	15	4.3	5.4	1.8	0.1
18	Lumberton	67	21	285	48	16	4.1	11.5	2.5	0.2
19S	NJAES Rutgers Agricultural Research	190	103	971	109	15	6.6	7.3	1.8	0.1
19G	and Extension Center, Upper Deerfield	284	128	702	155	18	6.9	5.3	1.5	0.1
20C	Horticulture Farm III, Rutgers, East Brunswick	123	125	1072	157	35	6.2	8.3	2.0	0.1
21S	NJAES Snyder Research and Extension	32	103	1332	162	19	6.9	8.5	3.0	0.1
21A	Farm, Pittstown	133	120	1629	96	22	6.9	9.5	2.5	0.1

Table 3.4 Selected chemical properties of the soil subsurface (18-50 cm) layer

Site No.	Location	P	K	Ca	Mg	Na	pH	CEC	SOM	EC
		---------- mg kg^{-1} ----------						meq/100g	%	S m^{-1}
1	Oxford	9	60	1550	65	20	7.8	8.5	2.5	0.2
2	Bilyck	22	50	500	60	13	6.3	4.4	2.5	0.2
3	Hope	51	188	850	130	14	7.1	5.9	2.5	0.2
4	Readington	9	41	1500	120	23	7.8	8.7	1.8	0.2
5	Flemington	33	53	850	180	32	5.6	9.6	1.9	0.2
6	West Trenton	21	39	850	145	20	7.5	5.6	2.3	0.2
7	Blawenburg	17	61	750	265	33	5.8	8.7	1.5	0.2
8	Belle Meade	3	73	950	295	36	4.8	14.8	1.6	0.2
9	Skillmans	51	61	1050	180	26	6.7	8.2	2.3	0.2
10	Leone-Harrison	217	134	400	65	15	5.2	5.4	1.2	0.2
11	Coles-Elk	135	52	300	30	16	6.3	2.0	0.6	0.1
12	Wood-Quinton	32	72	550	165	15	6.1	5.6	1.4	0.1
13	Gershal Avenue	109	35	350	55	14	6.2	3.6	0.7	0.1
14	Linden Pit	1	18	150	25	17	4.3	1.1	0.8	0.1
15	Rustin-Groveville	4	9	436	50	11	3.3	14.5	0.7	0.6
16	Shore	86	73	1000	122	19	5.7	8.7	2.4	0.1
17	Route 33, Freehold	8	6	214	31	12	4.2	3.8	2.3	0.1
18	Lumberton	94	30	547	68	16	3.5	19.0	2.0	0.7
19S	NJAES Rutgers Agricultural Research and Extension Center, Upper Deerfield	100	87	761	150	15	6.6	5.3	1.6	0.1
19G		233	59	1033	126	17	6.6	7.6	1.0	0.1
20C	Horticulture Farm III, Rutgers, East Brunswick	18	85	1071	147	29	6.4	8.1	1.4	0.1
21S	NJAES Snyder Research and Extension Farm, Pittstown	4	49	848	216	20	5.9	7.5	1.8	0.1
21A		10	54	976	195	24	6.5	7.9	1.7	0.1

Table 3.5 Residual contaminant concentrations in soils amended with alkaline-stabilized biosolids

Site	Biosolids Application Rate	NP		NP_1EO		NP_2EO		OP		BPA	
		0-17 cm	18-50 cm	0-17 cm	18-50 cm	0-17 cm	18-50 cm	0-17 cm	18-50 cm	0-17 cm	18-50 cm
	Mg ha^{-1}	μg kg^{-1}									
1	14.8	14.6	6.60	2.39	0.74	2.49	3.89	0.94	2.57	0.27	0.17
2	9.9	4.78	4.82	1.00	0.63	1.25	0.26	1.14	0.57	0.13	0.09
3	14.8	7.35	3.48	1.72	0.56	1.69	0.16	0.66	0.64	0.24	0.07
4	14.8	14.6	3.04	1.74	0.51	4.23	0.32	1.13	0.74	0.21	0.13
5	9.9	5.80	7.07	1.26	0.80	0.67	0.19	0.70	0.89	0.07	0.04
6	11.8	6.73	2.76	1.64	0.50	2.18	0.11	0.55	0.36	0.07	0.07
7	15.8	4.62	3.92	1.72	0.70	0.34	0.12	0.80	0.50	0.24	0.03
8	11.8	4.70	3.21	0.85	0.75	0.46	0.32	0.72	0.73	0.12	0.10
9	17.7	5.87	3.89	0.81	0.74	0.39	0.20	0.59	0.26	0.03	0.19
10	9.9	2.32	1.63	0.38	0.26	0.74	1.18	0.55	0.30	0.01*	0.10
11	9.9	3.60	3.11	0.49	0.60	0.86	0.15	0.55	0.39	0.03	0.03
12	9.9	2.98	2.31	0.30	0.46	1.88	0.79	0.49	0.38	0.03	0.18
13	14.8	2.04	2.33	0.44	0.21	0.20	0.15	0.39	0.27	0.09	0.01*
14	47.5	8.74	1.74	1.14	0.25	1.24	0.12*	0.71	0.24	0.14	0.03
15	11.8	5.61	0.52	1.15	0.32	0.49	0.39	0.72	1.98	0.06	0.02
16	75.0	6.86	0.03*	1.37	0.20	1.23	0.16	0.69	0.21	0.07	0.01*
17	147.8	28.3	1.77	3.14	0.44	6.08	5.63	1.90	0.24	0.11	0.05
18	12.8	2.88	3.95	1.44	0.18	2.09	0.86	0.40	0.15	0.04	0.01
Min		2.04	0.03*	0.30	0.18	0.20	0.12*	0.39	0.15	0.01*	0.01*
Max		28.3	7.07	3.14	0.80	6.08	5.63	1.90	2.57	0.27	0.19
Mean		7.35	3.12	1.28	0.49	1.58	0.83	0.76	0.63	0.11	0.07
Median		5.71	3.08	1.21	0.50	1.24	0.23	0.70	0.38	0.08	0.06

*Detection limits

Table 3.6a Summary of paired *t*-test of means of pollutant concentrations within 2 soil depths

Pollutant	Soil Depth	Treatment 1		Treatment 2	
		Mean†	*p*-value*	Mean†	*p*-value**
NP	0-17 cm	4.92	0.0005	10.90	0.6390
	18-50 cm	2.52		15.93	
N_1PEO	0-17 cm	0.89	<0.0002	0.18	0.9304
	18-50 cm	0.39		0.17	
N_2PEO	0-17 cm	0.88	<0.0002	0.07	0.6351
	18-50 cm	0.20		0.10	
OP	0-17 cm	0.53	0.0005	1.68	0.6412
	18-50 cm	0.32		2.07	
BPA	0-17 cm	0.04	0.0279	0.31	0.4362
	18-50 cm	0.08		0.20	

†Mean is geometric mean (mean of log concentration values, converted back to concentration); units are μg kg^{-1} dry weight

* Significant at p<0.05

** Not significant at p<0.05

Table 3.6b Summary of independent *t*-test of means of pollutant concentrations between biosolids+pesticides (Treatment 1), pesticides only (Treatment 2) and control plots (Treatment 3)

Pollutant	Treatment	Mean†	*p*-value	Treatment	Mean†	*p*-value
NP	Treatment 1	3.47	<0.0002	Treatment 2	13.80	<0.0002
	Treatment3	0.76		Treatment3	0.32	
N_1PEO	Treatment 1	0.58	0.00005	Treatment 2	0.20	0.0309
	Treatment3	0.31		Treatment3	0.44	
N_2PEO	Treatment 1	0.45	0.0022	Treatment 2	0.09	0.0189
	Treatment3	0.21		Treatment3	0.23	
OP	Treatment 1	0.42	<0.0002	Treatment 2	1.47	<0.0002
	Treatment3	0.23		Treatment3	0.21	
BPA	Treatment 1	0.05	0.7150**	Treatment 2	0.26	0.4238**
	Treatment3	0.05		Treatment3	0.21	

†Mean is geometric mean (mean of log concentration values, converted back to concentration); units are μg kg^{-1} dry weight

** Not significant at p<0.05

Table 3.7 Residual contaminant concentrations in soils with pesticide application

Site	NP		NP_1EO		NP_2EO		OP		BPA	
	0-17 cm	18-50 cm	0-17 cm	18-50 cm	0-17 cm	18-50 cm	0-17 cm	18-50 cm	0-17 cm	18-50 cm
	---------- $\mu g\ kg^{-1}$ ----------									
S19	7.68	9.60	0.13	0.13	0.12*	0.12*	0.10	0.22	0.06	0.02
G19	67.9	31.7	1.76	1.79	0.26	0.22	0.68	0.44	0.99	0.43
C20	23.1	13.5	0.45	0.40	0.97	0.50	0.56	0.20	0.78	0.09
A21	12.9	13.9	0.11	0.08	0.12*	0.12*	1.56	1.20	0.47	0.43
S21	36.7	15.8	0.27	0.17	0.12*	0.28	2.39	4.89	0.60	0.13
Min	7.68	9.60	0.11	0.08	0.12*	0.12*	0.10	0.20	0.06	0.02
Max	67.86	31.65	1.76	1.79	0.97	0.50	2.39	4.89	0.99	0.43
Mean	29.65	16.89	0.54	0.51	0.32	0.25	1.06	1.39	0.58	0.22
Median	23.12	13.91	0.27	0.17	0.12	0.22	0.68	0.44	0.60	0.13

