3-23-2015

Emergence and Fate of Siloxanes in Waste Streams: Release Mechanisms, Partitioning and Persistence in Three Environmental Compartments

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DOI: 10.25148/etd.FI15032134

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

EMERGENCE AND FATE OF SILOXANES IN WASTE STREAMS: RELEASE
MECHANISMS, PARTITIONING AND PERSISTENCE IN THREE
ENVIRONMENTAL COMPARTMENTS

A dissertation submitted in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

in

CIVIL ENGINEERING

by

Sharon Czarina Surita

2015

To: Dean Amir Mirmiran
College of Engineering & Computing

This dissertation, written by Sharon Czarina Surita, and entitled Emergence and Fate of Siloxanes in Waste Streams: Release Mechanisms, Partitioning and Persistence in Three Environmental Compartments, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Florida International University, 2014

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DEDICATION

I dedicate this dissertation to my husband, son and mother. Without their patience, understanding, support, and love the completion of this work would not have been possible.

ACKNOWLEDGMENTS

This dissertation would not have been completed without the support of numerous people. I wish to thank the members of my committee, Dr. Shonali Laha, Dr. Krishnaswamy Jayachandran, Dr. Omar Abdul-Aziz, Dr. Walter Tang and Dr. Berrin Tansel, as well as Dr. Fuentes, the Associate Chair of the Department for their support, patience, and insight. Their gentle, but firm direction has been most appreciated. Dr. Berrin Tansel, as my academic advisor, was particularly helpful in guiding me toward a comprehensive understanding of research methodologies. I would also like to thank Dr. Tansel for having confidence in my abilities to excel in my studies and propel me towards publication of several papers in high-impact journals and providing me with the opportunity to participate in significant research endeavors such as evaluating fate and transport mechanisms of siloxanes in the environment.

I would like to thank the Hinkley Center for Solid and Hazardous Waste Management of University of Florida, Gainesville, Florida for providing funding for research, sampling and analytical procedures. I also would like to acknowledge and thank Florida International University for financial support provided by the FIU Graduate School Dissertation Year Fellowship and allowing me the opportunity to focus exclusively on my research.

I thankfully acknowledge the contribution of many individuals involved in field sampling and analysis. Mr. Myers and staff at the South Florida Water Management District, Rodney Sasina, Collin Douglas and Jorge Fernandez provided immeasurable help in sample collection. Dr. Yusuf Emirov's help with micro-analysis was very instrumental in my research. Technical Advisory Group (TAG) members including,

Manny Moncholi, Tarek Abichou, and Wieland Uchdorf offered intellectual guidance to continue the flow of research efforts.

My coursework throughout the Curriculum and Instruction program equipped me with the tools to explore and decipher present issues and predict future trends in my subject area.

Finally, I would like to thank my husband, Kenneth for his support and encouragement and my ever-cheerful son, Xavier who gives me happiness and has been a blessing in my life.

ABSTRACT OF THE DISSERTATION

EMERGENCE AND FATE OF SILOXANES IN WASTE STREAMS: RELEASE
MECHANISMS, PARTITIONING AND PERSISTENCE IN THREE
ENVIRONMENTAL COMPARTMENTS

by

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Florida International University, 2015

Miami, Florida

Professor Berrin Tansel, Major Professor

Siloxanes are widely used in personal care and industrial products due to their low surface tension, thermal stability, antimicrobial and hydrophobic properties, among other characteristics. Volatile methyl siloxanes (VMS) have been detected both in landfill gas and biogas from anaerobic digesters at wastewater treatment plants. As a result, they are released to gas phase during waste decomposition and wastewater treatment. During transformation processes of digester or landfill gas to energy, siloxanes are converted to silicon oxides, leaving abrasive deposits on engine components. These deposits cause increased maintenance costs and in some cases complete engine overhauls become necessary.

The objectives of this study were to compare the VMS types and levels present in biogas generated in the anaerobic digesters and landfills and evaluate the energetics of siloxane transformations under anaerobic conditions. Siloxane emissions, resulting from disposal of silicone-based materials, are expected to increase by 29% within the next 10 years. Estimated concentrations and the risk factors of exposure to siloxanes were

evaluated based on the initial concentrations, partitioning characteristics and persistence. It was determined that D4 has the highest risk factor associated to bioaccumulation in liquid and solid phase, whereas D5 was highest in gas phase. Additionally, as siloxanes are combusted, the particle size range causes them to be potentially hazardous to human health. When inhaled, they may affix onto the alveoli of the lungs and may lead to development of silicosis. Siloxane-based COD-loading was evaluated and determined to be an insignificant factor concerning COD limits in wastewater.

Removal of siloxane compounds is recommended prior to land application of biosolids or combustion of biogas. A comparison of estimated costs was made between maintenance practices for removal of siloxane deposits and installation/operation of fixed-bed carbon absorption systems. In the majority of cases, the installation of fixed-bed adsorption systems would not be a feasible option for the sole purpose of siloxane removal. However they may be utilized to remove additional compounds simultaneously.

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ABBREVIATIONS AND ACRONYMS

acfm	actual cubic feet per minute
AD	Anaerobic digester
BOD	Biochemical oxygen demand
C&D	Construction and demolition
Conc	Concentration
CHP	Combined heat and power
COD	Chemical oxygen demand
CMAR	Carcinogenic, mutagenic, astmagenic or reproductive
CWNS	Clean Watersheds Needs Survey
DMSD	Dimethylsilanediol
D2	Hexamethyldisiloxane
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
D6	Dodecamethylcyclohexasiloxane
EDS	Energy dispersive spectroscopy
EPA	Environmental Protection Agency
FBCAS	Fixed bed carbon adsorption system
FDEP	Florida Department of Environmental Protection
GC	Gas chromatograph
GHG	Greenhouse gas
GWh	Gigawatt hour
L2	Hexamethyldisiloxane

L3	Octamethyltrisiloxane
L4	Decamethyltetrasiloxane
L5	Dodecamethylpentasiloxane
LF	Landfill
LFG	Landfill Gas
LMOP	Landfill Methane Outreach Program
MDL	Minimum detection limit
MS	Mass Spectrometry
MSW	Municipal solid waste
POTW _s	Publicly owned treatment works
SDLF	South Dade landfill
SDWWTP	South District wastewater treatment plant
scfm	standard cubic feet per minute
SEM	Scanning electron microscopy
SiO ₂	Silicon dioxide
ThOD	Theoretical oxygen demand
TMS	Trimethylsilanol
TMSOH	Trimethylsilanol
VMS	Volatile methyl siloxanes
WAS	Waste activated sludge
WM	Waste management
WRRF	Water resource recovery facilities
WWTP	Wastewater treatment plant

SYMBOLS

C	Concentration in water phase (mg/L)
C_A	Total adsorber system equipment cost
C_C	Cost of carbon contained within system
C_i	Concentration of species i (mg/L)
C_v	Cost of carbon vessel
dC_i	change in concentration of species i
DEC	delivered equipment cost
G	Concentration in gas phase (mg/L)
G_{MSW}	Per capita generation of MSW (3.18 kg/day)
H	Henry's constant (atm-m ³ /mole)
H^*	Dimensionless Henry's constant
F_{MSW}	Fraction of siloxane present in MSW (% w/w)
f_{oc}	Fraction of organic carbon (assumed 0.2 for soil, 0.8 for sludge)
F_{WW}	Concentration of siloxane in wastewater (mg/L)
γ_i	rate of conversion of species i (mg/L-d)
G_{WW}	Per capita generation of wastewater (378.54 liters/day)
k	reaction rate constant (d ⁻¹)
K_{AW}	air-water partition coefficient
K_{OA}	Octanol-air partition coefficient
K_{oc}	Organic carbon partition coefficient (L/Kg)
K_{OW}	Octanol-water partition coefficient
K_p	Soil water partition coefficient (L/Kg)

K_{SW}	Partition coefficient (ratio of concentration in biosolids to liquid phase)
kPa	kilopascal
MGD	million gallons per day
MW	megawatt
μm	microgram
μm	micrometer
N_T	number of carbon vessels
P	number of patents filed (as discussed in Section 2)
P_b	Atmospheric pressure – barometer (PSIA)
ppb	parts per billion
ppmV	parts per million by volume
ppbV	parts per billion by volume
P_S	Standard pressure (PSIA)
PSS	percent of silicone present per sector (i.e., paper, C&D)
PSW_s	projected silicone waste per sector in a given year (tons)
PV_a	Saturated vapor pressure of water at actual temperature (PSI)
PV_s	Saturated vapor pressure of water at standard temperature (PSI)
Q	flue gas flow, acfm
R_a	Actual pressure (PSIA)
R_c	ratio of total adsorber equipment cost to cost of vessels and carbon
RH_a	Actual relative humidity
RH_s	Standard relative humidity
S	surface area of contact for carbon vessel

scfm	standard cubic feet per minute
SiOC	Silicon-Oxygen-Carbon
S_p	Siloxane projection (g/ca-day)
SP	total annual silicone production (236,000 tons)
T	Temperature (K)
T_a	Actual temperature ($^{\circ}\text{R}$)
T_s	Standard temperature ($^{\circ}\text{R}$), where $^{\circ}\text{R} = ^{\circ}\text{F} + 460$
TIC	total installed equipment costs
w/w	weight basis
X	Concentration in soil phase (mg/Kg)

1. Introduction

The increasing demand for energy and dependency on fossil fuels has created opportunities for renewable energy sources. Regions with high potential for bioenergy production (i.e., from waste materials) have implemented programs and facilities to utilize the bioenergy (Blaschke et al., 2013). It has been estimated that by the year 2050, half of the world energy demand in developing countries will stem from improved biomass energy (Demirbas, 2008).

Biogas is generated from landfills and wastewater treatment plants (WWTPs) during the step-wise degradation process when microorganisms decompose the organic material under anaerobic conditions (Demirbas, 2008). The reuse of biogas eliminates much of the greenhouse gas emissions from landfills and can be further upgraded for pipeline use.

Siloxanes are widely used in personal care and industrial applications due to their soft texture, low surface tension, antimicrobial and hydrophobic properties, among other characteristics. They may be found largely in construction and automotive materials as a water-repelling, anti-abrasive coating as well as cosmetics because of their ability to spread easily and carry/release active ingredients (van Egmond et al., 2012). As a result of their extensive use, they are disposed of in both landfills and wastewater treatment facilities where they partition into the different phases (air, water and solids). During waste decomposition, siloxanes concentrations have been noted to have increasing trends.

Despite the reduction in greenhouse gas (GHG) emission, the presence of siloxanes is causing concern among landfill gas operators (Sevimoglu and Tansel, 2013). Deposits of silicon dioxide have been reported on engine components due to the combustion process that allows for utilization of biogas to energy (Surita and Tansel, 2014a; Naja et al, 2011; Arnold and Kajolinna, 2010). Once released, the transformation of siloxanes may expand diffusion and partitioning among phases (i.e., water, soil, sediments).

This dissertation will focus on various components of the transfer mechanisms of siloxanes from patent to decomposition. Paper one (**Chapter 2**) entitled “Siloxanes in MSW: Historical and projected trends in waste fractions with increasing siloxane use evaluates the trends in patent applications for silicon based products and increasing use of siloxane in consumer products. The fractions of silicone in the products and estimated degradation times were utilized to estimate siloxane release quantities from landfills The study assumes two scenario under the assumption of 5 % and 15% increases in silicone containing products within 10 years and 25 years respectively. Decompositional lag time variations in paper products and construction debris were accounted for.

Paper two published in Environmental Toxicology and Pharmacology, (**Chapter 3**) entitled “Oxidation of siloxanes during biogas combustion and nanotoxicity of Si-based particles released to the atmosphere” estimates siloxane particle size ranges post-combustion. Particle sizes are expected to range from 50 to 100 nm. Once released to the environment, nanoparticles interact with the environment and change in surface properties. Potential health impacts of SiO₂ from siloxanes in biogas generated from waste management facilities were accessed. Potential health risks associated with the

inhalation of Si-based nanoparticles were evaluated based on nanotoxicity studies available.

Chapter 4 presents a “Characterization of deposits forming during combustion of biogas from anaerobic digesters and landfill gas” as published in Renewable Energy. The objective of this study was to compare and contrast the composition of deposits collected from facilities in Florida, USA. Morphological characteristics and elemental composition of samples were analyzed using scanning electron microscopy and energy dispersive spectroscopy. Samples from both biogas and landfill gas were analyzed to determine if differences among the two exist with respect to combustion deposits forming.

The **5th chapter** evaluates persistence profiles and release mechanisms of two cyclic siloxanes are evaluated as presented in a paper entitled “Emergence and fate of cyclic volatile polydimethylsiloxanes (D4, D5) in municipal waste streams: Release mechanisms, partitioning and persistence in air, water, soil and sediments” (published in Science of the Total Environment. Analyses were conducted based on fate and transport mechanisms after siloxanes enter the waste stream. Due to individual compound characteristics of high volatility, the majority of D4 and D5 compounds are expected to end up in the biogas during decomposition. D5 is approximately 10 times more likely to partition into biosolids and have approximately 15 to 18 times higher concentrations in wastewater influent and biogas respectively as compared to D4 siloxanes.

Persistence and fate of specific siloxane compounds is further evaluated in **Chapter 6** in a paper titled “A Multiphase Analysis of Partitioning and Hazard Index Characteristics of Siloxanes in Biosolids” (published in Ecotoxicology and

Environmental Safety. The previous paper discussed in chapter 5 addressed persistence profiles for only D4 and D5 siloxanes, whereas this paper addresses the persistence, fate and transport mechanisms of the siloxanes consistently found at the study site, Miami-Dade County's South District Wastewater Treatment Plant. These compounds consisted of L3, D3, D4, D5 and D6. Based on initial concentrations, reaction rates and partitioning characteristics, hazards potential for these siloxanes was investigated and it was determined that D4 poses the highest hazard potential in liquid and biosolids whereas D6 posed highest risk in gas phase.

Chemical Oxygen Demand (COD) loading as a resulting from the presence of siloxanes in the wastewater industries is investigated in **Chapter 7**. The research paper, published in Chemosphere, entitled "Contribution of siloxanes to COD loading at wastewater treatment plants: Phase transfer, removal, and fate at different treatment units" uncovers the relationship between initial concentrations and COD along the treatment train. The fate and removal of selected cyclic siloxanes (D4, D5 and D6) is evaluated to determine removal efficiencies within each unit. Contributions of the siloxanes present in the influent and effluent were estimated with respect to COD levels based on their theoretical oxygen demand.

Finally, **Chapter 8** investigates manual maintenance practices related to siloxane removal and comparing costs associated with manual removal to costs of adsorption system installation and operating costs. This preliminary investigation aims to establish a range of biogas generation to which installation of carbon adsorption systems would become cost efficient. Further research is necessary to specify removal efficiency for

target compounds and would become instrumental for design aspects in both wastewater treatment systems and landfills utilizing biogas for energy and the synergistic effects of a myriad of contaminants in the waste stream.

A side study focusing on removal or treatment systems is found in the **Appendix**. The short technical report titled “Evaluation of a Full-Scale Water-Based Scrubber for Removing Siloxanes from Digester Gas: A Case Study” briefly discusses the efficiency of the scrubbing system for siloxane removal. Trimethylsilanol (TMSOH), Octamethyltrisiloxane (L3), Hexamethylcyclotrisiloxane (D3), Octamethylcyclotetrasiloxane (D4), Decamethylcyclopentasiloxane (D5), and Dodecamethylcyclohexasiloxane (D6) were detected in the digester gas. D4 and D5 were present at the highest concentrations, 5000 and 1800 $\mu\text{g}/\text{m}^3$, respectively. Sampling results have indicated that scrubbers employed for hydrogen sulfide (H_2S) removal at the facility do not provide effective removal of siloxanes due to their high Henry’s Constant and low water solubility. Post scrubber treatment is needed to remove siloxanes from the digester gas prior to combustion.

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2. Siloxanes in MSW: Historical and projected trends in waste fractions with increasing siloxane use

2.1 Introduction

Commercial applications of nanoparticles are primarily developed from silicon, carbon transition metals and metal oxides (Tansel and Surita, 2014). Silicon was discovered during investigation of reduction processes of potassium fluorosilicate with potassium by Berzelius in 1824 (Colas and Curtis, 2006). The first silicon organic compound was synthesized in 1863. Organosilicon chemistry flourished during the period from 1901 to 1930s when different types of silanes were synthesized. In the following decade, commercial materials were made available, when Dow Corning verified thermal stability and electrical resistance of resins made from silicone (Colas and Curtis, 2006). Between the period of 1947 through 1950, silicone fluids and resins were developed; expanding the product range into antifoaming agents, surface coatings and textile impregnates for stain resistance (Wacker, 2013).

Silicones (also known as polymerized siloxanes or polysiloxanes) are polymeric compounds which silicon atoms as well as carbon, hydrogen, oxygen atoms. Silicones can also include other elements. Because the silicon is larger than the carbon atom, it can form bonds that are longer and flexible with wider bond angles. Therefore, silicone type polymers have flexible molecular structures and can form longer chains while maintaining their flexibility in comparison to organic polymers. Because of their flexibility, they are able to align more effectively at interfaces, allowing them to coat the surfaces. Siloxanes contain alternating silicon and oxygen atoms with organic groups

attached to the silicon atom. Because of their flexibility, siloxane chains can vary in their configurations.

Siloxanes are used in many industries including electronics, automotive industry, textiles, construction, medical equipment, food industry, medicine and cosmetics, because of their antimicrobial properties, hydrophobicity and biocompatibility (Colas and Curtis, 2006).). These compounds come in two structural configurations, linear (denoted by an L or M nomenclature) and cyclic (denoted by D). The trends in patent application for silicone-based materials show an exponential increase for siloxane use in consumer products (**Fig. 2.1**). Silicone use in consumer products impacts the carbon footprint by allowing for improved energy efficiency and reduction of raw materials consumption. Specifically, their use in the automotive industry, construction and solar-energy has significantly reduced greenhouse gas (GHG) emissions. For every kg of CO₂ used in manufacturing and disposal of silicones, nine times less greenhouse gasses are generated due to post-production energy saving technologies and sustainability via reduced water use, product life and energy consumption (Brandt et al., 2012). Products containing silicon have yielded decreased GHG of approximately 54 million tons of CO₂ (Brandt et al., 2012). Despite the reduction in GHG emission, the presence of siloxanes is causing concern among landfill gas operators (Sevimoglu and Tansel, 2013). Deposits of silicon dioxide have been reported on engine components due to the combustion process that allows for utilization of biogas to energy (Surita and Tansel, 2014a; Naja et al., 2011; Arnold and Kajolinna, 2010).

The objectives of this study were to evaluate the use of siloxanes in materials and estimate the projected siloxane content in municipal solid waste (MSW) based on the

trends in patent applications for silicone based materials and siloxane use in consumer products. MSW trends were developed using the historical data for different MSW fractions. The silicone-containing waste products were categorized into five sectors. The analyses showed that the two most prevalent waste fractions with high silicone content are paper/paperboard and construction (wood) materials. The fractions of silicone per silicone-containing product were used as a basis for comparing generation of silicone to the siloxane releases projected from landfills.

Fig. 2.1 Historical silicon patents (Google Patents, 2014: 1957 – 2013)

Trend analysis MSW was undertaken for the United States for years between 1960 and current. The categories representing the highest composition of waste in landfills included paper/paperboard, food waste, wood, total metals, plastics, textiles, and rubber/leather as noted in **Fig. 2.2** Paper and paperboard use has decreased in recent years due to prevalent use of computers and internet; however this category substantiates a bulk of waste products in landfills even today due to slow degradation. The average composition of wastes over the study period of 1960 – 2012 is illustrated in **Fig. 2.3** and highlights the primary categories of consumer wastes found in municipal solid waste. Of these categories, siloxanes are found extensively in paper/paperboard, textiles, wood (construction) and food waste.

Food waste decomposes relatively quickly in comparison to paper, textile and wood. Additionally siloxane application in textiles has only recently been implemented. Although plastics disposal in the waste stream has increased, the quantity of silicone-based material utilized in its manufacture is minimal (Brandt et al., 2012) Therefore this study will focus on the paper/paperboard and construction (wood) industries.

Fig. 2.2 Categories and composition of waste products in U.S. landfills (United States Environmental Protection Agency (USEPA, 2014)).

Fig. 2.3 Average composition of MSW over the study period of 1960 – 2012 (USEPA, 2014)

In the United States, siloxane sales reached 236,000 tons in 2009 (Oxford Economics, 2010). The number of cumulative patents from that time period was 169. As such, a factor of total tons per patent was undertaken (approximately 1,397 tons per patent per year). Assuming the current trend of the end-of-life analysis over Europe, North America and Japan remains the same, approximately 30.9 % of silicone-containing products are used in construction industry primarily as exterior coatings. Currently, the amount of silicone used in paper industry is relatively small (1.5%) (Brandt et al., 2012). However; because relative quantity of the paper products in waste streams are large and the product use life time is relatively small, siloxanes utilized in the paper industry will have significant impact on the quantities of siloxanes entering the landfills and the anticipated levels of siloxanes in landfill gas.

According to the Florida Department of Environmental Protection (FDEP), the management practices for the municipal waste fractions in Florida, USA, primarily involve landfill disposal and recycling (2012). Based on the data provided by FDEP (2012), it was assumed that approximately 61% of construction waste is disposed in landfills and 39% is recycled (**Table 1**). Similarly, for the paper industry, an average of 72% waste is disposed in landfills and 28% is recycled. This includes corrugated cardboard, newspapers and office paper.

Table 2.1 Waste management practices used for paper products and construction and demolition wastes (FDEP, 2012).

Waste Management Practice	Paper Products (% w/w)	Construction& Demolition (% w/w)
Disposal	71.8	60.5
Recycled	28.2	39.5
Total	100	100

2.2. Methodology

2.2.1 Silicone trend analysis

The patent applications for silicone containing products were evaluated in relation to the year of publication of the patent in the patent directory (Google patents, 2014). The number of silicone related patents over time was estimated by regression analysis (Fig. 2.1). The trends of cumulative number of patents filed were estimated using three different growth models described below.

Model 1: Exponential growth

$$P = 2 \times 10^{-60} \cdot e^{0.0711x} \quad (1)$$

where,

P : total number of patents;
 x : year (i.e., 2012)

However the saturation growth curve is expected to be a better fit for patent filing rates and is suggestive of a smooth transition from exponential growth to steady-state.

While patent generation continues to increase, the resistance to further patent development is expected to concurrently increase. As such, equation 2 can be used to estimate the patent generation rate.

Model 2: Saturated growth

$$P = P_u(1 - e^{-kt}) \quad (2)$$

where,

P_u : ultimate patent generation count (assumed at 550 patents)
 k : patent rate constant
 t : time since patent generation began (1957; $t = 0$)

The patent rate constant (k) was calculated under the assumption that patent generation is finite. The maximum patent yield corresponds to the inflection point of the logistic curve, therefore, equation 3 can be used to estimate the patent rate constant where t_d is equivalent to the length of time to reach the half the maximum patent yield (assumed at 250 patents, approximately equivalent to 55 years).

$$k = \ln 2/t_d \quad (3)$$

Observing the stability of patent development from 1957 until 1980, the model was revised to include the lag time before notable growth occurs. The corrected saturated

growth curve expressed in equation 4 incorporates the lag time (t^*) as 23 years based on the number of patent filings since the first silicone patents filed.

Model 3: Corrected saturated growth

Since there was a lag in the number of silicon patent filings after the first silicon patent filing, the saturated growth model was modified to account for the lag time as follows:

$$P = P_u(1 - e^{-k(t-t^*)}) \quad (4)$$

where,

t^* : lag time (years).

Analysis of data showed that a t^* value of 23 years was adequate to describe the trend of cumulative silicone patents.

2.2.2 Justification of sector alignment

A study covering silicon production, use and end-of-life analysis over Europe, North America and Japan was used as a framework for consolidating waste categories and for alignment purposes (Brandt et al., 2012) as indicated in **Table 2.2**. The divided sectors included construction, electronics, industrial, personal and transportation as sectors A through E respectively. Silicone use as illustrated in **Fig. 2.4** in electronics (57%) and transportation sectors (7%) are anticipated to have long life-spans and therefore were not considered in waste assessment projection for the time period of this study. Personal care products that are primarily discarded in wastewater stream with minor amounts of waste being landfilled as residual amounts left within containers (i.e., shampoo bottles, creams, make-up containers). Therefore, the category of personal care

products are excluded from the analyses due to their relatively small contribution to siloxane levels in landfills.

The primary landfilled waste components include paper/paperboard, wood, food waste, and textiles; therefore the sectors aligned with these components that are evaluated in this study. **Table 2.3** provides silicone use in the two critical sectors utilizing silicone containing products (Brandt et al., 2012). The primary sectors include Sector A, which represents construction (wood); and Sector C, which represents the paper (paper/paperboard). Construction and demolition (C&D) waste comprises a substantial amount of total US landfilled waste and is commonly buried in segregated landfills. With segregation, moisture, nutrients and seed, bacteria are reduced thereby creating an environment with slower decomposition rates (Barlaz, 2006).

Based on the current practices, paper and wood (construction) industries are the two areas where silicone-based materials are used extensively. There has been a significant decrease in paper products in MSW. Construction wood has increased slightly but remained between the range of 5 and 10 percent of the waste composition during the past 25 years.

Table 2.2 Consolidated Waste categories for alignment

Industry	Category	Products/applications
Construction	Sector A	sealants, water repellents, insulation
Electronics	Sector B	insulation, cooling liquid, isolators, chlorosilane
Industrial	Sector C	antifoaming, coatings, additives, adhesion
Personal	Sector D	antifoaming, application
Transportation	Sector E	rubber in motor construction coatings and bonding

Fig. 2.4 Distribution of silicone use in industrial applications (Brandt et al., 2012).

Table 2.3 Silicone use in construction and other industrial applications (Brandt et al., 2012)

Industry	Products/application	Production (tons/yr)	Silicone content (%)	Silicone in product (tons/yr)
Construction	Sealants kitchen/bathroom	79.4	90	71.5
	Sealants windows IG unit	56.7	90	51.0
	Sealants expansion joints	38.9	45	17.5
	High quality sealants and adhesives	10.1	45	4.5
	Masonry water repellent concrete	2.5	100	2.5
	Masonry water repellent bricks	10.1	100	10.1
	PU additives for thermal insulation	9.3	100	9.3
Miscellaneous industrial use	Anti-foaming in paper production	10.2	20	2.0
	Paint additives	1.9	100	1.9
	Silanes for glass fiber coating	1.9	100	1.9
	Heat resistant industrial coatings	3.2	100	3.2
	Adhesion promoter for coatings	1.9	100	1.9

2.2.3 Municipal waste degradation

Wastes products entering landfills degrade at different rates. In a lysimeter study conducted by Martin et al. (1997), simulated waste was composed of food and paper waste at 44.2 and 55.8%, respectively. Biogas production followed week 19 of the study after methane concentrations began to rise and steadily increased until week 40, where the production was maintained steady until week 51.

In regards to wood degradation, Ximenes et al. (2007) demonstrated that prior laboratory research study overestimated the decomposition of wood products in landfills. With optimum moisture content ranging from 40 to 70 percent, excavated samples from the study showed no visible deterioration of the majority of the wood recovered after 19 to 46 years. According to Jang and Townsend (2003), C&D waste is composed primarily of wood (33.2%) concrete (29.2%), roofing shingles (13.7%), drywall (12.4%) and cardboard (8.0%). Siloxanes and silanes are the most common penetrating sealers used in the construction industry.

Fig. 2.5 illustrates the fate and estimated decomposition times for paper and C&D wastes as well as estimated release times of siloxanes during decomposition. Despite the extended degradation times of paper and wood products, siloxane volatilization happens rather quickly because of its application to surfaces. In landfills, the most common siloxanes detected are octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), hexamethyldisiloxane (L2) and trimethylsilanol (TMS) (Rasi et al., 2010; Sevimoglu and Tansel, 2013; Surita and Tansel, 2014a). The composition of gas from MSW landfills is indicative of the siloxane compounds used in the paper/paperboard industry and coatings used in construction materials.

Assuming first order kinetics, D4 and D5 are estimated to degrade by 90 percent within 37 and 23 days, respectively (Surita and Tansel, 2014b). Dow Corning (1999) has specified a general lifetime of volatile methylsiloxanes (VMS) to be within the range of 10 to 30 days. No biodegradation data were found pertaining to L2; however, it has been noted that they are resistant to biodegradation (Pubchem, 2005). Degradation of D4 has been estimated to vary from 49 to 588 days at temperatures of 5 to 25 degrees Celsius (Wang, 2012). Pierce (2005) determined that siloxane concentrations decreased with waste age exponentially. The highest levels were estimated to be present 5 years after landfilling and decreasing by about 90 % during the 10 year period after landfilling (i.e., waste age of 10 years). Due to the high volatility of siloxanes, they are released from the wastes prior to decomposition of the wastes in the landfills. As presents in Fig. 2.5, the siloxane release is likely to occur with the 0.5-10 years for paper products and with the 5 to 35 years for C&D wastes.

2.2.4 Silicone-containing waste projections

The projected silicone-containing waste per sector in a given year is estimated as the product of annual silicone production, the percent of silicone use per sector (i.e. paper, construction) and number of patents, estimated from corrected saturated growth curve (Model 3), as follows:

$$PSW_s = SPF \cdot PSS \cdot P \quad (5)$$

where:

- PSW_s : projected silicone waste per sector in a given year (tons)
- SPF : total annual silicone production factor (1,397 tons/patent)
- PSS : percent of silicone present per sector (i.e., paper, C&D)
- P : number of patents filed (estimated by Equation 4)

Fig. 2.5 Life expectancy of silicon-containing products from product manufacture to product decomposition

2.3 Results

Based on the saturated growth rate curve, patent generation rates will tend to decrease while cumulative patent counts increase as indicated in the methodology (Model 3). Although the exponential growth model fits the current patent generation trend, saturation is anticipated at approximately 550 patents (doubling rate at 55 year, growth rate constant approximately 0.0126). Since the saturation growth curve fits the predicted trend (t-test; p-value = 0.7237, α = 0.05), indicating a resistance to future patent development, the model was adjusted for the lag time in conceptual patents. **Fig. 2.6** provides an illustration of the models leading to the use of Model 3 for cumulative patents incorporating a lag time of 23 years prior to consistent growth. The figure identifies the actual cumulative patents developed beginning in 1957 and culminating in 2013. Although model 3 underestimates the three most current years, the covariance is not significant (R^2 =0.87).

Table 2.4 presents the estimated disposal of silicone containing wastes from the paper/paperboard and C&D industries. Assumptions for growth during the 23-year time span were made consistent with the actual patents generated during this time period to correct for negative values that resulted from utilizing the corrected saturated growth model. Uncertainties related to assumptions were accounted for by using conservative values for estimates of silicone-containing waste materials disposed of in the landfill.

Fig. 2.6 Cumulative patents observed from 1957 to 2013 and prediction models for exponential and saturated growth curves.

Table 2.4 Estimated and predicted silicone use quantities in paper/paperboard and C&D industries.

Year	Paper and Paperboard (tons/year)	Construction waste (tons/year)
1960	168	3,452
1970	293	6,041
1980	356	7,336
1990	973	20,040
2000	2,222	45,768
2010	3,323	68,451
2020	4,294	88,447
2030	5,149	106,076
2040	5,904	121,617
2050	6,569	135,318

With an average 1 year lag time on paper/paperboard industry and a 30 year lag time for construction materials prior to disposal, the amount of wastes containing siloxane has been estimated. Siloxane releases based on the estimated 5% and 15% release scenarios are presented in **Fig.2.7**. These projections indicate that the siloxane content of landfill gas is likely to increase by 29% during the next 10 years and by 78% during the next 25 years based on the assumption that 5% of the siloxanes entering the landfills will partition to the landfill gas. Fig. 7 compares for the scenarios corresponding to 5% and 15% release of siloxanes into the gas phase from wastes originating from paper/paperboard products and construction (wood) activities.

Fig. 2.7 Projected siloxane release quantities based on the trends of silicone patents and siloxane use in consumer products assuming 5 and 15 percent of siloxane is released as VMS during MSW decomposition at landfills: a) MSW originating from paper/paperboard products, b) MSW originating from construction (wood) related activities.

2.4 Conclusions

The projected siloxane quantities in MSW were estimated based on the use of siloxane-based materials in consumer products, trends in historical MSW composition, as well as trends in patent applications for silicone-based inventions (i.e., chemicals, products). Exponential growth has been observed from inception of silicone patents in 1957 to current however, the logistic growth curve was adapted as a more feasible model.

The primary sectors with the highest silicone content include the paper and construction industries. The fractions of silicone per silicone-containing product were used as the basis for comparing the use of silicone and siloxanes based materials, in order to project the amounts of siloxane releases from landfills during decomposition of waste products. Based on the historical trends, it is estimated that the quantities of siloxanes entering landfills will increase by approximately 29 % in conjunction with a 5% increase in silicone containing products within next 10 years and 78 % within the next 25 years. These percentages were estimated by taking into account the lag time between the use and decomposition of consumer products. The lag times used were one year for the paper/paperboard industry and a 30 year lag time for the construction materials.

Acknowledgments

Partial funding for this research has been provided by Hinkley Center for Solid and Hazardous Waste Management of University of Florida as well as the Florida International University Graduate School Dissertation Year Fellowship.

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3. Oxidation of siloxanes during biogas combustion and nanotoxicity of Si-based particles released to the atmosphere (published in *Environmental Toxicology and Pharmacology*)

3.1 Introduction

Nanotoxicity is a newly recognized area of toxicology which primarily involves exposure by inhalation of nanoparticles. There are limited studies addressing the risks and toxicity of nanoparticles for human health and environmental impacts. Nanotoxicity studies have gained interest after the increasing interest in nanotechnology (NSF and USEPA, 2003; Dreher, 2004). The relatively high potential for toxic effects of nanofibers and the general importance of nanoparticle geometry for toxic effects has been compared to those with asbestos (Biskos and Schmidt-Ott, 2012). Nanoparticles with large aspect ratios (e.g., carbon nanotubes) have been shown to cause asbestos-like effects (Poland et al., 2008). Most nanoparticles used in commercial applications are developed from transition metals, silicon, carbon and metal oxides (Dreher, 2004). Nanoparticles also form from the gaseous compounds that are either directly or indirectly released to the environment.

Siloxanes are released with the biogas from landfills and wastewater treatment facilities. Siloxanes and Si-based nanoparticles may also be emitted during the combustion of biogas. After release, siloxanes can transform into new Si-based nanoparticles. When released to the environment, nanoparticles interact with air, water and soil, resulting in changes in the surface properties (Randy, 2008). Siloxanes are low molecular weight polymers commonly ranging in size from 50 to 100 nm (Zydex, 2013). Table 1 presents the characteristics of linear and cyclic siloxanes detected in biogas.

Si-based and C-based nanoparticles have similarities in their chemical characteristics and structure geometries due the similar electron configurations of Si and C atoms (i.e., electron configuration of Si: $2s^2 2p^2$; and C: $3s^2 3p^2$). Both Si and C can form linear and cyclic compounds. Siloxanes are saturated organosilicon-oxygen compounds with unbranched or branched chains of alternating silicon and oxygen atoms. The use of siloxane based materials in consumer products (e.g., electronics and computers, home and garden products, cosmetics) has shown a significant increase in the recent years (Sevimoglu and Tansel, 2013). Due to their high Henry's constants and vapor pressures, they exhibit low water solubility; allowing them to be transferred to the gas phase during decomposition of organic matter (i.e., municipal solid waste and wastewater). The siloxanes are heavier than air. Table 3.1 provides characteristics of selected volatile methyl siloxanes commonly used consumer products. D4 and D5 constitute the majority of the total siloxanes released to the atmosphere (Surita and Tansel, 2014).