*Detection limit

Table 3.8 Residual contaminant concentrations in control soils

Site	NP		NP_1EO		NP_2EO		OP		BPA	
	0-17 cm	18-50 cm	0-17 cm	18-50 cm	0-17 cm	18-50 cm	0-17 cm	18-50 cm	0-17 cm	18-50 cm
	---------- $\mu g\ kg^{-1}$ ----------									
1	0.23	1.09	0.15	0.11	0.25	0.12*	0.50	0.25	0.10	0.01*
2	1.04	0.54	0.13	0.25	0.12*	0.12*	0.50	0.50	0.04	0.18
3	1.93	1.16	0.16	0.13	0.37	0.12*	0.61	0.22	0.02	0.01*
4	2.27	0.93	0.10	0.11	0.12*	0.49	0.18	0.25	0.01*	0.01*
5	1.54	0.89	0.14	0.23	0.30	0.29	0.27	0.15	0.2	0.48
6	0.68	0.75	0.86	0.87	0.21	0.12*	0.61	0.13	0.01*	0.01*
7	0.22	0.61	0.13	0.75	0.93	0.36	0.34	0.38	0.1	0.06
8	1.50	1.40	0.86	0.11	0.12*	0.12*	0.28	0.34	0.01*	0.01*
9	1.77	1.32	0.29	0.79	0.74	0.48	0.28	0.20	0.01*	0.01*
10	0.61	0.30	0.92	0.70	0.55	0.13	0.16	0.15	0.08	0.01*
11	0.95	0.53	0.33	0.41	0.96	0.12*	0.17	0.12	0.16	0.01*
12	1.75	0.23	0.67	0.77	1.12*	0.39	0.31	0.07	0.01*	0.10
13	0.74	0.61	0.48	0.45	0.12*	0.12*	0.68	0.18	0.01*	0.01*
14	0.51	1.38	0.11	0.53	0.39	0.24	0.23	0.19	0.01*	0.01*
15	1.52	0.77	0.10	0.83	0.46	0.14	0.26	0.26	0.01*	0.06
16	0.50	0.58	0.31	0.47	0.43	0.76	0.37	0.21	0.01*	0.01*
17	1.94	0.23	0.21	0.41	1.06	0.42	0.16	0.24	0.06	0.01*
18	0.33	0.33	0.67	0.22	0.81	0.12*	0.16	0.07	0.01*	0.01*
19	0.29	0.27	0.58	0.37	0.61	0.21	0.56	0.11	0.08	0.01*
20	0.58	0.32	0.12	0.57	0.18	0.17	0.16	0.28	0.01*	0.20
21	0.79	0.11	0.98	0.53	0.16	0.24	0.26	0.18	0.01*	0.25
Min	0.22	0.11	0.10	0.11	0.12*	0.12*	0.16	0.07	0.01*	0.01*
Max	2.27	1.40	0.98	0.87	1.11	0.76	0.68	0.50	0.17	0.48
Mean	1.03	0.68	0.40	0.46	0.48	0.25	0.34	0.21	0.05	0.07
Median	0.79	0.61	0.29	0.45	0.39	0.17	0.28	0.20	0.01*	0.01*

*Detection limits

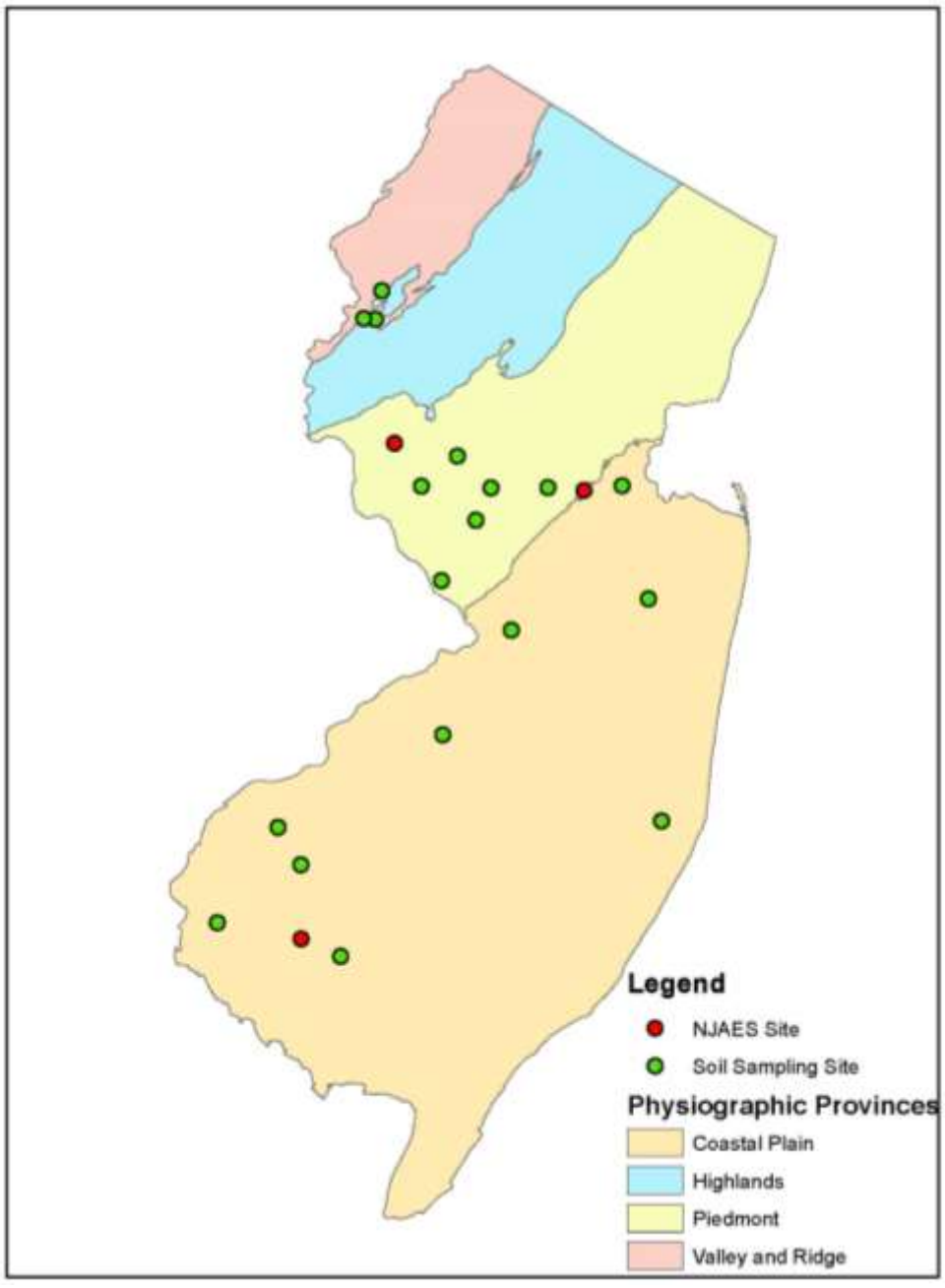

Figure 3.1 Locations of study sites

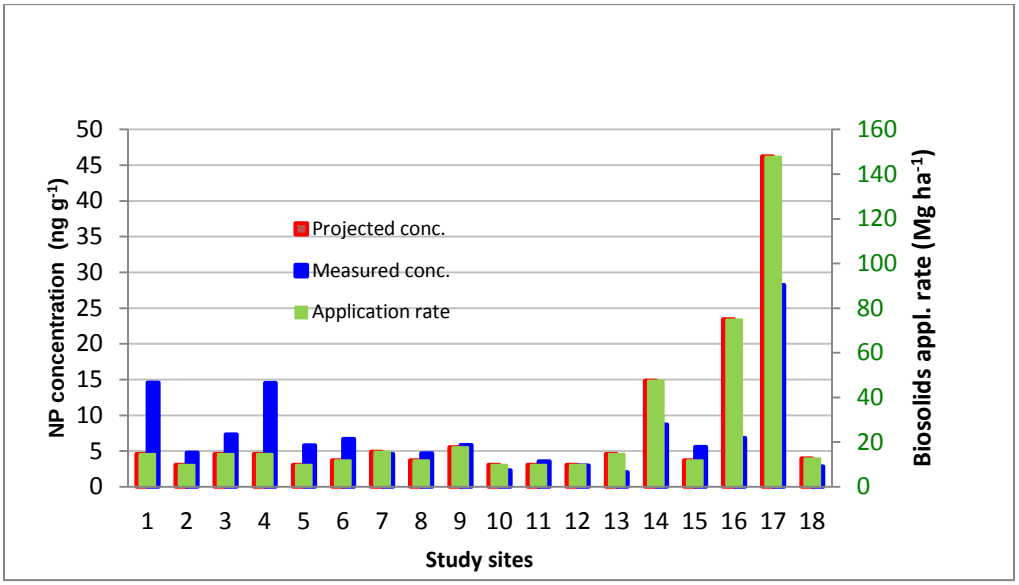

Figure 3.2 Relative proportions of nonylphenol (NP) detected in soils in comparison to projected concentrations calculated with equation 3.1 based on biosolids application rate and NP concentration in biosolids.

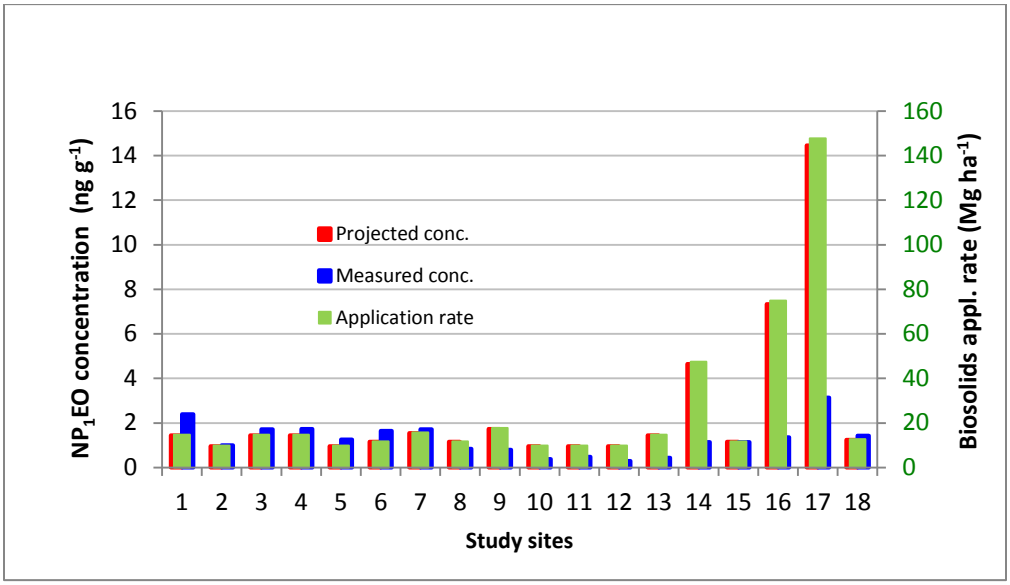

Figure 3.3 Relative proportions of nonylphenol monoethoxylate (NP_1EO) detected in soils in comparison to projected concentrations calculated with equation 3.1 based on biosolids application rate and NP concentration in biosolids.

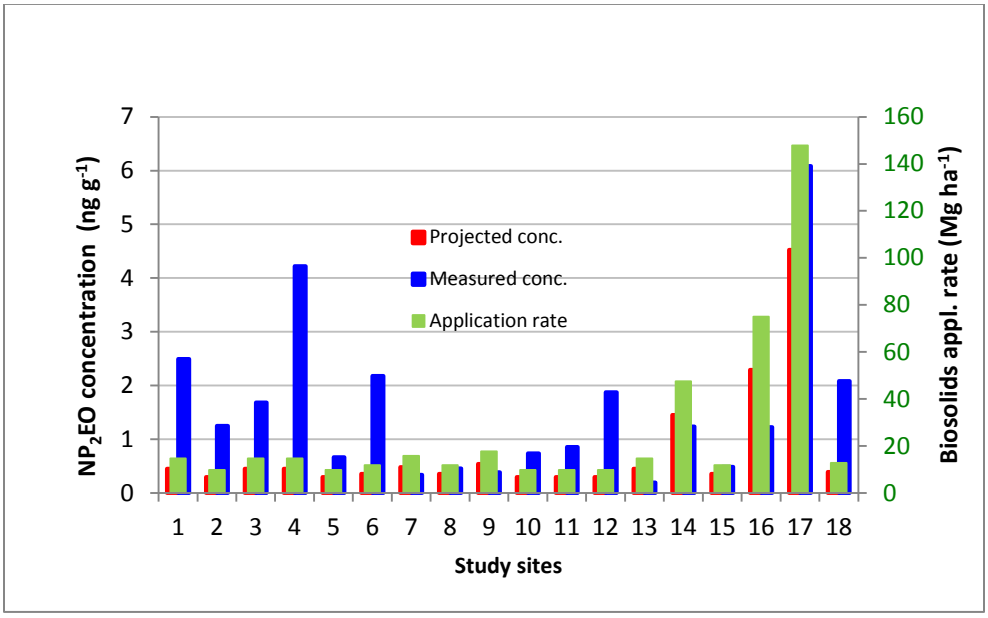

Figure 3.4 Relative proportions of nonylphenol diethoxylate (NP_2EO) detected in soils in comparison to projected concentrations calculated with equation 3.1 based on biosolids application rate and NP concentration in biosolids.

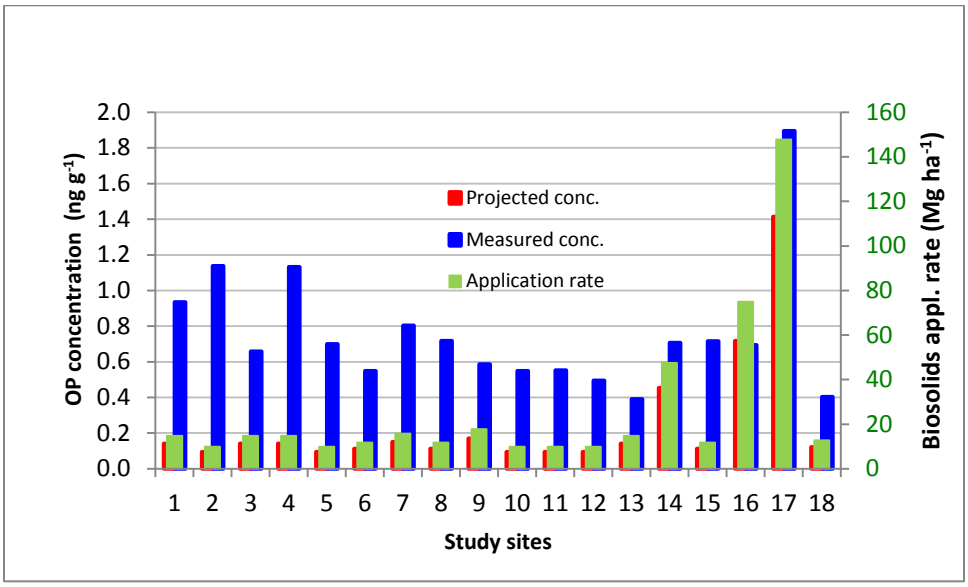

Figure 3.5 Relative proportions of octylphenol (OP) detected in soils in comparison to projected concentrations calculated with equation 3.1 based on biosolids application rate and NP concentration in biosolids.

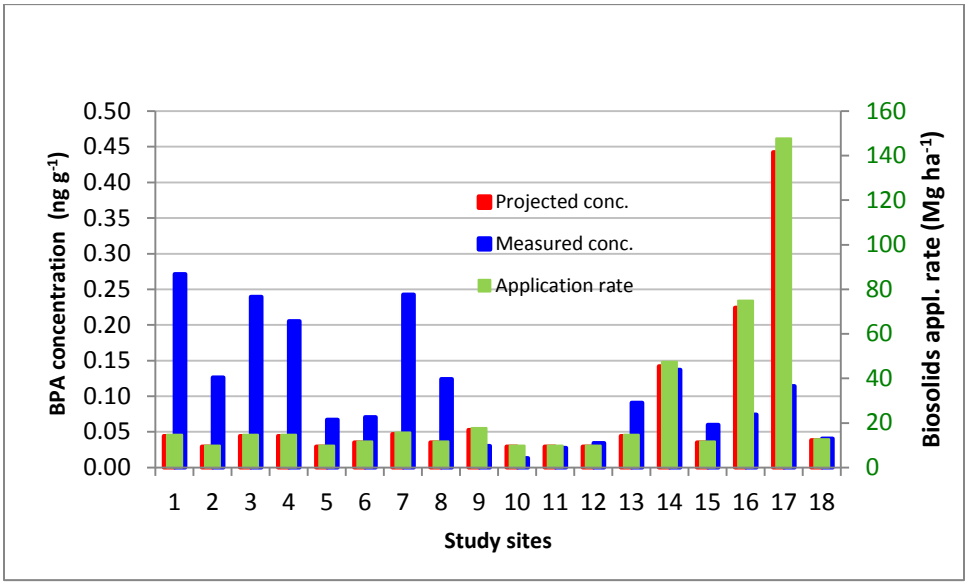

Figure 3.6 Relative proportions of bisphenol A (BPA) detected in soils in comparison to projected concentrations calculated with equation 3.1 based on biosolids application rate and NP concentration in biosolids.

CHAPTER 4

MODELING ENVIRONMENTAL CONCENTRATIONS OF NONYLPHENOLS AND BISPHENOL A IN SLUDGE, BIOSOLIDS AND BIOSOLIDS-AMENDED SOILS USING P*h*ATE MODEL

4.1 Introduction

Risk assessment is needed to understand the implications of chemical pollutants in the environment, and having an estimate of the concentrations of chemical pollutants in the environment is a necessary prerequisite. Environmental concentrations can be obtained by direct measurement, laboratory experiments, or by using predictive tools such as models. Environmental models offer the advantage of being able to provide initial quantitative assessment of impacts of environmental processes and predict concentrations of chemicals entering the environment. This could save enormous time and cost being invested in field and laboratory data collection.

Most environmental models are essentially mass balance models based on mathematical equations that reflect known processes taking place. Depending on the number of assumptions and how close they are to the real field processes they represent, models offer a reliable estimate of pollutant concentrations in the environment.

In this study, the Pharmaceutical Assessment and Transport Evaluation (P*h*ATE) model was utilized to predict the concentrations of nonylphenol and bisphenol A in wastewater, sludge (prior to treatment), biosolids (after treatment), and soil following land application of the biosolids. Presently, such modeling of the pollutant concentrations in sludge, biosolids, and biosolids-amended soils has not been reported. This is probably because actual monitoring of these pollutants in these media is possible though tedious

and time-consuming. However, modeling and monitoring are complimentary and this study presents the comparison of predicted values with actual monitoring data in the three media, and in the process shows the applicability of this model as a predictive tool that can be used to estimate the concentration of thousands of chemicals passing through the WWTP and eventually ending up in soils.

4.2 P*h*ATE Model Overview

P*h*ATE is a mass balance model that uses known physical-chemical data of the compounds along with assumptions of their behavior to calculate an estimated concentration. P*h*ATE was initially designed as a screening level model for predicting environmental concentrations of active pharmaceutical ingredient (API) in drugs entering surface water through wastewater effluent discharge (Anderson et al., 2004). During wastewater treatment, sorption and biodegradation are the key mechanisms determining the fate of organic pollutants in the waste stream. Sorption to solids and partition into biomass facilitate their transfer into the sludge, which is then removed for treatment and endpoint management such as application to soil as fertilizer. As a result of such transfer to soil and potential of exposure to pollutants through soil, the model was subsequently expanded with an additional module to predict the API in sludge, biosolids and soils amended with biosolids (Cunningham et al., 2012).