Per capita emissions of siloxanes are expected to increase continually as the percentage of silicon-containing products increases. Levels of D5 are approximately 16 times higher than D4 in wastewater influent and 18 times higher in biogas. D5 tends to partition into the solid phase (i.e., soil, biosolids). Per capita estimates based on siloxane concentrations in wastewater influent are $0.02 \mu\text{g/L}$ and $32 \mu\text{g/L}$ for D4 and D5 siloxanes, respectively (Egmond et al., 2012; Surita and Tansel, 2014). When oxidized, siloxanes are converted to silicon dioxide (SiO_2) and silicates (Chagger and Hainsworth, 1996; Panda et al., 2009). The oxidation reactions for D4 and D5 are provided below.

For the combustion of D4:

For the combustion of D5:

The combustion of methane requires only two moles of oxygen gas per mole of methane as presented below:

Oxidation of siloxanes requires between 12 and 22 moles O_2 /mole of siloxane in comparison to 2 moles O_2 /mole of methane as presented in **Table 3.1**. Therefore, the presence of siloxanes in the biogas can reduce the availability oxygen for oxidation of methane during the combustion process resulting in combustion inefficiencies.

The SiO_2 particles that are not deposited inside the combustion chamber are emitted to the atmosphere. The health impacts of SiO_2 particles in the atmosphere depend on the particle size, morphology, and emission levels. The objectives of this study were to evaluate the formation and quantities of SiO_2 from siloxanes in biogas generated at the waste management facilities (i.e., landfills and wastewater treatment plants); released quantities and potential nanotoxicity of SiO_2 released to atmosphere from energy-generating facilities. Potential health risks associated with the inhalation of Si-based nanoparticles were evaluated based on data available from nanotoxicity studies.

Table 3.1 Properties of selected volatile methyl siloxanes (adapted from Venture Technical Brief, 2009 and Schweigkofler, 2001)

Compound	Symbol	Acronym	Chemical formula	Molecular weight (g/mol)	SiO ₂ yield (mg/mg)	O ₂ required ^b (mole/mole)
Trimethylsilanol		TMS MOH	C ₃ H ₁₀ OSi	90.2	0.666	6
Hexamethyldisiloxane		L2	C ₆ H ₁₈ OSi ₂	162.4	0.740	12
Octamethyltrisiloxane		L3	C ₈ H ₂₄ O ₂ Si ₃	236.5	0.762	15
Decamethyltetrasiloxane		L4	C ₁₀ H ₃₀ O ₃ Si ₄	310.7	0.773	20
Dodecamethylpentasiloxane		L5	C ₁₂ H ₃₆ Si ₅ O ₄	384.8	0.781	24
Hexamethylcyclotrisiloxane		D3	C ₆ H ₁₈ O ₃ Si ₃	222.5	0.810	12
Octamethylcyclotetrasiloxane		D4	C ₈ H ₂₄ O ₄ Si ₄	296.6	0.810	16
Decamethylcyclopentasiloxane		D5	C ₁₀ H ₃₀ O ₅ Si ₅	370.8	0.810	20
Dodecamethylcyclohexasiloxane		D6	C ₁₂ H ₃₆ O ₆ Si ₆	444.9	0.810	22
Methane (for comparison)		-	CH ₄	16.0	NA	2

^a in biogas (Schweigkofler, 2001)

^b O₂ requirement for complete combustion to CO₂ and H₂O.

3.2 Siloxane levels in biogas

Siloxanes have been found both in biogas produced at municipal solid waste landfills and wastewater treatment plants due use of siloxane based materials in consumer products. D4 and D5 have been reported to be the primary siloxanes detected in biogas.

Table 3.2 presents the levels of D4 and D5 detected in biogas from landfills and wastewater treatment plants. Accumulation of deposits on engine parts and spark plugs of gas engines operated with biogas have been observed due to oxidation of siloxanes to silicon dioxide. Silicon dioxide at sizes below 100 nm may partially deposit on the engine parts, remain in bottom ash or released to the atmosphere (Gordon and McBride, 1984). SiO₂ particles that are not deposited on the walls of the combustion device will be vented to the atmosphere and thus contribute to the particulates in the environment.

3.2.1 Quantities of silicon dioxide deposited and released to the atmosphere

Silicon dioxide based on 10% deposition was calculated for D4 and D5 for typical biogas usage. The calculations were performed for temperature and pressure of 27 °C and 762 mm Hg, respectively. Molecular weights as provided in **Table 3.1** were used to estimate the combustion yields for SiO₂.

Assumptions:

Engine: 1 MW

Biogas: 19.5×10^6 scf/month = 6.63×10^6 m³/yr

D4 concentration: 1 ppm = 14.1 mg/m³

D5 concentration: 1 ppm = 15.1 mg/m³

For D4 in biogas (for 1 ppm concentration):

$$6.63 \times 10^6 \text{ m}^3/\text{yr} \times 14.1 \text{ mg}/\text{m}^3 = 93.48 \times 10^6 \text{ kg}/\text{yr} = 206.09 \times 10^6 \text{ lbm}/\text{yr} = 252 \text{ moles}/\text{yr}$$

SiO₂ produced:

$$252 \text{ moles}/\text{yr} \times 4 = 1008 \text{ moles}/\text{yr} = 60.58 \text{ kg}/\text{yr} = 133.56 \text{ lbm}/\text{yr}$$

If 10% is deposited in the combustion chamber:

$$0.10 \times 60.58 \text{ kg}/\text{yr} = 6.06 \text{ kg}/\text{yr} = 13.4 \text{ lbm}/\text{yr}$$

SiO₂ released 90%:

$$0.90 \times 60.58 \text{ kg}/\text{yr} = 54.52 \text{ kg}/\text{yr} = 120.20 \text{ lbm}/\text{yr} \text{ (per MW)}$$

For D5 in biogas (for 1 ppm concentration):

$$6.63 \times 10^6 \text{ m}^3/\text{yr} \times 15.1 \text{ mg}/\text{m}^3 = 100 \times 10^6 \text{ kg}/\text{yr} = 220 \times 10^6 \text{ lbm}/\text{yr} = 270 \text{ moles}/\text{yr}$$

SiO₂ produced:

$$270 \text{ moles}/\text{yr} \times 5 = 1350 \text{ moles}/\text{yr} = 81.12 \text{ kg}/\text{yr} = 178.84 \text{ lbm}/\text{yr}$$

If 10% is deposited in the combustion chamber:

$$0.10 \times 81.12 \text{ kg}/\text{yr} = 8.11 \text{ kg}/\text{yr} = 17.9 \text{ lbm}/\text{yr}$$

SiO₂ released 90%:

$$0.90 \times 81.12 \text{ kg}/\text{yr} = 73.00 \text{ kg}/\text{yr} = 160.97 \text{ lbm}/\text{yr} \text{ (per MW)}$$

The calculations conducted for 1 ppm which corresponds to 14.1 mg/m³ and 15.1 mg/m³ for D4 and D5 levels in biogas, respectively, are slightly higher than most places. However, the biogas levels reported from a wastewater treatment facility are as high as 62.1 mg/m³ and 296 mg/m³ for D4 and D5 which appear to be between 10-20 times of the typical levels reported at other locations.

Table 3.2 Siloxane (D4 and D5) concentrations in biogas from municipal solid waste landfills and wastewater treatment plants.

Sampling site	Siloxane type		Location
	D4	D5	
Landfills (mg/m ³)	12.53	4.73	Asten, Austria ^a
	4.8–5.1	0.60–0.65	Augsburg, Germany ^b
	7.97–8.84	0.50–1.09	Augsburg & Munich, Germany ^c
	10.6–15	3.0–3.3	Germany ^d
	2.8	1.26	4 landfills in Canada ^e
	<0.67	<0.30	4 Landfills in Finland ^f
	5.47	48.2	China ⁱ
	6	3.7	Istanbul, Turkey ^j
	3.8	1	Miami, FL, USA ^k
WWTPs (mg/m ³)	0.93	6.03	Asten, Austria ^a
	6.12	9.09	4 WWTPs in Munich, Germany ^c
	0.03–0.87	0.10–1.27	Finland ^f
	24.9	36.4	6 WWTPs in England ^g
	0.59	2.4	California, USA ^h
	62.1	296	China ⁱ
	5	1.8	Miami, FL, USA ^k
a. Accettola & Haberbauer (2005)			g. Griffen (2005)
b. Schweigkofler & Niessner (2001)			h. Hayes et al., (2003)
c. Schweigkofler & Niesser (1999)			i. Zhang et al., (2001)
d. Urban et al. (2009)			j. Sevimoglu and Tansel (2013)
e. McBean (2008)			k. This study (2013)
f. Rasi et al., (2010)			

3.2.2 Characteristics of Si-based particles formed during combustion of siloxanes

Thermodynamic analyses show that silicon-containing combustion products formed in gas engines are primarily silicon oxide (SiO) and silica (SiO₂) (Mokhov, 2011). This is similar to the formation of CO and CO₂ that are produced during the combustion of hydrocarbons. SiO is in gaseous form at the temperature ranges within the combustion chamber; however, SiO₂ can be present in condensed and gas phases depending on the temperature. The concentrations of SiO and SiO₂ in the flue gas depends on the of temperature and mole fraction siloxanes present in the biogas as presented in **Fig. 3.1**.

Silicon dioxide formed during the combustion of siloxanes can be in the form of nanoparticles that are in agglomerated state with particles size ranging from 5 nm up to about 100 nm. At low flame temperatures, SiO₂ forms as the primary product and condenses in the combustion chamber (Mokhov, 2011). The condensed SiO₂ can volatilize at high temperatures, as gaseous SiO₂ and SiO. The SiO₂ volatilizes in the flame entirely at temperatures above 2100 and 2500 K when the Si mole fraction in the biogas is between 100 and 1,000 ppm (Mokhov, 2011). Combustion of biogas containing over 1,000 ppm Si causes the condensation of SiO₂ because of the heat losses which lower the flame temperature to below 2200 K (Mokhov, 2011). However, the wall temperatures of the combustion chambers are cooler than the flame temperatures causing some of the SiO₂ to condense on the walls even at low siloxane concentrations in the biogas. For example, at the 5 ppb level, condensation of SiO₂ can occur at flame temperatures less than 1600 K (Mokhov, 2011).

Experiments on combustion of hexamethyldisiloxane (D2) with methane and air showed that flame color changes even at very low concentrations (1.3 mol %) of D2 in the gas stream (Chagger and Hainsworth, 1996). SiO_2 particles were observed in the post combustion gases. Analysis of the particles showed fused silica particles forming outside the flame zone. The particles were initially about 10 nm in size but increase in size. Butler and Hayhurst (1996) also reported that samples taken early in the flame were 5-10 nm in diameter, however, those that were sampled downstream from the flame had diameter of 20-30 nm.

The studies conducted with different air flows indicate that fuel-air mixing ratio has a significant effect on particle size as it affects the flame temperature (Panda et al., 2009). Increasing air flow rate increases the formation size of the silica particles. In general the silica particle size ranged from 47 to 69 nm with larger particles corresponding to higher air flows when hydrogen gas was used as the fuel (Panda et al., 2009).

Fig. 3.1 Characteristics and behavior of Si-based particles formed from siloxanes during biogas combustion (after Mokhov, 2011)

3.3. Nanotoxicity assessment of Si-based nanoparticles

3.3.1. Classification of nanoparticles with respect to toxicity

The nanoparticles have large surface to volume ratios, which can make them biologically active. Nanoparticles can enter the human body via skin, gastrointestinal tract or respiratory tract. Nanoparticles may gain access to the body via airways, ingestion, or dermal routes. They may also have the ability to translocate into secondary organs at small quantities (Oberdorster, 2010). Relatively few of the inhaled nanoparticles are translocated to secondary organs due to clearing by macrophages in the airways and alveoli (Simko and Mattsson, 2010). Nanoparticles that are passed from the respiratory tract may subsequently be ingested into the gastrointestinal tract depending on their surface characteristics (Jani et al., 1989) and size (Hillyer and Albrecht, 2001).

In medical applications, nanoparticles can be modified to penetrate the brain-blood barrier which suggests that this may also occur by exposure to nanoparticles in the environment. Determination of the absorption, distribution, metabolism, and excretion (ADME) properties of nanoparticles requires specialized detection methods in different biological matrices (e.g. blood and organs) (Hagens et al., 2007). The cell studies provide limited information from a risk assessment perspective on how the body reacts to particulate objects. The size, morphology, composition and agglomeration state can affect the responses (e.g., presence of macrophages and other inflammatory cells) (Bystrzejewska-Piotrowska et al., 2009). Different types of cells and tissues behave differently in the presence of particles due to their varying metabolic rates, permeability, and functions.

A document published by the British Standards Institution (BSI, 2007) categorizes nanoparticles with respect to toxicity as presented in **Fig 2**. Based on this classification SiO₂ particles released to the atmosphere (40-70 nm) can be described as fibrous dusts and as carcinogenic, mutagenic, ast

magenic or reproductive toxic (CMAR) nanoparticles as presented in **Fig. 3.2**.

3.3.2. Nanotoxicity of SiO₂ particles

The risks associated with SiO₂ particles for human health depends on their persistence in the environment, bioaccumulation potential, and toxicity. The toxicity (cytotoxicity) of nanoscale SiO₂ particles is size and time-dependent, increasing as the particles become smaller (at the nanoscale) (Wang et al., 2009). This may be due to the induction of antioxidant enzymes for the larger 100 nm SiO₂ particles. The higher toxicity observed for the 20 nm particles may be attributed to the larger specific area of the particles that enhances cellular interaction. On the other hand, antioxidant enzymes may not be released for the SiO₂ particles that are less than 20 nm (Passagne et al., 2012, Al-Mubaddel et al., 2012). A strong correlation ($R^2 = 0.956$) was observed between the decreased cell viability and increased ROS production post-exposure to 20 nm SiO₂ particles (Wang et al., 2009). Rabolli et al. (2001) reported that microporosity can directly influence toxicity of the SiO₂ particles.

In addition to pulmonary damage, SiO₂ nanoparticles can be transported into target organs causing toxic effects. Jaganathan and Godin (2012) reviewed the literature on biocompatibility of Si-based nano- and micro-particles by different exposure routes. In

<p>Fibrous</p> <ul style="list-style-type: none"> - Nanoparticles with high aspect ratios - Consist of insoluble materials <p>SiO₂</p>	<p>CMAR</p> <p>Nanoparticles consisting of substances classified as:</p> <ul style="list-style-type: none"> - Carcinogenic - Mutagenic - Astmagenic - Reproductive toxics <p>SiO₂</p>
<p>Soluble</p> <p>Nanoparticles not in fibrous or CMAR category</p>	<p>Insoluble or poorly soluble</p> <p>Nanoparticles not in the fibrous or CMAR category</p>

Fig. 3.2 Classification of SiO₂ particles according to toxicity categorization of nanoparticles British Standards Institution.

general, the use of Si-based materials is not considered harmful to humans. However, the short and long term effects of human exposure to Si-based and SiO₂ particles are not completely understood. Generally, crystalline SiO₂ is considerably more toxic than amorphous SiO₂ and Si particles.

The primary method of entry of nanoparticles in the atmosphere is through respiration (Donaldson et al., 2002). There is also evidence that nanoparticles have the ability to translocate from the lungs to the heart, spleen, liver and the potential to impact other organs (Choi et al., 2010) via the olfactory bulb which may be hazardous to the central nervous system (Liu et al., 2009). Poland et al. (2008) has reported that carbon nanotubes and asbestos show similar pathogenicity. Particle size, surface, shape, and chemistry affect the response of the cells; therefore, it is reasonable to anticipate that these effects will be translated to toxicity levels. However, there are very limited research results available from systematic studies on the effect of size, geometry and surface properties of nanoparticles on the toxicity levels in cells and tissues.

The human body exhibits similar response when airborne particles enter through inhalation. Nanoparticles deposit in the upper respiratory system, conducting airways, and the alveoli (Biskos and Schmidt-Ott, 2012). **Fig. 3.3** presents the fate of SiO₂ particles in the human body. Size ranges between 5 and 50 nm show effective deposition in the alveoli where toxic effects are higher. Deposition of these ranges can cause pulmonary inflammation, damage to epithelial cells, liver, spleen, silicosis and may potentially impair the central nervous system as demonstrated (Donaldson et al, 2002, Choi et al., 2009, Liu et al., 2009, and Wiesner et al., 2006).

For a particle size perspective, the inhaled particles are categorized as: 1. inspirable (capable of being inhaled into the nose or mouth; $< 100\ \mu\text{m}$); 2. Thoracic (reach past mouth and nasal region; $< 25\ \mu\text{m}$); and 3. Tracheobronchial ($5\text{-}25\ \mu\text{m}$). **Fig. 3.4** compares the deposition efficiencies of inhaled particles in the upper respiratory system, in the trachea, and in the alveoli (as reported by Biskos and Schmidt-Ott, 2012). In general, tendency for size-dependent reactivity decrease with increasing particles size (Wigginton et al, 2007).

3.5. Conclusions

Nanoparticles have a tendency to accumulate when the filtering mechanisms are limited. Toxic effects due to exposure to low levels may have a time delay of decades between exposure and outbreak of the toxic reactions. The calculations conducted for $14.1\ \text{mg}/\text{m}^3$ and $15.1\ \text{mg}/\text{m}^3$ for D4 and D5 levels in biogas, respectively, show that 54.5 and $73\ \text{kg}/\text{yr}$ of SiO_2 can be released during biogas combustion from a $1\ \text{MW}$ energy facility. Although for most facilities, the current D4 and D5 levels are about $\frac{1}{2}$ of these levels, there exists wastewater treatment facilities with D4 levels as high as $62.1\ \text{mg}/\text{m}^3$ and D5 levels as high as $296\ \text{mg}/\text{m}^3$. Ordinarily, the silica particles which can be released to the atmosphere would range from 40 to $70\ \text{nm}$ as the larger particles would be deposited within the combustions system. These particles have potential for deposition primarily in alveolar system during inhalation.