The model was developed around 12 watersheds containing 1302 WWTPs within the 48 contiguous United States. These watersheds, comprising approximately 19% of the United States land area and >14% of the U.S. population, were selected to reflect drinking water sources that are affected by WWTP effluent discharge. The spread encompasses wet and dry regions, streams with many and few WWTP, and rural and

highly populated areas (although, major metropolitan cities are not geographically included because their drinking water sources are not affected by WWTP discharges (Anderson et al., 2004).

The model has 3 modules – the surface water exposure module, the biosolids exposure module, and the human health effects module – that enable the user to generate a predicted environmental concentration (PEC) for surface and drinking water, sludge and biosolids within the WWTP, soil subsequent to land application of the biosolids, and estimate a predicted no-effect concentration (PNEC) on human health for drinking water, fish consumption, sludge, biosolids and biosolids-amended soils exposure. Detailed description of the principles, development, and operation of the model for estimating PEC in surface water has been presented by Anderson et al. (2004), and in sludge and biosolids by Cunningham et al. (2012).

P*h*ATE is a mass balance model, and uses both user-supplied and default physical, chemical and fate input data in a sequential series of calculations. The applicable user-supplied data input for the wastewater portion of this study are shown in Tables 4.1 and 4.2. Important default input data are tabulated in Tables 4.3, 4.4, 4.5 and 4.6. The output of one module is transferred into the next module; for instance, it is necessary to first run the surface water module before the biosolids module can be run. The mathematical expressions that were used in calculating various inputs and outputs have been well described by Anderson et al., (2004), Cunningham et al., (2012), and in the User's Manual (P*h*RMA, 2011).

4.3 Applicability of P*h*ATE Model to this Study

Most organic chemicals in wastewater stream can potentially be modeled using P*h*ATE if the requisite physicochemical input data is available and the main source of entry into the environment is through the POTWs since the same mechanisms affect their fate as that of an API. Similar to a pharmaceutical API, alkylphenol ethoxylates (APEOs) and bisphenol A (BPA) are ubiquitous chemicals whose primary entry into the environment is through wastewater treatment system. Previously, P*h*ATE has been used to predict chemicals other than pharmaceuticals (Anderson et al., 2004; Cunningham et al., 2012). An alkaloid stimulant (caffeine), a surfactant (linear alkylbenzene sulfonates, LAS), and an antimicrobial agent (triclosan, TCS) were used as surrogates to corroborate the model's PECs by comparison with measured environmental concentrations (MEC) available in the literature (Anderson et al., 2004; Cunningham et al., 2012). Thus it was demonstrated that P*h*ATE is directly applicable to predicting the environmental concentrations of chemicals and pollutants other than pharmaceuticals.

In the current study, the emphasis was placed on the pathway that generates PECs for NPs and BPA in sludge, biosolids and soil (i.e., biosolids module) rather than pathways that estimate PECs in surface water (rivers) and drinking water (dams), and estimates predicted no-effect concentrations (PNECs) on human health from water exposure. This was done in part because the hydrological data input required for the surface water module is not readily available.

4.4 Objectives

The objectives of this modeling exercise were to:

(1) predict the environmental concentrations of alkylphenols and bisphenol A in the WWTPs, sludge, biosolids, and soil-amended with biosolids.

(2) corroborate the predicted values with measured environmental concentrations (MECs) reported in Chapters 2 and 3 of this study; and

(3) assess the utility of the P*h*ATE model as a tool in predicting environmental concentrations of nonylphenol compounds and bisphenol A in sludge, biosolids and soils amended with biosolids.

4.5 Assumptions, Modifications and Limitations

The P*h*ATE model contains many assumptions. In this study, several assumptions were also made to streamline the complexity of the system. For example, as described in Chapter 1, commercial production of nonylphenol yields a mixture of branched nonyl chain isomers, hence separation by gas chromatography produces a cluster of peaks. As a result, a decision was made to treat NP and all substituted NP derivatives as one compound rather than individually. In addition, since the nonylphenol ethoxylates (NP_nEOs) can have as many as 50 ethoxy units (n=50), and the higher ethoxylated molecules degrade into lower ethoxylated NPEOs, modeling each of the units would be complex to near impossible as each one would be treated as a separate compound. This assumption also overcomes the unavailability of input data for each of the homologs.

A limitation was presented in sludge options. Four possible sludge treatment options were provided in the model: aerobic digestion, anaerobic digestion, composting, and no treatment. This limitation excludes many other sludge treatment processes such as alkaline stabilization, lime stabilization, thermal processes, and wet air oxidation sludge treatment. For this study, aerobic digestion was assumed.

Modification of the software to make portions of it more precise to this research work was not allowed by the Pharmaceutical Research and Manufacturers of America (P*h*RMA), however, a few changes described below were possible outside this limitation.

1. In the *Raritan watershed*, the biosolids handling option was changed from "no" to "yes" to indicate that POTW 2 applies its biosolids to soil. This change enables the model to generate PECs in soil for this POTW.
2. In the *Raritan watershed*, the population served by POTW 2 was changed from 381,803 to 750,000 to accurately reflect the POTW at the time the sample was collected.
3. Similarly, in the *Columbia watershed*, the population served by POTW 1 was changed from 28,000 to 31,600 as per the information provided by the WWTP at the time of sample collection.
4. In the "*Chemical Data*" section, under the "*Land Application Loss*" mechanism, the time interval was changed from 20 years to 10 years to align it with the time period for which MECs were obtained.
5. As a result of the change in item 4 above, the application frequency in the "*Biosolids*" tab of the data input would be "*# of applications over 10 y*" instead of "*# of applications over 20 y*".

While new chemicals can be readily added to the model, addition of new POTWs requires updating the line code of the software. Only 2 out of 14 POTWs sampled for the sludge and biosolids in Chapter 2 of this research are present in 2 watersheds in the P*h*ATE model; however they are important in that they represent both a small (3 MGD) and large (147 MGD) WWTP, and a low (31,600) and high (750,000) population service

areas. This is approximately the range of WWTP sizes in this dissertation. Therefore, only 2 watersheds containing the 2 WWTP were selected to run in the model.

4.6 Model Inputs

The data input into the model and source documentation for this study are shown in Tables 4.1 and 4.2. The fraction of the target compound removed in the WWTP is an important input that may affect the predicted environmental concentration. The literature offers various estimates of APEO removal from WWTP and different time scales for this removal (Ahel et al., 1994a; Thiele et al., 1997; Loyo-Rosales et al. 2007). This variation in removal during biological treatment may be due to factors such as the type of wastewater treatment system, sludge residence time (SRT), and hydraulic retention time (HRT). Loyo-Rosales et al. (2007) demonstrated this variation in removal rates between modified Ludzack-Ettinger, activated sludge followed by nitrification-denitrification, and nitrifying activated sludge treatment systems.

4.7 Model Calculations

Using both user-generated inputs and default values, the model used the following equations to calculate key parameters needed to produce predicted environmental concentrations (PECs):

Per capita usage:

$$U = \frac{Sales}{P_{US}} \qquad 4.1$$

where, U = average per capita usage, kg/person-yr
Sales = annual U.S. sales of the chemical, kg yr^{-1}
P_{us} = United States population

Mass Loading into the POTW:

$$M_{in} = \frac{U \times Population\ served}{365\frac{days}{yr}} \quad 4.2$$

where, M_{in} = mass loading into the POTW, kg day^{-1}

Influent Concentration:

$$C_{influent} = \frac{M_{in}}{Q \times CF_1} \quad 4.3$$

where, $C_{influent}$ = POTW influent concentration, kg L^{-1}
Q = Flow into the POTW, MGD (10^6 gal day^{-1})
CF_1 = Conversion factor, 3.78 L gal^{-1}

Concentration of pollutant in sludge (s):

$$C_{sludge\ (s)} = \frac{M_{sludge}}{S_{sludge} \times F \times CF_2} \quad 4.4$$

where, $C_{sludge(s)}$ = concentration of pollutant in the solid phase of untreated sludge, g kg^{-1}
M_{sludge} = daily mass of pollutant that is sorbed to untreated sludge, g d^{-1}
S_{sludge} = quantity of solids produced at municipal treatment plants per volume of water treated, kg m^{-3} (0.000135 for primary & 0.00022 for secondary wastewater treatment plants (Tchobanoglous & Burton in PhRMA, 2011)
F = POTW specific flow rate, m^3 day^{-1}
CF_2 = conversion factor, (3785 m^3 day^{-1})/MGD

Concentration of pollutant in sludge (aq):

$$C_{sludge(aq)} = \frac{C_{effluent} \times CF_3}{\%\ TSS} \quad 4.5$$

where, $C_{sludge(aq)}$ = concentration of pollutant in the aqueous phase of untreated sludge, g kg^{-1}
$C_{effluent}$ = POTW effluent concentration, mg L^{-1}
%TSS = Default value of 3.7 % Total Suspended

Solids in Sludge (Tchobanoglous & Burton, 1991 in PhRMA, 2011)

CF_3 = conversion factor, 1g 1000 mg^{-1}

Concentration of pollutant in sludge (total):

$$C_{sludge\ (s)} + C_{sludge(aq)} \quad 4.6$$

Concentration of pollutant in biosolids (s):

$$C_{biosolids\ (s)} = \frac{C_{sludge(s)} \times \left[e^{(-K_S \times D)}\ or\ (1-Loss)\right]}{(1-SR)} \quad 4.7$$

where, $C_{biosolids(s)}$ = concentration of pollutant in the solid phase of biosolids, g kg^{-1}