Particle size			Fate in living systems		
Large	100 nm		Conducting airways	Respiratory mucus	Pulmonary inflammation, liver, spleen
	50 nm		Pulmonary inflammation	Damage to epithelial cells, liver, spleen	Formations of granulomas
Medium	20 nm		Pulmonary inflammation	Interstitial fibrosis and inflammation	Silicosis/ pneumoconiosis
	5 nm		Blood	Kidneys	Central nervous system

Persistence in body (day)

Fig. 3.3 Fate of SiO₂ nanoparticles in human body based on persistence and particle size

Fig. 3.4 Comparison of deposition efficiency of inhaled particles in the upper respiratory system, in the trachea, and in the alveoli (a reported by Biskos and Schmidt-Ott, 2012) with the general tendency for size-dependent reactivity change with particle size (adapted from Wigginton et al., 2007).

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Zydex, 2013, Zycosyl, Zydex Fact Sheet.

4. Preliminary investigation to characterize deposits forming during combustion of biogas from anaerobic digesters and landfills (published in Renewable Energy)

4.1 Introduction

The increasing demand for energy and dependency on fossil fuels has created opportunities for renewable energy sources. Regions with high potential for bioenergy production (i.e., from waste materials) have implemented programs and facilities to utilize the bioenergy (Blaschke et al., 2013). It has been estimated that by the year 2050, half of the world energy demand in developing countries will stem from improved biomass energy (Demirbas, 2008). The United States accounts for the consumption of approximately 19 percent of the world's energy but only accounts for a population of 4.5 percent of the world. Approximately 84 percent of the energy supply comes from fossil fuels (Aslani and Wong, 2014). According to the International Energy Agency (IEA), biogas provides an estimated gross electricity generation of 9,281 gigawatt-hour (GWh) and heat production of 999 TJ (IEA, 2013). Additionally gross electricity generation from municipal waste and industrial wastes was estimated at 16,900 and 5,500 GWh. Gross heat production for these facilities was estimated at 11,700 and 3800 TJ, respectively.

Biogas is generated from landfills and wastewater treatment plants (WWTPs) during the step-wise degradation process when microorganisms decompose the organic material under anaerobic conditions (Demirbas, 2008). The gas produced is typically used as fuel for energy production, pumps and boilers (Pierce, 2013). Although utilization of biogas is more costly than energy derived from fossil fuels, the reuse of

biogas eliminates much of the greenhouse gas emissions from landfills and can be further upgraded for pipeline use. The potential energy of biomass from waste in the United States has been estimated to be 1.5 EJ/yr for the municipal solid waste industry, 0.8 EJ/yr for sewage sludge bio-solids, and 0.4 EJ/yr for industrial waste biodegradation (Chynoweth et al., 2001). In 2005, Demirbas et al. (2009) reported the top five of ten bio-electricity producers to be USA (30.7%), Germany (7.33%), Brazil (7.31%), Japan (5.13%) and Finland (4.85%). The composition of biogas is variable, but ranges between 40 and 60 percent methane, 40 to 55 percent carbon dioxide and the remainder consists of trace compounds such as nitrogen, oxygen, halogenated compounds, hydrogen sulphide and siloxanes.

Siloxanes in the wastewater stream originate from discarded consumer products (i.e. cosmetics, cleaning products, deodorants, and hair/skin care products, landfill leachate). Landfill origins can be traced to a multitude of consumer products including paper, construction debris, treated woods, and wastewater treatment sludge. With the increase of siloxanes found in consumer products, concentrations of siloxane compounds are intensifying in the waste stream. It was projected that the world demand for silicone has increased by 6.3 percent per year (Surita and Tansel, 2014; World Silicones, 2011). Siloxanes typically sorb onto solids due to their low solubilities or volatilize due to their inherent vapor pressures. **Table 1** provides mean siloxane concentrations found at different locations. **Fig. 1** provides the levels of the volatile methyl siloxanes in biogas from landfills and wastewater facilities which take only municipal discharges.

The comparison of the types and levels of siloxanes in biogas shows that volatile methyl siloxanes (VMS) presents in landfill gas are primarily TMSOH, D4 and D5 as well as small concentrations of L2 and L3. The VMS in biogas from anaerobic digesters are mainly D5, D4 and D3. It is interesting to note that the landfill conditions promote formation of TMSOH and D4 is present at higher concentrations than D5. On the other hand, in the biogas forming in anaerobic digesters, D% levels are significantly higher than those for D4. Lack of significant levels of linear siloxanes (L2-L4) and TMSOH in the biogas from anaerobic digesters in comparison to those in the biogas from landfills indicate that the reduction potential in the anaerobic digesters are significantly lower in comparison to those present in the landfills or formation of TMSOH, L2 and L3 occur through slow reduction processes.

Siloxanes are released from the solid phase (biomass) during anaerobic decomposition processes which result in release of the bound siloxanes through volatilizing when temperatures reach 60 °C (Ortega and Subrenat, 2009). When biogas is combusted, the siloxanes are oxidized, leaving white deposits on heated metal surfaces. Siloxane combustion yields silicon dioxide (SiO_2) or silicates, which is visible on engine components, pistons, cylinder heads, turbine blades, and spark plugs among others (Xebec Adsorption Inc., 2008; Sevimoglu and Tansel, 2013a). Deposits formed, contain mostly SiO_2 or silicates; however may contain calcium, zinc, phosphorus, sulfur and other trace elements.

Table 4.1 Siloxane concentrations (mg/m³) in landfill gas and biogas at different locations

Facility	Concentration of Si containing compounds (mg/m ³)								
	TMSOH	L2	L3	L4	L5	D3	D4	D5	D6
LF-1 ^a	-	6.07	0.32	-	NR	0.49	12.53	4.73	NR
LF-2 ^b	6.08	1.65	0.03	0.04	-	0.42	7.70	1.26	-
LF-3 ^c	0.30	0.33	0.01	-	-	0.10	0.67	0.30	-
LF-4 ^d	-	0.34	-	-	-	0.58	2.80	1.26	-
LF-5 ^{e,o}	35.7	-	-	-	NR	2.80	29.1	11.80	1.50
LF-6 ^f	10.10	0.10	-	-	NR	0.10	3.60	6.40	0.40
LF-7 ^g	6.70	0.10	-	-	NR	0.50	11.80	6.00	0.50
LF-8 ^h	12.70	1.50	-	-	NR	0.40	5.00	0.90	-
LF-9 ⁱ	7.25	0.72	0.10	-	NR	0.52	2.16	-	0.09
Averageⁿ	7.19	1.35	0.12	0.04	0.00	0.39	5.78	2.98	0.33
WW-1 ^a	-	0.02	0.02	-	-	0.04	0.93	6.03	-
WW-2 ^b	0.11	0.05	0.03	0.10	-	0.25	6.12	9.05	-
WW-3 ^c	0.04	0.01	0.20	0.04	-	0.04	0.45	0.69	-
WW-4 ^j	-	-	-	-	NR	1.60	0.50	5.30	0.10
WW-5 ^{k,o}	-	3.40	-	0.70	NR	-	8.10	340.7	8.70
WW-6 ^l	-	-	-	-	NR	2.80	0.90	11.90	0.20
WW-7 ^{m,o}	-	-	-	-	NR	0.10	1.00	48.40	2.50
WW-9 ⁱ	0.08	0.05	0.05	0.29	1.80	0.26	0.05	4.15	0.09
Averageⁿ	0.08	0.03	0.08	0.14	0.05	0.83	1.49	6.19	0.13

a Asten, Austria (Rasi et al., 2010)

d Canada ((Rasi et al., 2010)

g Germany-Baden-Wurttemberg (Piechota et al., 2013)

i Miami (This study)

m Poland-Woj. Pomorskie (Piechota et al., 2013)

b Germany (Rasi et al., 2010)

e Poland (Piechota et al., 2013)

h Germany-Sachsen-Anhalt (Piechota et al., 2013)

k Germany-Hessen (Piechota et al., 2013)

n Facilities which accept only municipal was

c Finland (Rasi et al., 2010)

f Poland – Woj. Podlaskie (Piechota et al., 2013)

j Germany-Niedersachsen (Piechota et al., 2013)

l Germany-Hessen (Piechota et al., 2013)

o Not included in the average

a. Biogas from landfills

b. Biogas from wastewater treatment facilities

Fig. 4.1 Comparison of the siloxanes in biogas from landfills and wastewater treatment facilities.

Deposits on spark plugs often cause premature engine failure, excessive fouling of heated surfaces, misfiring and noise. Pistons with excessive deposit accumulation may limit the expansion of piston rings thereby leading to higher oil consumption. When siloxane present in gas phase are burned, they form nanoparticles which accumulate when proper maintenance technologies and procedures are not employed (Sevimoglu and Tansel, 2013b; Tansel and Surita, 2014). Additional compounds present in engine deposits include metals in solid form (EA, 2013; Niemann et al., 1997; Hagmann et al., 1999) (i.e., calcium, copper, sodium, sulfur and zinc) (Venture E&C, 2014; Sevimoglu and Tansel, 2013b).

At energy facilities operated with biogas, the presence of VMSs reduce the engine performance and increase maintenance activities. Operation and maintenance costs can become increasingly high due to silicate deposition. No state, federal or regional mandates have been implemented for siloxane quantification and control; however several methodologies for sampling and analytical procedures have been developed (Surita and Tansel, 2014; Pierce, 2011; Arnold, 2010). Consequently, manufacturers have adapted equipment warranties for inclusion of deficiency due to these deposits.

Objectives of this study were to compare the composition of deposits forming in engines operated with biogas from anaerobic digesters and biogas from landfills. Engine deposit samples were collected from the facilities in Florida, USA. The morphological characteristics and elemental composition of the deposit samples were analyzed by scanning electron microscopy (SEM) which was used in conjunction with energy dispersive spectroscopy (EDS). Similarities and differences between the deposits

collected from the engines operated with biogas from anaerobic digesters were compared with those operated with biogas from landfills.

4.2. Background

The facilities used in this study are located in three different geographic areas of the state of Florida. Each of the facilities implements reciprocating engines of varying capacity. Site 1 is a wastewater treatment plant implementing digester recovered gas for cogeneration or combined heat and power. Efficiency gains are evident in the capture of both thermal energy and generation of electricity (EPA LMOP, 2014). Sites 2 and 3 utilize the landfill gas (LFG) for electricity generation versus direct use.

4.2.1 Facility 1

Samples were obtained from engine head and spark plug components of the combustion chamber at a wastewater treatment plant located in Facility 1 during a complete engine overhaul. The facility serves a population of approximately 2.3 million residents and includes conventional treatment including physical separation, neutralization, biological treatment and wet scrubbing for hydrogen sulfide removal. The treated wastewater is disinfected prior to disposal via deep well injection or reuse. The biogas from 12 on-site digesters receives pre-treatment from a water-based scrubbing system at a rate of 17 cubic feet per hour prior to cogeneration.

4.2.2 Facility 2

Facility 2 was opened in 1978 (EPA LMOP, 2014) and serves municipal, residential, industrial and commercial customers in the County and surrounding areas. The site is permitted by FDEP for Class I landfilling, yard waste mulching, tire collection

and solidification processes and does not accept hazardous waste. Approximately 1,700 tons of waste is received daily on a 700 acre site. Gas is collected through a series of gas extraction wells and is used to as fuel for electricity generation of approximately 4.8 MW (EPA, 2010). At the facility, 6 caterpillar engines are utilized, each being 4.9 mW. Approximately 11-12 scfm of LFG is utilized. Siloxane monitoring is conducted quarterly by a third party contractor. Engine deposition has been noted within engine head and operations and maintenance impacts have been noted, specifically from build-up on pistons which cause detonation.

4.2.3 Facility 3

Facility 3 is a Type I landfill, opened in 1999 (EPA LMOP, 2014) for disposal of MSW with designation of special-use areas for processing, storage and disposal. According to the EJ View Census 2010 Summary Report, the population density at a 1 mile radius from location is approximately 2,300. Samples were scraped from engine components replaced during a full-engine overall conducted in late February 2014. The facility is fitted with 2 caterpillar 3520's running at 1.6 mW and 1 smaller caterpillar 3516 running at 800 kW. Approximately 1100 scfm. LFG is utilized. Siloxane monitoring is not regularly conducted at this site; however deposition has been noted with minor impacts to routine maintenance.

4.3 Methods

When scanning electron microscopy (SEM) is used in conjunction with Energy Dispersive Spectroscopy (EDS), qualitative analysis of silicates can be determined. Because SEM uses wavelengths shorter than that of light, material observation can be

conducted down to the nanometer scale. The electron images in the SEM display compositional contrast resulting from mass and distributions, while EDS will identify the specific elements and their comparative proportions. EDS is used for elemental analysis and functions as a spectrum of the energy intensity of X-rays when Li-doped Si semiconductor detector and spectrum analyzer are combined. The JEOL 6330F Field Emission SEM with Energy Dispersive Spectroscopy was utilized for the characterization of siloxane deposition and microanalyses in this study.

Samples to be analyzed were scraped from engine components at three facilities and collected for future analyses (**Fig. 4.2**). Sample 1 was extracted from engine components utilizing digester gas whereas samples 2 and 3 were collected from landfills processing biogas for energy use. Samples were then processed for analysis in laboratory. The sample sizes were limited to less than 8 mm in size and were mounted on a metallic sample holder. Double sided conductive tape was used to affix samples to holder. The working distance was decreased and samples were aligned consecutively (one through three) for SEM followed by EDS microanalysis. Because the three samples lost resolution when magnified, due to poor conductivity, a thin coating of gold was applied to the samples using the PELCO SC-7 Auto Sputter Coater. This amendment improved the quality of the images and ensured reduced charge effect. However, because of the roughness of material, the charge effect could not completely be eliminated.

Fig. 4.2 Samples collected from facilities 1 through 3, respectively, a) scrapings from engine head operated with anaerobic digester gas, b) scrapings from engine head operated with landfill gas, and c) coated sparkplug from engine operated with landfill gas.

4.4 Results

Impurities in LFG include hydrogen sulfide, siloxanes, hydrochlorofluorocarbons, volatile halogenated hydrocarbons, benzene, toluene and xylene; however the most problematic of these are siloxanes due to their residues which develop on engine components during combustion. Samples collected from spark plugs and engine heads at WWTP and LFs were analyzed for elemental composition. **Figs. 4.3, 4.4 and 4.5** provide the SEM images for the three samples collected (Samples 1 through 3 respectively) to illustrate varying particle morphology. The magnifications and scales are indicated in each figure and vary depending on availability of high resolution image. Sample 1 as shown in Fig. 3 was consistent throughout producing an image of agglomerated dust-like particles. Deposits for sample 2 were affixed to scrapings from engine head that may have contained additional materials and roughness was more apparent. Sample 3 magnifications of 20,000 were reached, whereas samples 1 and 2, magnification of only 10,000 times were obtained due to clarity of image. In sample 3, observations of some

irregularity in structure were made (**Fig. 4.6**). These irregularities may be a result of sample extraction from the spark plug containing deposition.

Characteristic X-ray peaks for Facilities 1 through 3 respectively are provided in **Fig. 4.7**. Numerical comparison between net counts of samples indicated the following: Net counts for carbon in sample 1 were approximately four times higher than samples 2 and 3. Phosphorus and sulfur net counts were approximately thirteen and ten times higher in sample 1 when compared to samples 2 and 3 respectively. Calcium and zinc similarly presented higher ratios in sample 1. When compared with sample 2, calcium and zinc were five and eight times higher. Sample 1 comparison with sample 3 demonstrated eight and four times higher net counts for calcium and zinc respectively.

Fig. 4.3 Morphological characteristics of the deposits obtained from Facility 1 observed at different magnifications. a) X250, 100 μm ; b) X600, 10 μm ; c) X1,900, 10 μm ; d) X10,000, 1 μm

Fig. 4.4 Morphological characteristics of the deposits obtained from Facility 2 observed at different magnifications. a) X20, 1 mm; b) X1,000, 10 μ m; c) X2,500, 10 μ m; d) X10,000, 1 μ m

Fig. 4.5 Morphological characteristics of the deposits obtained from Facility 3 observed at different magnifications. a) X20, 1 mm; b) X2,500, 10 μ m; c) X5,000, 1 μ m; d) X20,000, 1 μ m

Fig. 4.6 Morphological characteristics of the deposits with irregularity in structure obtained from Facility 3 observed at different magnifications. a) X1,000, 10 μm ; b) X2,000, 10 μm ; c) X5,000, 1 μm ; d) X20,000, 1 μm

Fig. 4.7 Characteristic X-ray peaks observed in the deposit samples obtained from facilities 1, 2, and 3 respectively.

Elemental characterization of silicate deposits, formed during biogas combustion, is provided in **Table 4.2**. A graphical representation of the elemental characterization at each facility is depicted in **Fig. 4.8**. The prevalent compounds encountered at all three locations include carbon, oxygen, silicon, calcium, sulfur, phosphorus and zinc. Facility 2 indicated the highest elemental composition of oxygen and no potassium presence. Facility 1 and 3 were similar in both carbon and silicon compositions, however carbon ratios were not comparable. Misinterpretation of calcium and potassium overlap in sample 3 was not considered as two of the three samples indicated similar compositions. However, the overlap was considered negligible due to the quantitative comparison of elemental composition (w/w).

Similarity of elements in all three sample sites was evident; however, samples collected from engines operated with LFG did not indicate the presence of potassium and lesser quantities of calcium, sulfur and phosphorus. The difference was made up with the higher silicon content in comparison to those operated with anaerobic digester gas. In anaerobic digesters, the chemical form of some nutrients will be changed. Some potassium and phosphorus are released by decomposing material and mostly settle as sludge. Phosphorus, from zinc/phosphorus engine oil additives, separates from zinc at high temperatures as indicated in throttle deposit studies and confirmed by a manufacturer of the additive (Garrick, 2007). Calcium is commonly found in wastewater treatment systems, contributing to water hardness and has been noted to be essential for the growth of certain methanogens; however excess amounts lead to scaling on reactors and loss of buffering capacity (Chen et al., 2008). Moreover, calcium composition in

Table 4.2 Composition of deposits forming in engines during combustion of biogas

Element	Symbol	Facility 1 (WW)		Facility 2 (LF)		Facility 3 (LF)	
		Weight (%)	Elemental (%)	Weight (%)	Elemental (%)	Weight (%)	Elemental (%)
Carbon	C	24.64	34.98	15.51	22.62	26.46	37.50
Oxygen	O	47.51	50.63	54.33	59.47	42.98	45.73
Silicon	Si	11.49	6.97	24.96	15.57	22.29	13.51
Phosphorus	P	1.85	1.02	0.36	0.21	0.39	0.22
Sulfur	S	4.96	2.64	1.01	0.55	0.81	0.43
Potassium	K	0.10	0.04	-	-	0.00	0.00
Calcium	Ca	7.56	3.22	3.32	1.45	4.65	1.98
Zinc	Zn	1.88	0.49	0.51	0.14	2.41	0.63
Total		100	100	100	100	100	100

^a elemental composition was calculated by dividing the weight percent by the corresponding atomic weight normalized. Composition was adjusted to percentage.

Fig. 4.8 Elemental composition of the deposits forming during biogas combustion

deposits may be attributed to its addition as an amendment in engine oil. Residence time and release mechanisms (volatilization, solubilization and sorption) impact the conversion process and production of methane and other gas-phase constituents.

For these reasons, the relatively larger counts of potassium and calcium are expected in silicate deposits forming from digester produced biogas.

Large concentrations of zinc oxides, which enter the waste stream from the personal care products, inhibit methanogenesis (Mu et al., 2011). Delays in speciation/transformation process may contribute to ZnO stability and may be influenced by surface coating of formulations (Lombi, et al., 2012). Additionally, the relatively small elemental composition of zinc presented likely results from metallic elements within engine oils specifically used as friction modifier, antioxidant, antiwear or corrosion inhibitor (i.e. zinc dithiophosphate). Weathered nanoparticles present in

biological treatment have undergone transformation, including coating loss and reactivity before ending in sewage sludge (Brar et al., 2010). Some landfills are co-disposal facilities, accepting biosolids produced during anaerobic digestion. Organic complexes of zinc oxide may react with siloxanes, and because of volatility, may be released in biogas or LFG. Future studies should aim to understand the interaction of various nanoparticles between environmental compartments during various phases of treatment and with respect to degradation time.

A comparison of carbon-oxygen-silicon ratios are presented in **Table 4.3**. A correlation between silicate-based deposition on engine components and increasing CO emissions has been noted by Tower (2003). Because carbon exists in deposits sampled, it is indicative that the carbon bond with silicon and oxygen is too complex to break thus preventing carbon combustion. Furthermore, there is insufficient oxygen remaining to form bicarbonate. As a result, the siloxanes initially present in biogas may form other siloxane compounds in addition to varying crystalline, more complex structures. Atomic compositions have been estimated based on the molecular weights and elemental mass compositions. A study conducted by Yang et al., (2003) demonstrated that relative carbon content and porosity are significant factors of bonding. Bonding structures of SiOC have demonstrated caged silicon-carbon bonds with porosity enhancement.

Table 4.3 Comparison of the deposit compositions for the three elements with the highest concentrations relative to Si content.

Sample	C : O : Si
Facility 1	5.0 : 7.3 : 1.0
Facility 2	1.4 : 3.7 : 1.0
Facility 3	2.7 : 3.3 : 1.0

The relatively high levels of carbon present in the crystalline deposits were found in ratios of 5C:7O:1Si in the deposits obtained from the engines operated with biogas from the anaerobic digesters. The ratios were substantially different in engines operated with LFG at 2:3.5:1 establishing a lower silicon presence in engines operated with biogas.

4.5 Conclusions

The elemental composition of deposits formed during combustion of biogas or landfill gas was investigated using combined SEM/EDS methods. Three samples were collected from different facilities in the state of Florida processing biogas and LFG (one wastewater treatment plant and two landfills). Carbon-oxygen-silicon ratios in the deposits were compared. The analysis of the deposit composition show that carbon present in the deposits is not in carbonate form but in bound form to the crystal structure of the deposits. Relatively high levels of carbon were present in the crystalline deposits forming during the combustion of biogas. C:O:Si ratios were about 5:7:1 in the deposits obtained from the engines operated with biogas from the anaerobic digesters and 2:3.5:1 in the deposits from the engines operated with landfill gas. In general, the silicon content in the deposits in the facilities operated with biogas from the anaerobic digesters was

lower than those operated with biogas from landfills. The difference was made up with the higher phosphorus, sulfur and calcium content in the deposits from the engines operated with anaerobic digester gas in comparison to those operated with landfill gas. Future studies should aim to differentiate compound interactions and transport mechanisms between environmental compartments with respect to time in addition to other significant contributing factors such as waste age, composition of waste, organic content etc., as contributions to landfill gas generation.

Acknowledgements

Partial funding for this research has been provided by Hinkley Center for Solid and Hazardous Waste Management of University of Florida as well as the Florida International University Graduate School Dissertation Year Fellowship.

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**5. Emergence and fate of siloxanes (D4, D5) in municipal waste streams:
Release mechanisms, partitioning and persistence in air, water, soil and
sediments (published in Science of the Total Environment)**

5.1 Introduction

Since their introduction in 1943, silicone based compounds have been used in a variety of industrial applications either as coatings or as additives because of their surface properties and ability to repel moisture (Owen, 2005; Kochetkov et al., 2001; Tragoonwichian et al., 2011; Lu et al., 2011). Siloxanes are the basic building block of silicones which are used as sealants and antifouling agents. Due their super-hydrophobic characteristics, their use in consumer products have expanded from personal care products (i.e., make up, shampoo) to surface coatings in construction materials (i.e., wood, concrete) and fabrics. The World demand for silicones is anticipated to increase by 6.2% per year through 2015 (World Silicones, 2011) and the global market for silicone is forecasted to reach \$17.2 billion by the year 2017, driven by increasing end-use markets (i.e., construction, automotive, healthcare and chemical) (PR web, 2012).

Silicones and silicone based products are widely used in consumer products by different industries (i.e., automotive coating, electronics, paints and coating, textile manufacturing, beauty and personal care products, health care products, paper manufacturing, construction coating) (Dow Corning, 2012). Coatings made from silicone based polymers have significant benefits over the traditional organic polymers. These benefits include chemical resistance to organic and inorganic acids, alkalis and solvents; thermal resistance; resistance to abrasion; resistance to ultraviolet light degradation and microbiological growth; and prevention of water intrusion into porous surfaces (and ease

the removal of graffiti from surfaces) (Silicone Derivatives, 2012). As a result, in recent years, use of silicon based coatings has increased significantly. Siloxane hard coats are used on non-ferrous metal surfaces (brass, bronze, copper, aluminum); ferrous metal surfaces (carbon steel, cast iron); masonry surfaces (stucco, cement, clay pavers, limestone); plasters, and grouts; natural stones and tiles (slate, marble, granite, travertine, limestone); plastic and vinyl surfaces to add UV protection and prevent oxidation and fading (European Coatings, 2012).

Siloxanes have a chemical backbone structure of silicon and oxygen atoms, alternating in position with hydrocarbon groups attached to the silicon side chain. When silicon containing compounds are burned, the hydrocarbon fraction is lost and silicon is converted to silicates (SiO_2 or SiO_3^{-2}) (Ajhar et al., 2010). Siloxanes can be in linear configuration, cyclic form, or tetrahedral formation with organic groups. Some widely used cyclosiloxanes are hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6). Cyclosiloxanes are typically formed during depolymerization or reversion reactions. **Table 5.1** provides the selected properties for the volatile methyl siloxanes found in the environmental samples (i.e., gas, water, and soils).

Siloxanes from anthropogenic sources have been found in the ambient air samples near industrial areas, landfills and wastewater treatment plants, and outdoor air samples (Wang et al., 2001; Navea et al., 2011; Kaj et al., 2005, McLachlan et al., 2010). Landfill gas contains small amounts of compounds such as hydrogen sulphide, mercaptans, halogenated hydrocarbons and siloxanes (Eklund et al., 1998; Sevimoglu and Tansel, 2013) and trace metals (Suziki et al., 2002). Among these, volatile methyl siloxanes

Table 5.1 Properties of selected volatile methyl siloxanes (adapted from Ajar et al., 2010)

Compound	Abbr	Chemical formula	Vapor pressure ^a at 25 °C (kPa)	Water solubility at 25 °C (mg/L)
Hexamethyldisiloxane	L2	C ₆ H ₁₈ OSi ₂	5.626 ^a	0.93 ^b
Octamethyltrisiloxane	L3	C ₈ H ₂₄ O ₂ Si ₃	0.52 ^b	0.05 ^c
Decamethyltetrasiloxane	L4	C ₁₀ H ₃₀ O ₃ Si ₄	0.073 ^b	0.007 ^d
Hexamethylcyclotrisiloxane	D3	C ₆ H ₁₈ O ₃ Si ₃	1.147 ^a	1.56 ^a
Octamethylcyclotetrasiloxane	D4	C ₈ H ₂₄ O ₄ Si ₄	0.132 ^a	0.056 ^a
Decamethylcyclopentasiloxane	D5	C ₁₀ H ₃₀ O ₅ Si ₅	0.023 ^a	0.017 ^a

a. Schweigkofler (2001)

b. Venture Technical Brief (2009)

c. Pierce (2011)

d. Korchetkov et al. (2001)

siloxanes (VMS) have been reported to have the most adverse effects on utilization of biogas (Ohannessian et al., 2008; VDI, 2008; Ajhar et al., 2010; Gaur et al., 2010). The siloxane content in landfill gas is expected to increase in the future with the increasing use of siloxanes in consumer products. At the energy generation facilities operated with LFG, volatile methyl siloxanes (VMS) reduce the engine performance due to deposit formation inside the combustion chambers (Ohannessian et al., 2008; VDI, 2008; Ajhar et al., 2010; Ryckebosch et al., 2011; Rasi et al., 2010; Cheng et al., 2001; Sevimoglu and Tansel, 2013).

The presence of volatile methyl siloxanes in biogas reduces the efficiency of energy recovery from biogas. During combustion, siloxanes are converted to silicon dioxide deposits, leading to abrasion of engine parts or the build-up of layers that inhibit essential heat conduction or lubrication (Ajhar et al., 2010). Plant operators are facing a

choice between installing gas purification equipment or controlling the problem with higher maintenance costs. When the siloxane levels are relatively small, the investment and operating costs of the installed gas purification system may exceed the maintenance costs caused by siloxanes (e.g., due to more frequent oil changes, engine inspections, downtime) (Doczyck, 2003). Engine warranties linked to silicon levels in biogas have become significantly more stringent between 2002 and 2008 (McBean, 2008). Patent applications involving silicone containing organic compounds have also significantly increased in recent years. As the new silicone containing consumer products enter the market, the waste quantities will increase over time. The potential impacts of increasing quantities of siloxane containing waste materials may necessitate monitoring of siloxanes in LFG and digester gas at wastewater treatment plants.

Rasi et al., (2010) studied the organic silicon compounds in biogas samples from landfills, wastewater treatment plants (WWTPs), and biogas plants processing sewage sludge. Analysis of 48 samples showed that the most common compounds in WWTPs and in biogas plants processing sewage sludge were octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) while in landfill gas the most common compounds were D4, D5 and hexamethyldisiloxane (L2) followed by trimethylsilanol (Rasi et al., 2010; Sevimoglu and Tansel, 2013). One of the most common methods of siloxane removal is the use of activated carbon for adsorption. Because of the difficulty in desorbing siloxane from material, regular replacement is essential. Weekly activated carbon replacement has been reported for a facility in the UK, Trecatti. Alternative methods of treatment include absorption via the use of high boiling organic solvents, cryogenic condensation and chemical abatement (Dewil et al., 2006).

The objectives of this study were to evaluate the release mechanisms of two cyclic siloxane compounds (D4 and D5) which have been detected both at landfills and wastewater treatment plants; evaluate their partitioning into water and soil phases; estimate the persistence times in different media; and project release quantities over time in relation to their projected use in consumer products. Analyses were conducted based on the fate and transport mechanisms of siloxanes after they enter waste streams (i.e., municipal solid waste and/or wastewater). Per capita emission rates were estimated using their projected levels in waste stream (i.e., municipal solid waste and wastewater).

5.2 Methodology

Once released to the environment, the transformation of siloxanes may occur due to diffusion and partitioning among phases (i.e., water, soil, sediments). Analyses were conducted to characterize the fate and transport of D4 and D5 which have been detected in biogas from landfills and wastewater treatment plants. D4 and D5 have been reported to be the dominant siloxanes comprising approximately 90% of the total volatile siloxanes (Tower, 2003). **Fig. 5.1** presents a schematic of the environmental release mechanisms and transport routes considered in the analyses. The decomposition reaction sequence of siloxanes in the various environmental compartments is illustrated in **Fig. 5.2**.

Fig. 5.1 Release mechanisms of siloxanes in waste streams into the environment

Fig. 5.2 Decomposition reaction sequence of siloxanes in different media.

Analyses were performed to estimate (1) Concentrations in water, soil, and sludge based on the levels detected in biogas; and (2) anticipated release quantities to wastewater and solid waste. Ratios for partitioning into different media were used to estimate the siloxanes entering solid waste and wastewater. Fate and transport mechanisms were analyzed to estimate the current and projected per capita quantities in biogas solid waste and wastewater.

The ranges of D4 and D5 concentrations reported in biogas from landfills and wastewater treatment facilities are provided in **Table 5.2**. For the equilibrium conditions, the concentrations in water, sludge and soil phases can be estimated from the gas concentrations as follows (Kuo, 1999):

$$C = G / (H^* \times 1000) \quad (1)$$

$$X = K_p \times C \quad (2)$$

$$K_p = f_{oc} \times K_{oc} \quad (3)$$

where,

- X : Concentration in soil phase (mg/Kg)
- K_p : Soil water partition coefficient (L/Kg)
- K_{oc} : Organic carbon partition coefficient (L/Kg)
- f_{oc} : Fraction of organic carbon (assumed 0.2 for soil, 0.8 for sludge)
- C : Concentration in water phase (mg/L)
- H^* : Dimensionless Henry's constant
- G : Concentration in gas phase (mg/L)

Table 5.2. Ranges of D4 and D5 concentrations in biogas from landfills and wastewater treatment plants (WWTP)

Sampling location	Concentration (mg/m ³)			
	Range D4	Average D4	Range D5	Average D5
Biogas from landfills	1-15 ^a	5.2	1-5 ^b	7.1
Biogas from WWTP (digesters)	1-102 ^c	14.3	1-80 ^c	50.3

^a high concentration reported by Urban et al. (2009)

^b high concentration reported by Accettola and Haberbauer (2005)

^c high concentration reported by Griffin (2004)

5.3. Results

5.3.1 Partitioning characteristics and degradation

The partition of volatile siloxanes can be estimated based on the partition coefficients of the compounds between different media. **Table 5.3** provides the partition coefficients for octanol-water (K_{OW}), octanol-air (K_{OA}), air-water and organic carbon partition coefficient (K_{OC}) for D4, D5, and D6. The K_{AW} was estimated from the ratio of K_{OW} and K_{OA} .

Based on the levels of D4 and D5 detected in biogas, the maximum levels in water, soil, and sludge phases were estimated for the equilibrium conditions. **Fig. 5.3** presents the estimated concentrations water and soil phases based. In multimedia environments, D4 and D5 (cyclic volatile methyl-siloxanes) will readily partition to the gas phase due to their low water solubility and high vapor pressures. Therefore, the gas phase (i.e., atmospheric partitioning) is the main environmental sink for D4 and D5. Due

Table 5.3 Organic compounds found in biogas containing silicon (adapted from Wang et al., 2012)

Compound	log K _{OW} ^a	log K _{OW} ^b	log K _{OA} ^c at 25 °C	log K _{AW} ^d at 25 °C	log K _{OC}	H ^{*j}	Half-life (days)	
							Atmospheric ^h	Soil- sediment ⁱ
D4	4.45	4.45	4.34	2.69	4.22 ^e	536 ^j	10	4.1-5.3
D5	5.20	5.2	5.06	3.13	5.17 ^f	17.9 ^k	20	9.7-12.5
a. Bruggrenan et al., 1984			e. Miller, 2007			i. Xu, 2007		
b. Kochetkov et al., 2001			f. Durham, 2007			j. GuideChem, 2013a		
c. Xu, 2006			g. Brooke et. al, 2009b (linear extrapolation)			k. GuideChem, 2013b		
d. Xu and Kropscott, 2007			h. Atkinson, 1991					

to the relatively high octanol-water coefficient, siloxanes also have high tendency to partition into the soil and biosolids. Adsorption characteristics of siloxanes in organic media exceed aliphatic or cyclic hydrocarbons (Everaert and Baeyens, 2004) with similar molecular weights due to their relatively higher octanol-water partition coefficients. Therefore, the estimated levels in biosolids are significantly higher in comparison to soil due to the high organic content of biosolids (organic content of about 20% for soils vs. 80% for biosolids).

Table 5.4 presents the mass fractions which partition into different phases in the environment for D4 and D5. For D5, the ratio of mass fractions for air:soil:water:sediments were estimated to be 64:2:1:33 (Siloxane D5 Board of Review, 2012). Mass distributions were derived for D4 based on the K_{AW} ratio for air and water percentages and K_{WS} for sediment partitioning. Soil partitioning was determined by taking the remaining balance into account.

Fig. 5.3. Estimated partitioning characteristics of D4 and D5 between water, soil, and gas phase, a. air-water equilibrium for D4, b. water-soil equilibrium for D4, c. air-water equilibrium for D5, and d. water-soil equilibrium for D5. The maximum levels detected in biogas from landfills and wastewater treatment plants are indicated

Table 5.4. Partitioning of D4 and D5 (%w/w).