$C_{sludge(s)}$ = concentration of pollutant in the solid phase of untreated sludge, g kg^{-1}

K_s = first order loss coefficient, d^{-1} (during biosolids processing)

Loss = user-defined fixed loss of pollutant during biosolids processing (fraction)

SR = reduction in solid mass during sludge treatment; 0.38 for treated sludge

Concentration of pollutant in biosolids (aq):

$$C_{biosolids\ (aq)} = \frac{C_{effluent} \times CF_4}{\%\ TSS} \times \left[e^{(-K_S \times D)}\ or\ (1 - L_S)\right] \quad 4.8$$

where, $C_{biosolids(aq)}$ = concentration of pollutant in the aqueous phase of biosolids, g kg^{-1}

CF_4 = conversion factor, g $1000mg^{-1}$

D = assumed duration that the sludge is held during treatment (60 days)

Concentration of pollutant in biosolids (total):

$$C_{biosolids(s)} + C_{biosolids(aq)} \quad 4.9$$

Concentration in biosolids-amended soil initially (t_0):

$$C_{soil} = \frac{C_{biosolids} \times AR \times AF \times CF_5}{\rho \times d \times Y \times CF_6} \qquad 4.10$$

where,

C_{soil} = soil pollutant concentration immediately following application, mg kg^{-1}
$C_{biosolids}$ = pollutant concentration in biosolids, mg kg^{-1}
AR = application rate, Mg ha^{-1}
AF = application frequency (no. of applications), yr^{-1}
ρ = soil bulk density, kg m^{-3}
d = mixing depth, m
Y = no. of years for which PEC is being calculated, yr.
CF_5 = conversion factor, 1000 kg Mg^{-1}
CF_6 = conversion factor, 10000 m^2 ha^{-1}

In the model, predicted concentration in biosolids-amended soil was calculated based on the biosolids pollutant concentration, biosolids application rate and the number of applications (frequency), and the result evenly spread over the number of years for which soil decay is desired. The resultant value is then added each year as additional input to the previous year's decay result. This approach assumes that biosolids was applied each year, at the same rate, whereas this is not always the case as consideration is usually made for nutrient loading, and for soil pH in the case of alkaline-stabilized biosolids. In addition, this approach does not predict the desired concentration for this study where only one biosolids application occurred within a period of 10 years. Therefore, to obtain the true predicted pollutant concentrations, equation 4.10 was modified to equation 4.11, and was used in addition to equation 4.12 in calculations carried out outside the model.

$$C_{soil} = \frac{C_{biosolids} \times AR \times CF_5}{\rho \times d \times CF_6} \qquad 4.11$$

Concentration in biosolids-amended soil after 10 years (t_{10}):

$$C_t = C_o e^{-kt} \qquad 4.12$$

where, C_t = pollutant concentration in soil after time t, mg kg^{-1}
C_o = soil pollutant concentration immediately following application, mg kg^{-1}
k = first-order decay coefficient, 0.00812 day^{-1}
t = time, day (3650 days for 10 years)

4.8 Sensitivity of the model to first-order soil decay coefficient (k) values

Biodegradation of organic pollutants in soil is often described by first-order degradation kinetics (Kvestak & Ahel, 1995; Veeh et al., 1996; John et al., 2000; Roberts et al., 2006). This is understandable when it is considered that the growth of microorganisms, that are responsible for the degradation, often takes the exponential form for a period of time, and is best described by the first-order reaction rate (Chapelle, 2001). First-order is a reaction in which the rate is dependent on the initial concentration (C_o) of the substrate or reactant. A single soil decay value is not universally applicable to all soil types since it was derived for a specific soil and under different experimental conditions. It is important then to evaluate how the model will respond to different decay values in predicting soil NP and BPA concentrations.

As different half-life and decay values are reported for biodegradation studies by different authors, a range of decay values in Table 4.5 were assembled or calculated from published half-life derived from laboratory and field experiments involving NP and BPA biodegradations. To calculate *k*, equation 4.12 can be re-written as,

$$\ln C_t = \ln C_o - kt \qquad 4.13$$

$$\ln \frac{C_t}{C_o} = -kt \qquad 4.14$$

A linear plot of $\ln \frac{C}{C_o}$ against t yields a straight line with a slope of –*k*, where

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \qquad 4.15$$

and

$$t_{1/2} = \frac{0.693}{k} \qquad 4.16$$

where,

$t_{½}$ = half-life (days)
k = decay coefficient (day^{-1}).

4.9 RESULTS AND DISCUSSION

4.9.1 Sensitivity Analysis

The model's response to different k values was evaluated using a few of the decay values from Table 4.5 and the results are shown in Figures 4.1 for nonylphenol and 4.2 for bisphenol A. The analysis shows that soil accumulation of NP occurs at slow biodegradation rates (low *k* values), and it is increasingly below instrumental detection capability as biodegradation rates increases (higher *k* values). The same pattern was observed for bisphenol A, even though only two decay values found in the literature were evaluated. Using a soil decay value of 0.231 day^{-1} and the same biosolids application rates above, the model predicted no detectable bisphenol A in soil10 years after biosolids application. Overall, soil pollutant concentration decreases rapidly as the decay value gets larger.

4.9.2 Sludge and biosolids

The surface water module of the model was first run, where estimates of the target chemicals in the influent and effluent were obtained; and concentrations of the chemicals sorbed by raw sludge and biosolids (treated sludge) were calculated (Table 4.6). These concentrations were then input into the biosolids module where predicted environmental concentrations (PEC) in biosolids-amended soils (Table 4.7) were determined.

In order to properly determine the appropriate soil pollutant concentrations for this study, as opposed to the P*h*ATE calculation approach discussed above, biosolids PEC from Table 4.6 was used in calculations outside the model to produce the initial soil pollutant concentration following land-application using equation 4.11, and at the end of 10 years using equation 4.12. Decay coefficients of 0.00812 day^{-1} for nonylphenol and 0.213 day^{-1} for bisphenol A were used.

Sludge nonylphenol PECs were higher than measured environmental concentrations (MECs) for both POTW 1 and POTW 2 by a wide margin (Table 4.7 and 4.8). Over-prediction for both POTWs by the model may suggest that the assumption that pollutant loss during wastewater treatment was relatively low fixed proportion of the pollutant's mass within a POTW may not be accurate, although this assumption and the associated default value were useful to streamline the calculation in the model. Efficiency of POTWs vary as reflected by operational data such as sludge retention time (SRT), hydraulic residence time (HRT), and by performance indicators such as biochemical oxygen demand (BOD), total suspended solids (TSS), and fecal coliforms, that are routinely conducted to assess plant efficiency. In addition, higher PECs may be explained, in part, by per capita chemical concentration input into the model which assumes that the United States population consumes equal amounts of products

containing these chemicals, i.e. the concentration entering POTW 1is the same as that entering POTW 2 without provision for local or regional variation in consumption. Factors such as age demographics, urbanization, and industrialization could affect the use of products containing these chemicals such that their discharge may be concentrated in different areas or population centers than others. An illustration of this variation in consumption (hence discharge into sewer) is seen in the measured sludge bisphenol A which is 5 times higher in POTW 1 than POTW 2, although the population served and hydraulic capacity of POTW 2 is about 24 times that of POTW 1. This higher MEC may be due to wastewater discharge from a plastics manufacturing company located within the same town with POTW 1. Another real possibility is that much of the per capita use calculated does not end up in the sewer system, but is instead used (for example, in pesticide application) or disposed of (for example, as solid waste) in other ways.

Similar to the sludge, biosolids nonylphenol PECs for POTWs 1 and 2 are higher than MEC by a wide margin (Table 4.8). Most of this difference is undoubtedly because of the difference between the sludge PEC and MEC. An additional factor may be that biosolids PEC for POTW 2 is higher possibly because aerobic digestion was assumed by the model as the sludge treatment (stabilization) method whereas sludge was actually treated by alkaline stabilization. The model does not provide the alkaline stabilization treatment option. Aerobic digestion has the potential to reduce mass but concentrate pollutants present in the sludge, while alkaline stabilization has a diluting effect due to addition of alkaline material. In addition, NP concentration could potentially have been reduced during alkaline stabilization due to volatilization as a result of the high temperature generated during sludge treatment. In both sludge and biosolids, the predicted results are several orders of magnitude above the measured values.

As with nonylphenol, the model predicted higher bisphenol A concentrations in both sludge and biosolids. Sludge and biosolids PEC in POTW 1 are consistently higher than in POTW 2, although somewhat less so than was obtained for nonylphenol. As stated above, the lower BPA concentration may also be due to the low fixed loss value applied during wastewater treatment.

While biodegradation and sorption to the solid phase are the main mechanisms in operation during wastewater treatment, it appears that the model gives sorption a greater emphasis for being responsible for the removal of these pollutants from the wastewater. Photodegradation of bisphenol A in water and atmosphere, specifically by photolysis and photooxidation, has been suggested (Staples et al., 1998) but it is not known if this mechanism accounts for BPA loss in sludge. Rather than an increase in predicted BPA concentration in biosolids due to aerobic digestion, BPA concentration actually decreased in both POTWs.