Siloxane	Air	Soil	Water	Sediment
D4	55.2 ^a	6.3 ^b	2.3 ^a	36.2 ^c
D5 ^d	64	1	2	33

^a Air and water percentage for D4 calculated based on K_{AW} ratio

^b Soil percentage for D4 calculated by difference

^c Sediment percentage calculated based on K_{WS} ratio

^d Siloxane D5 Board of Review, 2012

5.3.2 Persistence in the environment

The atmospheric lifetimes of D4 and D5 have been estimated as 11.5 days and 7.5 days, respectively, with significant variability reported by different researchers (Atkinson, 1991; Karl et al., 2001; Navea, 2011). Atkinson (1991) estimated the half-lives of D4 and D5 as about 10 days and 20 days, respectively, based on first order kinetics. After release to the atmosphere, siloxanes either converted to monomeric dimethylsilanediol (DMSD) which can degrade by UV-induced reactions or returned with rainfall to soil (Atkinson, 1991).

In soil, the siloxanes can hydrolyze to siloxanols (DMSD) as the ultimate product (Lehmann et al., 1994; Carpenter et al., 1995). The DMSD, can degrade to CO₂ and inorganic silicate (Lehmann, et al., 1994; Lehmann, et al., 1998; Sabourin, et al., 1996). The production of CO₂ from DMSD degradation has been reported as from 0.4-1.6% per week (Lehmann, et al., 1998). DMSD also volatilizes from soil at about 1-7% per week, with higher losses from sandy soils (Lehmann and Miller, 1996).

Fig. 5.4 presents the degradation profiles of D4 and D5 in atmospheric, freshwater, marine water and soil-sediment environments derived from half-lives reported in different media (as provided in **Table 3**). The reporting limit (RL = 0.009 µg/L) was used to estimate the persistence times of D4 and D5. Maximum ranges for D4 and D5 in various media as reported by Wang, et al (2012) were used to conservatively estimate the initial concentrations. D4 concentrations observed in air, water and soil-sediment were reported at 6.226, mg/m³, 1.1 µg/L and 9.5 µg/g, respectively. Similarly, D5 concentrations were reported at 1.275 mg/m³, 0.41 µg/L and 0.21 µg/g in air, water and soil-sediment, respectively. **Fig 5.5** presents the estimated persistence times (days) for D4 and D5 to reach an RL of 0.009 µg/L in the different media based on the first order kinetics and siloxane concentrations reported by Wang et al. (2012).

Fig. 5.4 Change in concentrations of D4 and D5 in the environment: a. D4, b. D5.

Fig. 5.5. Persistence times of D4 and D5 to reach MDL of 0.009 µg/L in different media.

5.5.3 Current and projected quantities

Current and projected quantities of D4 and D5 which can be released from municipal solid waste landfills and wastewater treatment plants were evaluated on per capita basis.

For the municipal solid waste, analyses were conducted from the fraction of siloxanes in the landfill gas, and their partitioning profiles between gas and solid and liquid phases for the per capita solid waste generation rate of 3.18 kg/day (average for US). The calculations were performed for the projected increases of siloxanes in solid waste.

For the waste wastewater facilities, analyses were conducted similarly from the fraction of siloxanes in the biogas at the wastewater treatment facilities, and their partitioning profiles between gas, biosolids and liquid phases for the per capita wastewater generation rate of 378.54 L/day (average for US corresponding to 100 GPD).

The partitioning percentages from Table 5.4 were taken into account to estimate the projected per capita siloxane generation from solid waste and wastewater. The example calculations for the per capita generation rates are provided below:

$$S_p = F_{MSW} \times G_{MSW} \times P_c \quad (4)$$

$$S_p = F_{WW} \times G_{WW} \times P_c \quad (5)$$

where,

S_p : Siloxane projection (g/ca-day)

F_{MSW} : Fraction of siloxane present in MSW (% w/w)

G_{MSW} : Per capita generation of MSW (3.18 kg/day)

P_c : Compartmental partitioning of siloxane to gas phase (Table 4)

F_{WW} : Concentration of siloxane in wastewater (mg/L)

G_{WW} : Per capita generation of wastewater (378.54 liters/day)

Example calculations for D4 are provided below:

$$\begin{aligned} D4 \text{ in MSW} &= 0.00001 \times 3.18 \frac{kg}{capita - day} \times 0.567 \times 1000 \frac{g}{kg} \\ &= 0.0180 \frac{g}{capita - day} \end{aligned}$$

$$D4 \text{ in WW} = 0.00002 \frac{mg}{L} \times 378.54 \frac{L}{capita - day} \times 0.567 = 4.2926 \frac{g}{capita - day}$$

The per capita generation rates in solid waste were estimated for siloxanes (D4 or D5) in MSW ranging from 0.001 to 0.008 % (w/w). For the wastewater, the per capita

estimates were performed based on siloxane concentrations in wastewater influent provided by van Egmond et al. (2012) (D4=0.02 µg/L and D5=32 µg/L). Incremental increases of 0.02 µg/L for D4 and 10 µg/L for D5 were used for future projections.

Tables 5.5 and 5.6 present the estimated per capita quantities that can partition into different phases during the decomposition of MSW or treatment of wastewater.

5.4 Conclusions

Fate and transport analyses were conducted for D4 and D5 based on the partitioning characteristics and first order transformation kinetics after siloxanes enter waste streams. Based on projections, per capita contributions of D4 and D5 in biogas from landfills are relatively small in comparison to digester gas produced at wastewater treatment plants. Due to high volatility, the majority of D4 and D5 end up in biogas during decomposition reactions. D5 is about ten times more likely to partition into the solid phase. D5 detection levels in wastewater influent and biogas are about 16 and 18 times higher respectively than D4.

Table 5.5 D4 per capita generation projected in different media

Municipal Solid Waste (g/capita-day)					Wastewater Treatment Plant (g/capita-day)				
D4 ^a (% w/w)	Biogas	MSW/soil	Leachate	Sediment ^c	D4 ^b (mg/L)	Biogas	Soil ^d	Water	Biosolids
0.001	0.0180	0.0012	0.0004	0.0122	0.00002 ^e	4.2926	0.2831	0.0878	0.0878
0.003	0.0541	0.0036	0.0011	0.0366	0.00004	8.5853	0.5663	0.1756	0.1756
0.005	0.0902	0.0059	0.0018	0.0611	0.00006	12.8779	0.8494	0.2635	0.2635
0.008	0.1442	0.0095	0.0030	0.0977	0.00008	17.1706	1.1326	0.3513	0.3513

^a percent in MSW (w/w)

^b influent concentration to wastewater treatment plants

^c can be added to MSW/soil fraction

^d can be added to biosolids

^e concentration in wastewater treatment plant influent (van Egmond et al., 2012)

Table 5.6 D5 per capita generation projected in different media

Municipal Solid Waste (g/capita-day)					Wastewater Treatment Plant (L/capita-day)				
D5 ^a (% w/w)	Biogas	MSW/soil	Leachate	Sediment ^c	D5 ^b (mg/L)	Biogas	Soil ^d	Water	Biosolids
0.001	0.0064	0.1280	0.0640	0.0033	0.0003 ^e	72.6797	2.2712	1.1356	1.1356
0.003	0.0192	0.3840	0.1920	0.0099	0.0004	96.9062	3.0283	1.5142	1.5142
0.005	0.0320	0.6400	0.3200	0.0165	0.0005	121.1328	3.7854	1.8927	1.8927
0.008	0.0512	1.0240	0.5120	0.0264	0.0006	145.3594	4.5425	2.2712	2.2712

^a percent in MSW (w/w)

^b influent concentration to wastewater treatment plants

^c can be added to MSW/soil faction

^d can be added to biosolids

^e concentration in wastewater treatment plant influent (van Egmond et al., 2012)

5.4 Conclusions

Fate and transport analyses were conducted for D4 and D5 based on the partitioning characteristics and first order transformation kinetics after siloxanes enter waste streams. Based on projections, per capita contributions of D4 and D5 in biogas from landfills are relatively small in comparison to digester gas produced at wastewater treatment plants. Due to high volatility, the majority of D4 and D5 end up in biogas during decomposition reactions. D5 is about ten times more likely to partition into the solid phase. D5 detection levels in wastewater influent and biogas are about 16 and 18 times higher respectively than D4.

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6. A Multiphase Analysis of Partitioning and Hazard Index Characteristics of Siloxanes in Biosolids (published in Ecotoxicology and Environmental Safety)

6.1 Introduction

Siloxanes are progressively being used in consumer products in the manufacture of furniture, cookware, cosmetics, electronics, and medical devices among others (Zhang et al., 2010) due to their hydrophobic and antimicrobial properties. They exhibit qualities such as ease of spreadability (for surface applications), increased absorption, high flexibility, and heat resistance. Additionally, they are being utilized in food industry as an oil substitute, allowing for the development of alternative low calorie food products such as potato chips and condiments (i.e. salad dressing, mayonnaise)(Jankoski, 2013).

Siloxanes have been detected beyond landfill boundaries in air samples, indicating they are partitioned between phases and transported via wind currents. At complete combustion conditions of siloxanes, silicon dioxide forms as the byproduct. Both silicon dioxide and other siloxanes can deposition on engine parts causing abrasion, in-turn inhibiting heat conduction and lubrication problems. To limit the effects of silicon dioxide deposition, additional gas treatment systems can be installed or maintenance practices need to be increased to remove the deposits before they result in significant performance loss. Currently there are no state or federal promulgated methods for siloxane quantification; however, several suitable methods for sampling procedures have been established (Pierce, 2011; Arnold, 2009).

The purpose of this study is to evaluate the release mechanisms of dominant siloxanes in waste streams, quantify current emissions, and investigate potential hazards

due to increasing emission levels. Octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) have been noted to constitute a large majority of total siloxanes detected in biogas and waste streams and have become a concern due to bioaccumulation potential and persistence (Sanchis, et al., 2013; Wang et al. 2013a; Yucuis et al., 2013; Badjagbo et al., 2010). However, one study providing contrasting results, indicated that D7 and D5 were the dominant cyclic siloxanes found in sediment and sludge while L10 and L11 combined accounted for 55% of the overall concentrations found in sludge samples (Zhang et al., 2010).

Biogas monitoring results from a wastewater treatment plant in Miami, Florida, validated that concentrations of D4 and D5 were prominent. First order kinetics was used to develop persistence profiles for these compounds in conjunction with their bioaccumulation potential post-digestion. Expected concentrations and the risk factors for exposure to siloxanes have been evaluated in different environmental compartments (gas, liquid, sludge). Comparison sites located in Greece and China were utilized to estimate sludge-water partitioning rates based on the reported data in the literature (Bletsou et al., 2013; Xu et al., 2013). Although characteristics of sewage sludge may differ, the air/water and sludge/water partition coefficients were assumed to be similar based on the individual compounds evaluated and the relatively small composition of siloxanes in contrast to other compounds found in wastewaters. Henry's law was used to estimate partitioning from gaseous phase to aqueous phase.

Bioaccumulation of siloxanes in biosolids due to low solubilities, may impact land applications. Persistent siloxanes present in materials used for land application may cause increased hazard potential by either increasing concentrations in solid phase or in

gaseous phase during subsequent volatilization. Cyclosiloxanes have been connected to disruption of the endocrine system and connective tissue disorders as well as adverse immunologic responses in laboratory animals exposed to the compounds (Granchi et al. 2005; Lieberman et al., 199; Quin et al., 2007; Zhang et al., 2010). In rats exposed at large doses, an increased liver weight and decreased ovary weight has been noted (Burns-Naas et al., 1998, 2002; Zhang 2010). Biogas and sludge concentrations for post-digester levels were estimated and taken into account for estimation of hazard potential and subsequent effects on agroecology.

6.2 Background

Synthetic volatile methylsiloxanes (VMS) are becoming more prominent in landfill and digester gas. Siloxane monitoring is generally not conducted for characterizing gas streams because they are not subject to air quality standards. Currently there are no state or federally promulgated methods for quantification of siloxanes exists. However, several methods for gas sampling suitable for determination of siloxane levels have been developed (Ortega et al, 2009; ALS Environmental, 2013).

Siloxanes affect the performance efficiency of the power-generating turbines. Preventing siloxanes and/or silicon dioxides from reaching turbines would reduce mechanical wear of turbines and particulate build up on boilers. As deposits accumulate, engine efficiency decreases which results in detonation in the combustion chambers. Unburned fuel contaminates the exhaust gas which may increase overall emissions. Without proper maintenance, severe damage can occur to valves, pistons, liners, cylinder heads, spark plugs and turbochargers, imposing downtime and costly repairs. Damage

from siloxanes can cost a 5 MGD wastewater treatment plant with a generator engine approximately \$60,000 per year or more (Tower et al., 2006).

6.2.1 Commonly encountered siloxanes

The most common siloxanes detected in landfill gas (LFG) have been reported to be trimethylsilanol, octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) for landfill gas (Badjagbo et al, 2010). Biogas observations indicate that both D4 and D5 were commonly encountered; however, trimethylsilanol was not (ALS Environmental, 2013). D4 has been listed by the U.S. Environmental Protection Agency (USEPA) for safety being considered both persistent and bioaccumulative (Bletsou et al., 2013). Dodecamethylcyclohexasiloxane (D6) concentrations have recently been added to the list of commonly encountered siloxanes. **Table 6.1** provides the chemical formula and molecular weights for Octamethyltrisiloxane (L3), hexamethylcyclotrisiloxane (D3), D4, D5 and D6 siloxane compounds, which were detected at the highest concentration at the South Dade Landfill (Miami, Florida).

6.2.2 Site Description

The Miami-Dade County's South District Wastewater Treatment Plant (SDWTP) is comprised of wastewater treatment processes that were constructed in the 1970's and prior. It serves nearly 2.3 million residents, treats 300 million gallons of wastewater per day (MDWSD, 2013). The treated wastewater is disposed via deep well injection (3,000 feet) into the confined aquifer. Currently, the plant's capacity is 225 MGD and is capable of treating peak wastewater flows of 690 MGD (Wang, 2013). Raw wastewater goes

Table 6.1 Properties of selected volatile methyl siloxanes: L3, D3, D4, D5 and D6.

Compound	Abbreviation	Formula	Molecular weight (g/mol)	Vapor pressure^a at 25 °C (kPa)	Water solubility^a at 25 °C (mg/L)	Boiling point (°C)^e
Octamethyltrisiloxane	L3	C ₈ H ₂₄ O ₂ Si ₃	236.5	0.52 ^b	0.05 ^c	153
Hexamethylcyclotrisiloxane	D3	C ₆ H ₁₈ O ₃ Si ₃	222.46	1.147	1.56	135
Octamethylcyclotetrasiloxane	D4	C ₈ H ₂₄ O ₄ Si ₄	296.61	0.132	0.056	175.5
Decamethylcyclopentasiloxane	D5	C ₁₀ H ₃₀ O ₅ Si ₅	370.77	0.023	0.017	210
Dodecamethylcyclohexasiloxane	D6	C ₁₂ H ₃₆ O ₆ Si ₆	444.9	4.6 ^d	0.005 ^d	245 ^d
a. Schweigkofler (2001)		c. Pierce (2011)		e. Soreanu et al., 2011		
b. Venture Technical Brief (2009)		d. ECHC, 2011				

through the conventional treatment of physical separation processes, biological treatment for dissolved converting organic matter to biosolids and neutralization prior to disposal or reuse. Treated wastewater is disinfected prior to disposal.

With respect to utilization of biosolids for land application, characteristics of sewage sludge are dependent on the quality of the sewage effluent and any subsequent treatment technologies (Singh et al., 2008). Biosolids are used as fertilizers due to the rich organic nature and nutrients. Usage of biosolids may eliminate the need for commercial fertilizers; however, with accumulation of siloxanes, impacts may become evident. Increased soil microbial activity resulting from sewage sludge amendments will impact soil respiration and enzyme activity (Banerjee et al., 1997). Agricultural soil application of biosolids may become arduous, due to the increasing levels and bioaccumulation potential of toxic compounds (Kulling et al., 2001; Bingham et al, 1975; Lopez-Mosquera et al., 2000).

6.3. Methods

6.3.1 Sampling

Gas sampling was conducted for siloxane analyses were conducted at the SDWTP. Specially prepared silicone tubing was utilized for biogas collection. Because samples were collected in tubes instead of methanol solutions, tedlar bags, or impingers; they did not represent a hazardous material or dangerous goods. Hold times for sorbent tubes are said to be approximately 14 days (ALS Environmental, 2013). The silicone tubing was secured into both sides of a T-fitting with one side being connected to the gas line and the other to a calibration tube. The slip stream was placed at the lowest point of the sampling

train to prevent water build-up within the sample. A rotameter was used to calibrate and adjust a flow rate of 0.2 liters per minute. The sample time was 30 minutes in order to obtain a volume of 6 liters.

The analysis of siloxanes was conducted by a third-party contractor using gas chromatography/mass spectrometry (GC/MS) to identify and quantify siloxane concentrations. A treated carbon tube was used for collection of samples and was subsequently extracted and analyzed using lab-developed method on GC/MS. The method utilized is applicable to siloxanes ranging from low ppbV to high ppmV concentrations. The sampling volume is directly related to ambient conditions at the test site. Specially prepared SPE cartridges combined with the high sensitivity and selectivity of the GC/MS ensures robust and accurate detection. Sample volumes up to 30 Liters at flow rates of 0.5 liters per minute have not indicated breakthrough. Storage of samples are stable at a temperature of 4C for up to 14 days. .

The National Environmental Laboratory Accreditation Program (NELAP) has established criteria including instrument tuning and calibration as well as second source standards verification, continuing calibration verification, laboratory control standards and duplicates and methods blanks which was followed by the laboratory contracted to perform analytical procedures. Additionally, OSHA's Organic Chemicals Air Sampling and Analysis Guidelines were adhered to for validation of sorbent-based methods. Method parameters such as sampling rate, volume, recoveries, field samples and field samples "over-spikes" were validated by the contracted laboratory conducting analysis.

6.3.2 Estimating concentrations in air, water and biosolids

Siloxane partitioning between gaseous and liquid phases were analyzed utilizing Henry's dimensionless constant as demonstrated in Equations 1 and 2. For the equilibrium conditions, the concentrations in gas, water, sludge can interchangeably be estimated, assuming the linear form of the Freundlich isotherm, as follows (Kuo, 1999):

$$H^* = (H / RT) \cdot 1000 \quad (1)$$

$$C = G / H^* \quad (2)$$

$$X = K C \quad (3)$$

where,

H^* : dimensionless Henry's constant;

H : Henry's constant (atm-m³/mole);

T : Temperature (Kelvin);

C : Liquid phase concentration (µg/L);

G : Gas phase concentration (µg/m³);

X : Concentration in biosolids (µg/Kg);

K : Biosolids-liquid partition coefficient (L/Kg).

Table 6.2 provides the concentrations reported for the gaseous phase. Liquid phase concentrations were first estimated using the air-water partition coefficients and subsequently the biosolids concentration was determined using the estimated aqueous phase concentration and sludge/water partition coefficients (L/Kg) as calculated from the

ratios of the sludge to liquid phase concentrations (Xu et al., 2013; Bletsou et al., 2013). Henry's constants were determined by taking ratio of vapor pressure to solubility for each compound studied.

First order kinetics was used for the reactions taking place within each environmental compartment (liquid, gas, biosolids). Half-lives for L3 (linear), and D3-D6 (cyclic) siloxanes were obtained from literature review (Xu et al., 2007; Atkinson, 1991; ECHA, 2013; Van Egmond et al., 2012; Kennedy, 2011; Brooke et al., 2009; Vesterager et al., 2004; Wang et al., 2013b; Steward et al., 1979; ECHC, 2013; Markgraf et al., 1997). Based on maximum sludge concentrations encountered and half-lives, the reaction rate constant was calculated. The first-order equation as per Kuo (1999) is as follows:

$$\gamma_i = dC_i/dt = -k C_i \quad (4)$$

where,

γ_i : rate of conversion of species i (mg/L-d)
 k : reaction rate constant (d^{-1})
 C_i : concentration of species i (mg/L)

The half-life for L3 was reported in terms of relative humidity; therefore, the local relative humidity of Miami was used to extrapolate the half-life from the data. Reaction rates for each compound in the three different environmental compartments (gas, liquid, and biosolids) were calculated with the exception of D3 for biosolids. There was no data available in the literature for the reaction rate for D3 in soil/sludge phase. Degradation of D3 has been reported to be minimal in the anaerobic tanks so the main process for disappearance of D3 is expected to be via mass transfer by volatilization (ECHA, 2013).

Table 6.2 Measured gas phase concentrations and estimated concentrations for liquid phase and biosolids for D4 – D6 siloxanes for the SDWWTP

Compound	Abbr.	Liquid concentration ($\mu\text{g}/\text{m}^3$)	Gas concentration ($\mu\text{g}/\text{m}^3$)	Biosolids concentration ($\mu\text{g}/\text{Kg}$)
Octamethyltrisiloxane	L3	0.21	300	0.17
Hexamethylcyclotrisiloxane	D3	7.79	520	2.95
Octamethylcyclotetrasiloxane	D4	10.20	5,000	6.01
Decamethylcyclopentasiloxane	D5	1.33	1,800	0.83
Dodecamethylcyclohexasiloxane	D6	16.55	98	9.40

An assessment of degradation of siloxane compounds over time was utilized to establish a hazard index. The maximum concentrations calculated and partitioned into gas, water and biosolids were assigned a risk factor of 1 being the lowest and 5 being the highest. Degradation rates were assigned a similar index: 1 being the most rapid degradation (least persistent) and 5 being the slowest degradation (most persistent). A product of the two indices was used to determine the accumulation risk based on initial local concentrations, estimated partitioning and expected persistence of the target compounds.

6.4 Results

Concentrations were evaluated based on equilibrium conditions for three environmental compartments: atmosphere, water and biosolids. **Table 6.2** provides the measured gaseous phase concentrations as well as the estimated concentrations partitioned into water and biosolids based on partitioning characteristics. Degradation curves have been developed assuming first order kinetics and utilizing the previously mentioned parameters. The persistence of L3, D3, D4, D5, and D6 siloxanes are presented in **Fig. 6.1** below for aqueous phase, gaseous phase and biosolids. D5 demonstrates the fastest degradation rate in aqueous phase, D3 in gaseous phase and D6 in solids. L3 is the most persistent in aqueous phase due to its initial concentration, reaction rate of 0.051day^{-1} and high sludge/liquid partition coefficient, calculated at 846 L/Kg based on concentrations reported by Bletsou et al. (2013)., whereas D6 persists

Fig. 6.1 Persistence of L3, D3, D4, D5 and D6 siloxanes in different phases; a. aqueous phase, b. gaseous phase, c. biosolids

more in gaseous phase and D4 in solids. The estimated duration 90% removal time, for each compound, with the exception of D3 in solids, is provided in **Table 6.3**. D3 in anaerobic tanks is expected to have minimal degradation.

Table 6.3 Estimated duration for 90% removal of L3, D3, D4, D5 and D6 in different phases

Compound	Abbr.	Time for 90% removal (days)		
		Liquid	Gas	Biosolids
Octamethyltrisiloxane	L3	45.5	29.1	17.2
Hexamethylcyclotrisiloxane	D3	1073.3	99.6	NA
Octamethylcyclotetrasiloxane	D4	149.4	36.5	15.6
Decamethylcyclopentasiloxane	D5	2256.9	23.2	36.8
Dodecamethylcyclohexasiloxane	D6	1330.9	19.9	597.4

The presence of siloxanes in sludge has been reported in Athens, Greece and northeast China (Bletsou et al., 2013; Zhang, et al., 2011) and has been compared with results estimated in this study based on partitioning coefficients. L3 and D3 were not reported in China and D7 was not reported in our study. Overall comparison suggests mean concentrations of siloxanes in Miami, FL are significantly lower than Greece and China in biosolids as shown in **Table 6.4**.

Table 6.4 Mean siloxane concentrations in biosolids

Compound	L3	D3	D4	D5	D6	D7	Location
Concentration [mg/kg]	0.0002	0.003	0.006	0.0008	0.009	NR	Miami, FL ^c
	0.22	0.009	0.11	15.1	5.03	0.8	Athens, Greece ^d
	NR	NR	0.0621	0.296	0.135	0.332	northeastern China ^e
	ND	0.108	1.096	1.705	1.509	NR	Beijing, China ^f

a. NR: not reported

b. ND: not detected

c. Evaluated partitioning from gas phase measured in this study

d. Bletsou et al, 2013

e. Zhang et al., 2011

f. Xu et al., 2013

Fig. 6.2 compares the estimated hazard potentials of the siloxanes present in different phases during wastewater treatment based on the data collected from the South Wastewater Treatment Plant in Miami, Florida. Varying initial concentrations have a significant effect in determining potential hazards. Because D3 is expected to have minimal anaerobic degradation, its hazard was ranked highest in the biosolids phase. In both liquid and biosolids, D4 has the largest exposure risk in Miami, Florida whereas D5 poses the highest risk gas phase. The lowest estimated exposure risks correspond to D5 within liquid phase, D3 in gas phase and L3 in biosolids.

Fig. 6.2 Estimated hazard potential in Miami for L3, D3, D4, D5 and D6 siloxanes in water, gas and biosolids

6.5. Conclusions

The multiphase analysis and persistence characteristics of siloxanes in different phases allow comparison of the relative hazard potentials and exposure risks to the siloxanes present in wastewater based on their partitioning and fate during wastewater treatment. The relative hazard potentials of the siloxanes were estimated based on their initial concentrations, projected degradation and partitioning characteristics between air, water and biosolids. The commonly found siloxanes include L3, D3, D4, D5 and D6 siloxanes. Although D5 has a high Henry's constant which allows for volatilization, its degradation rate is slowest in gaseous phase contributing to its high exposure risk. The elevated exposure risk for D4 in water is attributed to both the slow hydrolysis reaction

rate and low solubility. D4 exposure risks in biosolids can be attributed to the high sludge/water partition coefficient and low kinetic reaction rate.

For land application of biosolids, D3 and D4 siloxanes present the greatest hazard. Bioaccumulation of these compounds can become detrimental to usage of biosolids as an alternative to fertilizers. The addition of amendments targeting D3 and D4 siloxanes may become necessary as a pretreatment prior to land application. A thorough analysis of products contributing to the disparity of initial concentrations is necessary to determine the possible impact of additional confounding variables.

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7. Contribution of siloxanes to COD loading at wastewater treatment plants: Phase transfer, removal, and fate at different treatment units (Published in Chemosphere)

7.1 Introduction

Cyclic volatile methylsiloxanes (cVMSs) are among the most common siloxanes found in personal care products. Dimethicone, also known as polymethylsiloxane, is an ingredient listed on many common cosmetics products such as anti-aging creams, functioning as an antifoaming, skin conditioning agent (Surita and Tansel, 2014a). Octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) are high production compounds that display chemical characteristics capable of bioaccumulation (EC, 2001; Kierkegaard, 2011; CECBP, 2008). Environment Canada (EC) has taken the position that D5 is a bioaccumulative chemical based on evidence from 15 bioaccumulation metrics (EC, 2008). In an SGB meeting held December 4-5, bioconcentration factors for D4 were given as 12,400 L/kg, and greater than 5,000 for both D5 and D6 (CECBP, 2008). Because of their high vapor pressure and low solubility, siloxanes volatilize throughout the treatment system during wastewater treatment. Significant siloxanes levels are found in the biogas from the anaerobic digesters indicating that siloxanes are partitioning to sludge stream (i.e., biosolids) (Surita and Tansel, 2014b).

Table 7.1 below presents selected properties of D4, D5, and D6. High Henry's constant indicated higher volatility. Atmospheric half-lives of D4, D5, and D6 are reported as 10, 20, and 1.6 days, respectively (Wang et al., 2012, Surita and Tansel, 2014a). The half-lives of D4 and D5 were estimated assuming a specified tropospheric concentration of hydroxyl radicals (7.7×10^5 molecules per cubic centimeter over one

day period) and first order kinetics (Wang et al., 2012). MacLeod et al. (2013) estimated the half-life of D6 utilizing the Junge relationship from the GAPS dataset. The Junge relationship was derived from the spatial and temporal variability of gas phase concentrations and residence times in conjunction with empirical data (MacLeod et al., 2013). D4 and D5 are likely to undergo atmospheric transport by wind current offsite due to their slower degradation rates.

Because siloxanes have relatively high half-lives, they can contribute to COD loadings in influent and effluent. When siloxanes are degraded or oxidized, dissolved oxygen (DO) is decreased and affecting the quality of receiving water bodies. Chemical oxygen demand (COD) measures the amount of oxygen necessary for chemical oxidation of wastes, whereas biochemical oxygen demand (BOD) measures oxygen demand for biological degradation by microorganisms.

The purpose of this study was to evaluate the fate and removal of selected cyclic siloxanes during wastewater treatment. The siloxanes studied were D4, D5 and D6 which are the most commonly found cVMSs in the wastewater. Removal efficiencies of the wastewater treatment units were evaluated based on the partitioning characteristics of the cVMSs in gas, liquid, and biosolids phases. Adsorption is not significant for compounds when $\log K_{OW}$ is less than 4; however D4, D5, and D6 siloxanes have $\log K_{OW}$ values greater than 4 as reflected in **Table 1**. The contributions of the siloxanes present in the influent and effluent were estimated in terms of COD levels based on the theoretical oxygen demand of the siloxanes.

Table 7.1 Selected properties of D4, D5 and D6.

Property	D4	D5	D6
Chemical formula	C ₈ H ₂₄ O ₄ Si ₄	C ₁₀ H ₃₀ O ₅ Si ₅	C ₁₂ H ₃₆ O ₆ Si ₆
Molecular weight (g/mol)	296.6	370.8	444.9
Density (g/cm ³ at 25°C) ^a	0.95	0.954	0.963
Henry's constant (Pa·m ³ /mol at 25°C) ^a	1,214,000	3,342,000	14,667
Water solubility (µg/L at 25°C) ^b	56.2	17	5
Atmospheric half-lives (days)	10 ^c -15.8 ^d	6.9 ^e -60 ^f	2.6–12.8 ^d
Air-water partition coefficient (K _{AW})	2.69 ^g - 2.72 ^h	3.13 ^g - 3.16 ^h	0.80 ^h - 3.01 ^g
Soil-water partition coefficient (K _{SW}) ⁱ	3.38	3.71	3.25
Octanol-water partition coefficient (K _{OW}) ^j	6.98	8.07	8.87

^a CES, 2014

^b Wang et al., 2012; Varaprath et al., 1996

^c Wang et al., 2012

^d EA, 2009

^e Atkinson (1991)

^f MacLeod et al., 2013

^g Wang et al., 2012; Xu and Kropscott, 2012

^h Calculated from Henry's constant

ⁱ Bletsou et al., 2013

^j Xu and Kropscott, 2012

7.2. Methods

7.2.1 Partitioning from liquid phase

The air-water partition coefficient (K_{AW}) was estimated using Henry's constant as provided in the literature and dividing by the universal gas constant (in appropriate units) and respective temperature (K). Equations 1 through 3 (LaGrega et al., 2001) were utilized to determine the expected concentration in the gas phase after volatilization from liquid phase concentrations. **Table 1** provides the reported K_{AW} (Xu and Kropscott, 2012) and calculated K_{AW} based on compound characteristics. Additionally biosolids-water partitioning coefficients (K_{SW}) were obtained from the literature as 3.39, 3.71 and 3.25 for D4, D5 and D6 respectively (Bletsou et al., 2013). Utilizing this coefficient, we then estimated the concentration in biosolids as indicated in equation 3.

$$H^* = H/RT \times 1000 \quad (1)$$

$$G = H \times C \quad (2)$$

$$K_{SW} = X/C \quad (3)$$

where,

H^* : Henry's Constant (dimensionless)

H : Henry's constant (atm-m³/mole)

T : Temperature (K)

C : estimated concentration in liquid phase (mg/L)

G : measured concentration in gas phase (mg/L)

K_{SW} : partition coefficient (ratio of concentration in biosolids to concentration in liquid phase)

X : estimated concentration in biosolids (mg/kg)

7.2.2 Chemical Oxygen Demand

Silicon dioxides forms when siloxanes are completely oxidize as illustrated by equations 4 through 6 below for D4, D5 and D6, respectively (Tansel and Surita, 2014). The theoretical oxygen demand (ThOD) was used to estimate the COD for D4, D5 and D6.

7.2.3 Wastewater treatment process

The levels of siloxane-based COD were estimated based on the field study conducted at a wastewater treatment facility in Broadholme, United Kingdom by van Egmond et al. (2012). **Fig. 1** presents the general flow diagram of the treatment processes. The locations of the samples collected from different treatment units and locations reported by van Egmond et al. (2012) are also indicated in the figure. All measurements were reported in liquid phase ($\mu\text{g/L}$) with the exception of the primary settled sludge which was measured on dry weight basis as mg per kg. The concentrations reported in **Fig. 1** are the means of two sampling events conducted on different dates at the test site. The available liquid concentrations for siloxanes were used to estimate gas phase concentrations and removal efficiencies and extent of partitioning into the gas

phase during the treatment processes as well as extent of partitioning into the siloxanes into biosolids.

Fig. 7.1 Schematic of the wastewater treatment plant tracks and respective cVMSs, D4, D5 and D6 reported (µg/L)(adapted from van Egmond et al., 2012).

7.3 Results

7.3.1 Estimated partitioning between phases

Fig. 7.2 illustrates the minimum liquid phase concentrations for D4, D5 (0.01 and 0.141 µg/L respectively) which were found at the trickling filter post sand filter; however D6 concentrations presented slightly higher in the trickling filter (0.057 µg/L) than the

activated sludge channel settlement tank and oxidation tank channel effluent, 0.038 and 0.03 $\mu\text{g/L}$ respectively. The maximum concentrations for all three cyclic siloxanes evaluated were found in the activated sludge channel aeration tank as demonstrated in **Fig. 7.2**. This is indicative that a majority of cyclic siloxanes (approximately 99%) either sorb to the solids or volatilize during sludge aeration passing through the sludge settling tank. This supports a study by Parker et al. (1999) in which it was suggested that cyclic siloxanes are removed from wastewater via sorption to solids.

Using the partitioning coefficients calculated from Henry's constant and individual compound characteristics, the gas phase concentrations were estimated. The log concentrations of these estimates are illustrated in **Fig. 7.2** below. Gas phase estimates for D4, D5 and D6 siloxanes were highest in the activated sludge channel aeration tank. D4 and D5 were both estimated in lowest concentrations at the trickling filter, however D6 was estimated lowest in the oxidation tank channel effluent. This demonstrates the high molecular weight and lower solubility and Henry's constant for D6 prevents volatilization until aeration of sludge is provided. The particular treatment system investigated eliminates the bulk of the cyclic siloxanes D4, D5, and D6 in gas phase at 94.5, 98.5 and 98.1 percent respectively.

Additionally concentrations were estimated in biosolids based on partitioning coefficients between solid and liquid phases extracted from a study conducted in Athens, Greece (Bletsou et al., 2013). These estimates are provided in **Fig. 7.2** and demonstrate that each track of treatment units reduces overall concentrations of cyclic siloxanes D4, D5 and D6 to less than 1 mg/kg with the exception of the bypass primary settled sludge

which receives no further treatment in this study. It has been estimated that approximately 50% of cyclic siloxanes (D4, D5 and D6) entering the wastewater stream end in biosolids.