4.9.2 Biosolids-amended soil

Two sets of PECs were obtained for soil amended with biosolids. First, predicted environmental concentrations were obtained for NP and BPA in soil with the assumption that there was no loss of pollutants in the intervening 10 years. Second, predicted environmental concentrations were calculated for the soil using a first- order loss equation over the same period of time. In the former scenario, concentrations of NP (13.1 – 84.8 mg kg^{-1}) and BPA (7.22 – 46.6 mg kg^{-1}) were predicted in the topsoil as a result of one-time biosolids application to soil (Table 4.7). These concentrations might not be a true depiction of the reality in biotic environments, but it gives an indication of the worst case situation if the chemicals were to be resistant to biodegradation, or immobilized

within soil. In this case, these concentrations might be of concern from the standpoint of soil erosion, which could serve as a source of surface water pollution. However, bisphenol A may not be as high as predicted since it is readily biodegraded in soil; its continual presence in the soil is as a result of recurring use rather than from un-degraded residue (Fent et al., 2003; Flint et al., 2012). In addition, the values obtained for conserving the pollutants in soil without loss also represents the initial soil concentrations following land application of the biosolids.

Since these pollutants are rarely preserved in soil without loss, but rather their losses are usually described by first-order reaction kinetics, the second scenario may be a better indicator of expected soil concentrations. When decay was applied, the soil NP concentrations were depleted within 4 years of application, whereas soil BPA concentrations were below detection by the end of the first year. This difference is due mainly to the rate of decay or biodegradability. At the end of 10 years, the predicted environmental concentrations (Table 4.7) for both pollutants are virtually beyond any instrumental detection (2.77×10^{-12} to 1.02×10^{-11} mg kg^{-1} soil NP, and 1.02×10^{-35} to zero soil BPA). These PECs suggest that NPs and BPA are readily biodegradable in soil environments. Table 4.9 show comparisons of predicted and measured concentrations for biosolids-amended soils. For both compounds, the predicted concentrations are considerably lower than the measured environmental concentrations (MECs) of NP (5.9 – 18.5 mg kg^{-1}) and BPA (0.07 to 0.13 mg kg^{-1}) reported in Chapter 3. Models as predictive tools may under- or over-predict actual environmental values, but it is expected that most agricultural practices that utilize biosolids as a source of inexpensive fertilizer will apply biosolids more than once over a 10-year period, which would produce a higher predicted concentration than obtained here.

Also, as discussed in Chapter 3, there are additional sources of introduction into the environment, especially agricultural soils, that are not accounted for by the model since it considers POTW as the main source. In addition, actual per capita input may be higher than assumed in the model, and the values assigned to certain model inputs may be higher than they are in the field. However, biological degradation was not sufficient to eliminate all the NP and BPA, as low levels were detected through environmental monitoring. One explanation would be that biodegradation did not occur at the predicted rates

The observations between the PEC and MEC in this study are unlike the observations of Anderson et al. (2002) and Cunningham et al. (2012) in the development of the P*h*ATE model. In corroboration studies using compounds other than active pharmaceutical ingredients (API), PECs were compared with MECs published in the literature for triclosan (TCS) and linear alkylbenzene sulfonates (LAS) in sludge and biosolids, and for caffeine, TCS and LAS in surface waters (Anderson et al., 2004). An agreement of PEC and MEC within one to four orders of magnitude was considered a successful corroboration. This performance criterion was met for NP and, and sometimes BPA for sludge and biosolids in this study, but not for soil. The long (10-year) time interval being modeled probably added to this problem. If a shorter window of time, as in many experiments, was being considered, a closer agreement could have been possible.

While verification of model predictions like these is necessary, Oreskes et al. (1994) have argued that verification and validation of numerical models in earth sciences are not possible except in closed systems. They reasoned that to verify implies that the truth about the model has been established, and to validate implies that the model does not contain known or detectable flaws. Although PhATE is an attempt to simulate the actual processes taking place in the field, it under-predicts the soil concentrations while it

over-predicts the sludge and biosolids concentrations. This may be because sorption was given undeservedly more weight than biodegradation during the wastewater portion of the model, and biodegradation was weighted more than sorption in the soil portion of the model. Apart from the corroboration of the model prediction performed by the developers, it would have been much more satisfactory to perform a statistical comparison in this study, but sufficient PECs and MECs were not available. Nevertheless, the experimental data from Chapters 2 and 3 show that the assumptions and inputs into the model need to be refined to obtain a more successful corroboration.

4.10 CONCLUSIONS

Modeling of environmental processes and compartments is complimentary to direct monitoring of actual processes. When monitoring data is not available, or direct monitoring is not possible, modeling provides a quick and less expensive approach to examining the question at hand. As a result of default assumptions built into the model, it was assumed that sorption is the dominant mechanism affecting the fate of nonylphenol and bisphenol A in wastewater treatment, and sludge and biosolids processing, while biodegradation is the predominant mechanism controlling the fate of NP and BPA in the soil. As such, the predicted and measured environmental concentrations obtained did not yield a good comparison. Predicted NP and BPA concentrations by the P*h*ATE model are higher for sludge and biosolids, and lower for soil by several orders of magnitude compared to measured concentrations. This level of performance means that the model's ability to predict environmental concentrations of NP compounds and BPA in wastewater, sludge, biosolids and soils that are amended with biosolids is not yet as reliable as it is for the pharmaceutical compounds for which it was developed.

Future development of the model is needed to improve the accuracy of sludge and biosolids PECs, and increase its applicability to sludge and biosolids treatment. Currently, the model recognizes aerobic, anaerobic and composting methods of sludge treatment to the exclusion of others, such as alkaline stabilization, thermal treatment methods, and other methods used in *Process to Significantly Reduce Pathogens* (PSRP).

In addition, if all the 14 POTWs could have been modeled, there would have been more data for statistical comparison with a more robust conclusion, and a better comparative analysis all the 14 POTWs studied in Chapter 3 would have shown the effect of different sludge treatment or stabilization methods on the estimated concentrations or PECs. This is a potential exercise for the future. In the current work being reported, the model enabled comparison of PECs between a small and large POTWs, and suggests that the trace MECs obtained provide a better assessment of these environmental pollutants.

With more specific input values and refinement, the P*h*ATE model could be used to predict concentrations of NP and BPA, and potentially many chemicals, in wastewater treatment plants and in sludge, biosolids, and soils amended with those biosolids. This capability will be useful to determine potential threat or lack thereof in these media before time-consuming and expensive field sampling and analysis campaigns are embarked upon.

4.11 LITERATURE CITED

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Table 4.1 Model inputs for nonylphenols (chemical ID 151)

Parameter	Input value	Reference	Comment
Mass of nonylphenol (kg yr^{-1})	1.306344 x 10^{8}	Chemical Market Reporter (2007)	80% of USA demand[1] is used in detergent production.
US population	305529237		P*h*ATE default value
Per capita use (kg person-yr^{-1})	0.4275676		Calculated by P*h*ATE
Water solubility	4.9	Brix et al. (2001)	
Log K_{ow}	4.48	Ahel & Giger (1993)	
K_d (L kg^{-1})	22000 (10000-33000)	John et al. (2000)	
Henry's coefficient, (atm-m^{-3} $mole^{-1}$)	3.4 x 10^{-5}	MSDS	
Biodegradation rate, k (day^{-1})	0.00812	Jacobsen et al. (2004)	
Biodegradation rate, k (hr^{-1})	0.19488		Calculated from Jacobsen et al., (2004)
Distribution coefficient, Log D_{ow}	4.48		Estimated from Log K_{ow} by model
Bioconcentration factor	300 (280-320)	Thiele et al. (1997)	
Removal from aqueous phase in primary trmt.	0	Loyo-Rosales et al. (2007)	
Removal from aqueous phase in primary & secondary treatments	0.42	Loyo-Rosales et al. (2007)	
Fraction of solids adsorbed to primary sludge	0.19	Loyo-Rosales et al. (2007)	
Fraction of solids adsorbed to secondary sludge	0.42	Loyo-Rosales et al. (2007)	

[1] "Demand" is the sum of domestic production and import.

Table 4.2 Model inputs for bisphenol A (chemical ID 152)

Parameter	Input value	Reference	Comment
Mass bisphenol A (kg yr^{-1})	9.7×10^{8}	ICIS Chemical Business (2011)	
US population	305529237		P*h*ATE default value
Per capita use (kg person-yr^{-1})	3.174818		Calculated by P*h*ATE
Water solubility, mg L^{-1})	120-300	Howard (1989)	
Log K_{ow}	3.3	Howard (1989)	
K_d (L kg^{-1})			
Henry's coefficient, (atm-m^{-3} $mole^{-1}$)	1×10^{-10}	Howard (1989)	
pKa	9.6	Kosky et al.(1991)	
Biodegradation rate, k (hr^{-1})	0.154	Cousins et al., (2002)	Calculated from Cousins et al., (2002)
Distribution coefficient, Log D_{ow}	3.3		Estimated from Log K_{ow} by model
Bioconcentration factor	196	Howard (1989)	Calculated from log K_{ow}
Removal from aqueous phase in primary trmt.	0.329		Calculated by SimpleTreat v.3.1 (Struijs et al., 1991; Struijs , 1996)
Removal from aqueous phase in primary & secondary treatments	0.596		
Fraction of solids adsorbed to primary sludge	0.013		
Fraction of solids adsorbed to secondary sludge	0.013		

Table 4.3 Publicly-owned treatment works (POTW) input specific to the two facilities in this study

POTW	Watershed ID	Treatment Type	Population Served	Flow Rate (MGD)§	Sludge Handling ID
1	10 -- Columbia	6 – Advanced I	31600	5.6	2, Aerobic
2	12 -- Raritan	5 -- Secondary	750000	147	2, Aerobic

§ Million gallons per day. Expressed as MGD in the wastewater industry.

Table 4.4 Land use inputs into the model to generate PECs for biosolids-amended soils

Parameter	Type	Application Rate (Mg ha^{-1} dry wt.)	Frequency (application/10yr.)	Mixing Depth (cm)	Bulk Density (kg m^{-3})
Land Use	Agricultural	12.7	1	15	1400
	Reclamation	74	1	15	1400
	Recreational	18	1	15	1400

Table 4.5 Published NP and BPA half-life and decay (*k*) values in soil calculated from laboratory and field experiments

Compound	**Half-life, $t_{½}$ (Reported)**	**Decay (Reported)**	**Decay (Calculated from half-life)**	**Reference**	**Source of data**
	(day)	(day^{-1})	(day^{-1})		
NP	37	0.00812	-	Jacobsen et al., 2004	Lysimeter study
NP	4.5-16.7	-	0.154-0.0415	Topp & Starratt, 2000	Laboratory
NP	2.5-35	-	0.2772-0.0198	Kvestak & Ahel, 1995	Laboratory
NP	7.3-9.8	-	0.0949-0.0707	Gejlsbergs et al., 2001	Laboratory
NP	10.6	-	0.0654	Gejlsbergs et al., 2001	Laboratory
NP	1.4-10.6	-	0.495-0.0654	Roberts et al., 2006	Laboratory
NP	1-3	-	0.693-0.231 (at low NP conc.)	Roberts et al., 2006	Laboratory
NP	10-42	-	0.0693-0.0165 (at high NP conc.)	Roberts et al., 2006	Laboratory
NP	3-6	-	0.231-0.1155	Hesselsøe et al., 2001	Laboratory
NP	5-6	-	0.1386-0.1155	Hesselsøe et al., 2001	Laboratory
NP	4.6	-	0.1507	Ying & Kookana, 2005	Laboratory
BPA	3	-	0.231	Fent et al., 2003	Laboratory
BPA	7	-	0.099	Ying & Kookana, 2005	Laboratory

Table 4.6 Predicted NP (Chemical ID 151) and BPA (Chemical ID 152) concentrations in sludge and biosolids

*

						---------- POTW ----------				---------- Sludge (pre-stabilization) ----------				---------- Biosolids (post-stabilization) ----------			
POTW	Sludge Handling Type Id	Trmt. Type Id	Chem Id	Pop. Served	Flow Rate	Influent Mass	Influent Conc.	Effluent Conc.	Effluent Mass	Mass API Sorbed	Conc API Sorbed (solid phase)	Conc API Sorbed (aq. Phase)	Conc API Sorbed (total)	Mass API in Biosolids (solid phase)	Conc API Biosolids (solid phase)	Conc API Biosolids (aq. Phase)	Conc API Biosolids (total)
					MGD	kg d^{-1}	mg L^{-1}	mg L^{-1}	kg d^{-1}	kg d^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	kg d^{-1}	mg kg^{-1}	mg Kg^{-1}	mg kg^{-1}
1	2	6	151	31600	5.6	32.8	1.55	1.36	28.9	6.89	1477	36.81	1514	6.898	2383	22.70	2406
1	2	6	152	31600	5.6	274.9	12.97	5.24	111.0	3.58	766.2	141.6	907.8	3.57	1236	87.31	1323
2	2	5	151	750000	147	778.7	1.40	0.57	319.3	163.5	1336	15.51	1351	163.5	2154	9.56	2164
2	2	5	152	750000	147	6524	11.72	4.74	2636	84.8	692.8	128.0	820.8	84.8	1117	78.9	1196

Table 4.7 Predicted NP and BPA concentrations in soil 10 years after biosolids application

POTW	Chemical	Land Use Type	Application Rate (Mg ha^{-1} dry wt.)	Biosolids Concentration (mg kg^{-1})	Soil Conc. assuming no loss (mg kg^{-1})	Soil Conc. assuming first order loss (mg kg^{-1})
1	Nonylphenol	Agricultural	12.7	2406	14.5	1.95×10^{-12}
		Reclamation	74		84.8	2.77×10^{-12}
		Recreational	18		20.6	1.14×10^{-11}
	Bisphenol A	Agricultural	12.7	1323	7.99	0
		Reclamation	74		46.6	0
		Recreational	18		11.3	0
2	Nonylphenol	Agricultural	12.7	2164	13.1	1.76×10^{-12}
		Reclamation	74		76.3	2.49×10^{-12}
		Recreational	18		18.5	1.02×10^{-11}
	Bisphenol A	Agricultural	12.7	1196	7.22	0
		Reclamation	74		42.2	0
		Recreational	18		10.3	0

Table 4.8 Comparison of the predicted and measured NP and BPA concentrations in sludge and biosolids

POTW	Chemical	Sludge		Biosolids		Sludge	Biosolids
		Predicted Environmental Concentration (mg kg^{-1})	Measured Environmental Concentration (mg kg^{-1})	Predicted Environmental Concentration (mg kg^{-1})	Measured Environmental Concentration (mg kg^{-1})	Ratio of Predicted/Measured	
1	Nonylphenol	1514	16.4	2405	42.0	92.3	57.3
	Bisphenol A	907.8	0.42	1323	0.09	2161	14700
2	Nonylphenol	1351	6.73	2164	0.71	201	3048
	Bisphenol A	820.8	0.14	1196	0.04	5863	29900

Table 4.9 Comparison of the predicted and measured NP and BPA concentrations in biosolids-amended soil*

POTW	Chemical	Agricultural		Recreation		Reclamation	
		Predicted (mg kg^{-1})	Measured (mg kg^{-1})	Predicted (mg kg^{-1})	Measured (mg kg^{-1})	Predicted (mg kg^{-1})	Measured (mg kg^{-1})
1	NP	1.95×10^{-12}	-	2.77×10^{-12}	-	1.14×10^{-11}	-
	BPA	0	-	0	-	0	-
2	NP	1.76×10^{-12}	5.9	2.49×10^{-12}	6.86	1.02×10^{-11}	18.5
	BPA	0	0.11	0	0.07	0	0.13

*18 fields that were land-applied with biosolids from POTW 2 were sampled and analyzed.

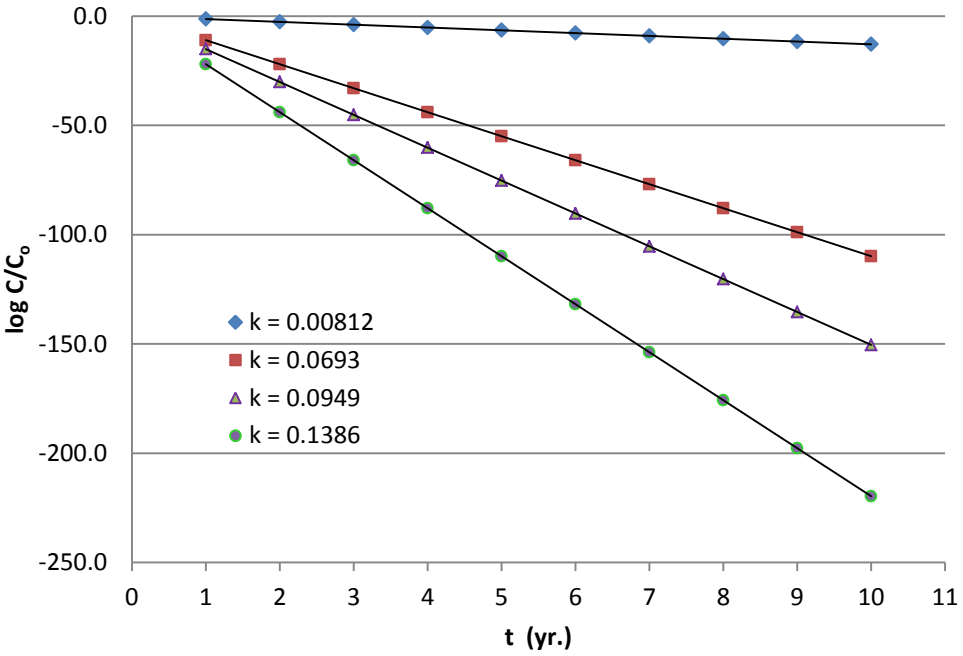

Figure 4.1 P*h*ATE model's response to selected soil decay (*k*) values from Table 4.5 for nonylphenol in biosolids-amended soils

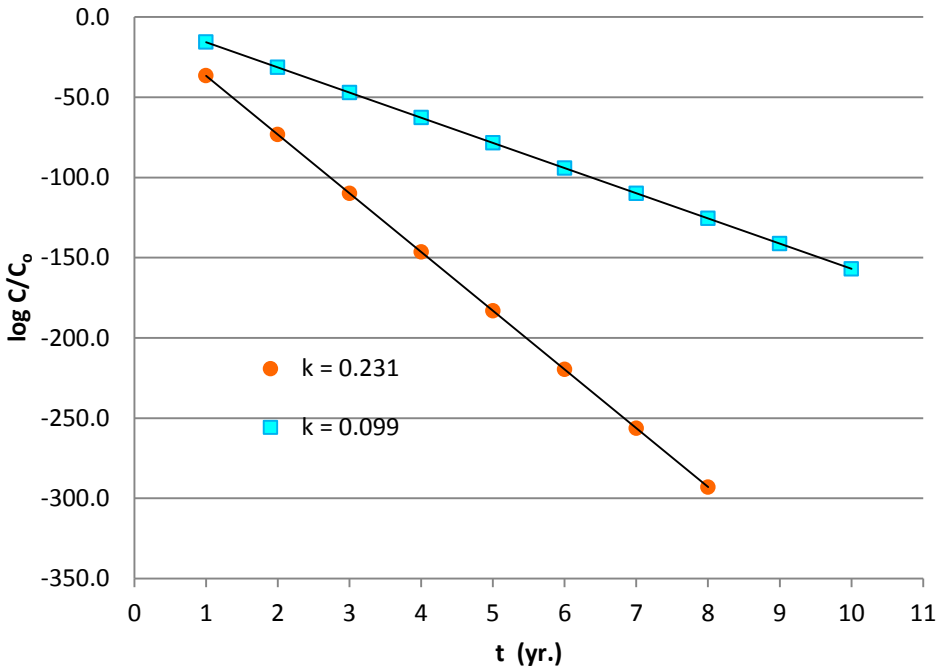

Figure 4.2 P*h*ATE model's response to selected soil decay (*k*) values from Table 4.5 for bisphenol A in biosolids-amended soils

APPENDICES

APPENDIX A

Retention Times, Quantitation Ions for Alkylphenol Ethoxylates and Bisphenol A

Parameter	Retention Time (min.)	Primary Ion	Secondary Ions
Acenaphthene-d_{10}†	14.63	164	140
Octylphenol	16.14	135	107, 91
Nonylphenol (NP)			
Isomer Group 1	17.25	121	107, 163, 220
Isomer Group 2	17.35	135	107, 121, 220
Isomer Group 3	17.46	149	135, 107, 220
Isomer Group 4	17.53	149	121, 220
Isomer Group 5	17.59	135	121, 107, 220
Isomer Group 6	17.70	149	121, 107, 220
Isomer Group 7	17.80	135	107, 163, 220
Isomer Group 8	17.81	149	121, 107, 220
Isomer Group 9	17.86	163	121, 107, 220
Isomer Group 10	17.90	135	107, 149, 220
Isomer Group 11	17.94	149	107, 212, 220
Isomer Group 12	18.01	135	149, 107, 220
Phenanthrene-d_{10}†	18.37	188	94, 160
4-n-Nonylphenol*	19.18	107	135, 220
Nonylphenol Monoethoxylate (NP_1EO)			
Isomer Group 1	20.06	165	207, 221, 264
Isomer Group 2	20.18	179	135, 107, 264
Isomer Group 3	20.26	179	193,107, 264
Isomer Group 4	20.28	179	193, 165, 264
Isomer Group 5	20.39	179	193, 165, 264
Isomer Group 6	20.52	179	207, 135, 264
Isomer Group 7	20.57	193	179, 221, 264
Isomer Group 8	20.65	207	165, 107, 264
Isomer Group 9	20.70	179	135, 193, 264
Isomer Group 10	20.82	193	179, 107, 264
4-n-Nonylphenol Monoethoxylate*	21.97	107	151, 264, 91
Bisphenol A	22.40	213	228, 119
Nonylphenol Diethoxylate (NP_2EO)			
Isomer Group 1	22.88	241	265, 209, 308
Isomer Group 2	23.03	223	135, 308
Isomer Group 3	23.08	237	223, 279, 308
Isomer Group 4	23.15	223	135, 237, 308
Isomer Group 5	23.22	233	135, 237, 308
Isomer Group 6	23.31	237	209, 279, 308
Isomer Group 7	23.36	237	223, 265, 308
Isomer Group 8	23.42	251	237, 223, 308
Isomer Group 9	23.49	223	135, 308
Isomer Group 10	23.61	237	223, 149, 308
4-n-Nonylphenol Diethoxylate*	24.63	107	195, 220, 308

† Internal Standard

* Surrogate

APPENDIX B

List of pesticides applied to the NJAES plots sampled for this study

Site	Crop	Pesticide Class	Brand	Application Rate (per acre)*
19G	Grapes	Herbicide	Prowl	3 qts
			Rely	3 qts.
		Fungicide	Captan80	4 lb/acre
			Pristine	10 oz.
			Rovral	1 pt.
		Insecticide	Assail	3 oz.
			Danitol	16 oz.
19S	Soybeans	Herbicide	Roundup	1 quart
			Lorox	1 lb.
			Dual mag	1 pt.
20	Corn	Herbicide	Lexar	2.75 qts
		Insecticide	Lambda-Cy AG Gold	6oz
21A	Asparagus	Herbicide	Glyphosate plus	2.5 qts
21S	Soybeans	Herbicide	Glyphosate plus	1 gal
			Solicam 80 DF	5 lbs
			Karmex DF	2 lbs
			Sandea DF	1 lb
		Insecticide	Sevin XLR Plus	1.5 qts.
		Surfactant	Surf 9010 nonionic surfactant	4 fl oz/100gal
		Herbicide	Glyphosate Plus	4 fl oz./gal

* Application frequency not known.

APPENDIX C

Calculation of surfactant concentration in field-applied pesticides assuming 0.25% and 1% surfactant concentration in the spray tank as per Green (1999)[§]

Location	Crop	Trade Name	Type of Pesticide	Active Ingredient	Pesticide Application Rate (per acre)		Surfactant Application Rate 0.25%	1%		Conc of Surfactant in soil @ 0.25%	@ 1%	
NJAES Pittstown	Soybean & Asparagus	Glyphosate Plus	Herbicide	Glyphosate 41%	1	gal/acre	0.0237	0.0946	L ha^{-1}	**11.19**	**44.75**	**µg/kg**
		Glyphosate Plus	Herbicide	Glyphosate 41%	2.5	Qt/acre	0.0148	0.0592	L ha^{-1}	**6.99**	**27.97**	**µg/kg**
		Glyphosate Plus	Herbicide	Glyphosate 41%	4	fl. oz/gal	0.0002	0.0008	L ha^{-1}	**0.09**	**0.37**	**µg/kg**
		Suf 9210	Surfactant	Alkyl & alkylaryl polyoxyethylene glycol 90%	4	fl. oz/100gal						
		Suf 9210	Surfactant	Alkyl & alkylaryl polyoxyethylene glycol 90%	1	Qt/100gal						
		Solicam 80 DF	Herbicide	Norflurazon 78.6%	5	Qt/acre	0.0296	0.1183	L ha^{-1}	**13.99**	**55.95**	**µg/kg**
		Karmex DF	Herbicide	Diuron 80%	2	lb/acre	0.0057	0.0227	kg ha^{-1}	**2.83**	**11.31**	**µg/kg**
		Sandea DF	Herbicide	Halosulfuron-Methyl 75%	1	oz	0.0002	0.0007	L ha^{-1}	**0.09**	**0.35**	**µg/kg**
		Sevin XLR Plus	Insecticide	Carbaryl 44.1%	1.5	Qt	0.0089	0.0355	L ha^{-1}	**4.20**	**16.78**	**µg/kg**
		Malathion	Insecticide	Malathion 56%	2	pints	0.0059	0.0237	L ha^{-1}	**2.80**	**11.19**	**µg/kg**
		Banvel	Herbicide	Dimethylamine salt of Dicamba 48.2%	1	pint	0.0030	0.0118	L ha^{-1}	**1.40**	**5.59**	**µg/kg**
		Stinger	Herbicide	Clopyralid 40.9%	10	fl. oz	0.0018	0.0074	L ha^{-1}	**0.87**	**3.50**	**µg/kg**

APPENDIX C CONTINUED

Location	Crop	Trade Name	Type of Pesticide	Active Ingredient	Pesticide Application Rate (per acre)		Surfactant Application Rate 0.25%	1%		**Conc of Surfactant in soil @ 0.25%**	**@ 1%**	
NJAES Deerfield	Grapes	Prowl H_2O	Herbicide		3	Qt	0.0177	0.0710	L ha^{-1}	**8.39**	**33.57**	**µg/kg**
		Rely	Herbicide		3	Qt	0.0177	0.0710	L ha^{-1}	**8.39**	**33.57**	**µg/kg**
		Captan 80	Fungicide		4	lb	0.0114	0.0455	kg ha^{-1}	**5.66**	**22.63**	**µg/kg**
		Pristine	Fungicide		10	oz	0.0018	0.0074	L ha^{-1}	**0.87**	**3.50**	**µg/kg**
		Rovral	Fungicide		1	pint	0.0030	0.0118	L ha^{-1}	**1.40**	**5.59**	**µg/kg**
		Assail	Insecticide		3	oz	0.0006	0.0022	L ha^{-1}	**0.26**	**1.05**	**µg/kg**
		Danitol	Insecticide		16	oz	0.0030	0.0118	L ha^{-1}	**1.40**	**5.59**	**µg/kg**
	Soybeans	Round-up	Herbicide		1	Qt	0.0059	0.0237	L ha^{-1}	**2.80**	**11.19**	**µg/kg**
		Lorox	Herbicide		1	lb	0.00284	0.0114	kg ha^{-1}	**1.41**	**5.66**	**µg/kg**
		Dual mag	Herbicide		1	pint	0.0030	0.0118	L ha^{-1}	**1.40**	**5.59**	**µg/kg**
NJAES East Brunswick	Corn	Lexar	Herbicide		2.8	Qt	0.0163	0.0651	L ha^{-1}	**7.69**	**30.77**	**µg/kg**
		Lambda-Cy AG Gold	Insecticide		6	oz	0.0011	0.0044	L ha^{-1}	**0.52**	**2.10**	**µg/kg**

[§]Green, J. M. 1999. Effect of nonylphenol ethoxylation on the biological activity of three herbicides with different water solubilities. Weed Technol. 13(4):840-842.

Mass of 1 acre-furrow slice

Area — 1 acre = 43560 ft^2

Plow layer = 0.5 ft

Volume — 1 acre = 43560 ft^2 x 0.5 ft = 21780 ft^3

Soil particle density — 1.3 g/cc = 62.43 lb/ft^3

Mass (dry) of soil — 1 acre = 21780 ft^3/acre x 63.43 lb/ ft^3 = 1767643.02 lb/acre

1767643.02 lb/acre = 803,474.1kg

2.2 lb/kg

1 hectare = 803474.1 kg x 2.5 acre/hectare = 2,008,685.3 kg