The estimated gas phase D6 siloxanes taper off in opposition to the liquid phase throughout the treatment train. D4 siloxanes exhibit the opposite phenomenon. In all cases and in both phases, the D5 siloxanes appear in highest concentration. Because of extremely high Henry's constant, it can be said that the D5 compounds present during activated sludge channel aeration are volatilized.

Fig. 7.2 Concentrations of cyclic volatile siloxanes from a sewage plant located in Broadholme (R. van Egmond et al., 2012) in alternative tracks; a. measured in liquid phase, and estimated in b. gas phase and c. solids phase.

7.3.2 Estimated siloxane-based COD loading

COD contributions were estimated in different treatment units utilizing concentrations reported from the Anglian Water's Broadholme sewage treatment plant in England (R. van Egmond et al., 2012). The sample calculation is provided in **Table 7.2** for the primary settled sludge treatment unit. In this unit, concentrations were measured in dewatered sludge versus the typical liquid measurement therefore the aqueous phase concentration was estimated. All of the other measurements were taken from liquid phase and theoretical oxygen demand was calculated directly. Typically in wastewaters, the BOD values are around 30 to 80 percent of the COD depending on wastewater type. This study utilizes the conservative value of 80 percent. **Table 7.3** provides measured siloxane concentrations in aqueous phase, estimated concentrations in gas phase and biosolids as well as estimates for the COD contribution in each treatment unit. **Fig. 7.3** illustrates the estimated siloxane-based COD loading following treatment within each unit track. The cumulative D4, D5 and D6 siloxane contributions for tracks 1, 2, and 3 respectively are 0.076, 39.103 and 0.029 mg/L. Considering a mass balance approach for cumulative D4, D5 and D6 concentrations, Track 1, Track 2 and Track 3 contributions are estimated at 0.5%, 61% and 1.7%.

Table 7.2 Sample calculation for estimating COD and BOD loading due to siloxanes in primary sludge solids.

Parameter	Siloxane		
	D4	D5	D6
Solids concentration in dewatered sludge (mg/kg) ^a	10.0	47.6	22.1
Siloxane concentration (mg/L)	2.96	12.83	6.80
O ₂ required (moles/mole siloxane)	16	20	24
Molecular weight (g/mole)	296.6	370.8	444.9
COD (mg/L) ^{b,c}	5.11	22.15	11.74
BOD (mg/L) ^d	4.09	17.72	9.39

^a van Egmond et al., 2012

^b COD (mg/L) = Siloxane concentration (mg/L) × ThOD

^c ThOD calculated for D4, D5 and D5 was 1.73

^d BOD/COD approximated at 0.8

Table 7.3 Measured and estimated concentrations of siloxanes (D4, D5, D6) at treatment units during wastewater treatment.

Treatment Unit within Track		Measured liquid phase concentration (µg/L)			Estimated gas phase concentration (mg/m ³)			Estimated biosolids concentration (mg/kg) ^b			COD (mg/L)		
		D4	D5	D6	D4	D5	D6	D4	D5	D6	D4	D5	D6
Track 1	Oxidation tank	0.98	38.5	4.22	479.25	51,830.39	24.93	3.31	142.84	13.72	0.002	0.066	0.007
	Final clarifier	0.02	0.2	0.03	8.56	275.31	0.17	0.06	0.76	0.09	-	-	-
Track 2	Primary settling tank	0.2	10.03	3.8	97.81	13,502.83	22.45	0.68	37.21	12.35	-	0.017	0.007
	Aeration tank	1.53	43.2	6.21	748.22	58,157.73	36.69	5.17	160.27	20.18	0.003	0.075	0.011
	Settlement tank	0.01	0.24	0.4	5.72	317.04	0.23	0.04	0.87	0.13	-	-	-
	Primary sludge ^a	2.96	12.83	6.8	1,446.8 4	17,272.56	40.18	10	47.6	22.1	5.107	22.14	11.73 8
Track 3	Primary settling tank	0.2	10.03	3.8	97.81	13,502.83	22.45	0.68	37.21	12.35	-	0.017	0.007
	Trickling filter bed	0.2	1.63	0.46	97.81	2,193.81	2.70	0.68	6.05	1.48	-	0.003	0.001
	Final clarifier	0.01	0.29	0.11	4.89	395.12	0.66	0.03	1.09	0.36	-	0.001	-
	Sand filter	0.01	0.16	0.07	5.62	220.78	0.39	0.04	0.61	0.21	-	-	-

Fig. 7.3 Estimated siloxane-based COD loading (mg/L) during treatment.

With stringent water quality regulations that limit effluent to BOD to 20 mg/L, siloxanes should be monitored to ensure that siloxane-based COD does not contribute to the effluent BOD. Analyses conducted show that siloxane-based COD in the effluent is relatively small. However, for systems bypassing treatment, with primary settled sludge, siloxane-based COD levels can be substantially high. The biosolids that may be further utilized as fertilizer have the potential to bioaccumulate. Additionally, co-disposal facilities receiving biosolids as waste will have increased siloxane concentrations that can potential impair energy recovery systems if no additional treatment is considered.

Track 1 consisting of oxidation indicates that siloxane-based COD is almost completely eliminated via oxidation as illustrated in **Fig. 7.4**. Track 2, which consist of aeration and final settling units also had significant removal of siloxane-based COD. However, the sludge from primary settling tank shows a significant increase in siloxane-based COD levels. Siloxane-based COD levels are also decreased during the treatment processed in Track 3 which consists of trickling filter and final clarifier and sand filter.

Fig. 7.4 Siloxane-based COD loading per treatment unit within each track; a. D4, D5 and D6 siloxane based COD loading; b) cumulative cyclic siloxane-based COD loading

Oxidation appears to eliminate D4 and D6 siloxane-based COD loadings while D5 COD loading in significantly smaller concentrations has been noted. D5 and D6 siloxanes appear to persist, therefore contributions to COD loading are anticipated in all other treatments units.

All treatment tracks provided at least 94% removal efficiency of siloxane-based COD in the liquid phase. However, in the sludge phase (biosolids), there is removal but accumulation of siloxanes. In Track 1, the COD due to D4 and D5 was removed entirely (100%) with D5 at 99% removal efficiency. In track 2, D4 was removed at 94% efficiency followed by D5 at 98% and D6 at 99% removal efficiency. In Track 3, COD due to D4 was removed at 100% followed by D5 and D6 both at 98% efficiency.

Accumulation of siloxanes in biosolids can lead to release of siloxanes with biogas during anaerobic digestion process. In the influent distribution channel of the wastewater stream, siloxanes contribute approximately 39 mg/L of COD loading. In the effluent, siloxane levels are negligible, contributing about 0.001 mg/L of the effluent COD.

7.4 Conclusions

As silicon patents continue to increase the presence of cVMSs in our wastewater treatment systems is also rising due to extensive use of “wash-off” products. Having both high vapor pressures and low solubilities, cVMSs are primarily volatilized or sorbed onto biosolids. The purpose of this research is to estimate the response and volatility of cyclic siloxanes (D4, D5 and D6) and to determine siloxane-based COD loadings during various stages of wastewater treatment.

In measured liquid phase and biosolids, as estimated, concentrations of D5 siloxanes surpass those of both D6 and D4. Gas phase cVMSs indicated higher concentrations of D5, subsequently followed by D4 and D6. Siloxane-based COD loading has been estimated to be negligible in active wastewater treatment systems in concentrations near 0.001 mg/L. However in systems utilizing bypass to primary settled sludge, cyclic siloxanes are anticipated to bioaccumulate due to sorption of approximately 50% of the influent siloxanes onto biosolids. Oxidation systems tend to eliminate more siloxane –based COD loading as compared to aeration tanks and filtration systems.

Acknowledgements

Partial funding for this research has been provided by Hinkley Center for Solid and Hazardous Waste Management of University of Florida as well as the Florida International University Graduate School Dissertation Year Fellowship. .

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8. Feasibility of siloxane management at landfill gas to energy facilities: Precombustion gas phase siloxane removal vs. post combustion deposit removal

8.1 Introduction

Utilization of biogas generated from anaerobic digesters and landfills for energy is a sustainable alternative for conventional fuels. Biogas has a heating value of approximately 500 Btu per cubic foot which is half that of natural gas (LMOP, 2009). Landfill gas (LFG) produced by degradation of municipal solid waste (MSW) contains about 40 to 60 percent methane, and 40 to 45 percent carbon dioxide as well as water vapor, nitrogen and small amounts of volatile organic compounds (i.e., hydrocarbons, hydrogen sulfide, and siloxanes). The composition of the biogas varies depending on climate as well as the composition and age of MSW. The estimated biogas yield ranges between 150 and 265 cubic meters per ton of MSW (Asgari et al., 2011; Bhide et al., 1990). Deficiency in mineral nutrients (carbon, oxygen, hydrogen, sulfur, phosphorus, potassium, calcium, magnesium and other trace elements), heavy metals, antibiotics, detergents, pH values below 6.2 have been noted to have inhibitory effects on methane generation (Asgari et al., 2011).

Siloxanes are man-made compounds containing silicon and oxygen with organic side groups (typically methyl groups) attached to the silicon atoms. They can have linear (denoted by L or M nomenclature) and cyclic (denoted by D) structural configurations. Organic side groups give siloxanes their strong hydrophobic properties. Because of their thermal stability, low solubility, hydrophobicity and antimicrobial characteristics, siloxane production and use in consumer products have increased significantly in recent

years. They are used in health care, personal hygiene and industrial products, as well as in paper and construction industry (due to their high water repelling characteristics).

During combustion of biogas, siloxanes form white crystal or amorphous deposits on engine components (engine heads and spark plugs) depending on the temperature. This accumulation affects the engine performance by causing detonation in combustion chambers, and decrease in efficiency of biogas to energy engines (Sevimoglu and Tansel, 2013a, 2013b). Removal of siloxanes prior to incineration is therefore becoming necessary to reduce engine maintenance needs.

Carbon adsorption is one of the most commonly used gas purification technologies. In general, adsorption is higher with higher surface area, pore volume, and pH values (Matsui and Imamura, 2010). Adsorbance of siloxanes by activated carbon depends on the type and concentration of siloxane species, temperature and relative humidity (RH) (Wheless and Pierce, 2004; Ajhar et al., 2010). Sorenau et al., (2010) has suggested that siloxanes can be both polymerized or degraded, therefore, new siloxanes may form based on the composition of the parent compounds and environmental conditions.

Adsorptive capacity of carbon depends on the type of siloxanes present in the biogas. For example, D5 has been reported to be adsorbed on different adsorbents (e.g., activated carbon, molecular sieves, and silica gel) more readily than other siloxane compounds (Seifers, 2010). Ortega and Subrenat (2009) conducted a study on adsorption of siloxanes by four types of media (i.e., activated carbon cloths, granular activated carbon, silica gel and zeolite gel) and observed that D4 was adsorbed more than L2 because of its molecular structure and contact with surface. Porosity of the adsorbent

was also an important factor in siloxane removal by different media. Activated carbon with a total pore volume of $0.670 \text{ cm}^3/\text{g}$ was more efficient in removing siloxane than the silica and zeolite gels which had total pore volumes of $0.2431 \text{ cm}^3/\text{g}$ and $0.328 \text{ cm}^3/\text{g}$, respectively. Adsorption capacity had an inverse relationship with temperature, which may be due to the tendency of siloxanes to volatilize. Humidity content of biogas can also affect the adsorption capacity (Ortega and Subernat, 2009). **Table 8.1** presents the effect of humidity on carbon adsorption process for some gaseous contaminants including hexamethyldisiloxane. The effect of humidity on removal of hexamethyldisiloxane was not significant when compared with other contaminants. The removal efficiency of hexamethyldisiloxane was between 76 and 100% for humidity ranges up to 70%.

Table 8.1 Effects of humidity on adsorption efficiency of activated carbon

Material	Texture	Carbon Properties		Compound Tested	Humidity (%)	Efficiency (%)	References
		Total pore volume (cm ³ /g)	BET surface area (m ² /g)				
FM 30K	Cloth	0.494	1000	Hexamethyldisiloxane (L2)	0	93	Ortega & Subrenat (2009)
NC 60	Granular	0.67	1220	Hexamethyldisiloxane (L2)	70	84	
					0	84	
A-10	Granular	0.69	1720	Trichloroethylene (TCE)	70	76	
					0	100	Miyake et al. (2002)
					50	87.5	
					55	45	
					65	12.5	
					75	10	
SGA-100	Granular		1100-1200	Benzene	0	85	Shin et al. (2001)
					40	62.5	
					60	20	
					90	0	
SGA-100	Granular		1100-1200	Toluene	0	90	Shin et al. (2001)
					40	80	
					60	75	
					90	15	
SGA-100	Granular		1100-1200	Ethylbenzene	0	92.5	Shin et al. (2001)
					40	85	
					60	82.5	
					90	45	

Prabucki et al. (2001) reported on the siloxane removal efficiencies for three methods utilizing activated carbon. One of the methods only uses a heat exchanger to increase the temperature to 35-40 °C, to prevent moisture build up within the adsorption unit. Since the gas is not cleaned prior to the adsorption unit, the operating costs are high. The second method first cools the gas prior to heating; in-turn removing up to 20 to 25 percent of siloxanes with the condensate trapping some of the siloxanes as well as hydrocarbons. The third method uses a freezing procedure to remove up to 90 percent of siloxanes; however, additional electrical power is needed for compressors and discharge equipment for ice production (Prabucki et al., 2011).

The purpose of this study is to compare the economic feasibility of landfill gas-to-energy systems for dealing with the operational challenges due to siloxanes in the landfill gas. Economic analyses were performed to compare the costs associated with the increased maintenance to remove the deposits accumulating on the engine components vs. installation of carbon adsorption systems to remove siloxanes. The effects of temperature and moisture on the siloxane removal by carbon adsorption were accounted for in estimation of the capital and operating costs.

8.2. Methodology

Economic feasibility analyses were performed for two operational practice options for addressing siloxane related operational problems and their management at LFG to energy facilities. These included (1) removal of siloxanes from LFG by carbon adsorption prior to energy generation, and (2) removal of siloxane deposits from engine parts by periodic maintenance after combustion of LFG.

8.2.1 Estimated quantity of siloxanes generated

Siloxane generation varies with location, waste profiles, temperature, humidity, landfill age, and landfill operation practices. The siloxane concentration in LFG is typically reported to be in the range 2 to 81 mg/m³ (Surita and Tansel, 2015). The rate of generation of siloxanes can be estimated from their concentration in the LFG and volumetric flow rate of the LFG. **Fig. 8.1.** presents the estimated quantity of siloxanes from LFG in relation to LFG generation rate and average global total siloxane concentrations (18 mg/ m³) for siloxane levels in LFG between 40% of the average (low), 140% of the average (high).

Fig. 8.1 Estimated siloxane concentration to be removed from LFG based on average concentrations reported globally (Surita and Tansel, 2015) with respect to biogas generated. Low levels correspond to 40% and high levels correspond to 140% the average siloxane concentration in LFG.

8.2.2 Fixed bed adsorption system

For removal of siloxanes from biogas, capital costs for installation of the carbon adsorption system and the operating and maintenance costs associate with the carbon adsorption process were considered. This capital cost is highly variable depending on the manufacturer as noted by Gas Technology Institute (GAS, 2014) even within the same flow rate ranges.

8.2.2.1 Fixed bed adsorption system capital costs

It is difficult to estimate the costs of adsorption system due to the use of different types of adsorbents used and variations in system design. In the early 2000s, the estimated cost was approximately \$40 to \$50 per actual cubic feet per minute (acfm) for a complete carbon-steel packaged unit with instrumentation, condenser, cooler, decanter, fan and flue gas throughput ranging from 5,000 to 10,000 acfm. Cost data from several adsorber installations and vendors were investigated by Vatauvuk (1996) and the following correlation was developed:

$$R_c = 6.98 \times Q^{-0.133} \quad (1)$$

where;

R_c : the ratio of the total adsorber equipment cost to combined cost of the adsorber vessels and contained carbon; and

Q : the flue gas flow, acfm

The adsorber vessel cost (C_v) is associated to its surface area (S), which typically ranges from about 100 to 2100 square feet including heads, as provided by equation 3. Surface area was estimated by the equation 2, which is based on the ratio of the gas inflow rate using linear interpolation between the typical ranges of 97 and 2,110 ft² and

4,000 to 500,000 acfm for surface area and flue gas flow, respectively (Cooper and Alley, 2011).

$$C_v = 420 \times S^{0.778} \quad (2)$$

Carbon beds generally have lengths equal to twice the width (or the diameter of the cylindrical vessel) of the housing the bed. Therefore, diameter is a critical parameter and must be at a minimum. If moderately or highly corrosive flue gas exists, more costly corrosion – resistant alloys will become necessary for adsorption vessel which could increase the relative cost by up to 4.5 times. With the relationships provided in equations 1 and 2, the total adsorption system equipment cost (C_A) can be estimated by equation 4 (Cooper and Alley, 2011). The number of vessels (N_T) required should account for regeneration vessels which minimize down time.

$$C_A = R_C(C_C + N_T \times C_v) \quad (3)$$

where

C_C : the cost of carbon contained within the system (\$1 to \$2 per pound)

Additionally the installed cost factors must be considered when estimating capital costs. Direct costs of equipment include control devices and auxiliary equipment, instruments and controls, taxes and freight. The delivered equipment cost (DEC) are approximately 1.18 times the equipment cost (Equation 4) (Cooper and Alley, 2011). Installation costs include foundations and supports, erection and handling, electrical, piping, insulation, painting, site preparation, facilities; while installation indirect costs include engineering and supervision, construction and field expenses, construction fees,

start-up, performance test, pilot suites and contingencies. Total installed costs (TIC) are about 1.75 times the DEC (equation 5) (Cooper and Alley, 2011).

$$DEC = 1.18 \times C_A \quad (4)$$

$$TIC = 1.75 \times DEC \quad (5)$$

This cost can be annualized by considering its present worth as an ordinary annuity using the following equation:

$$AOC = C_R \left[\frac{i(1+i)^n}{(1+i)^n - 1} \right] \quad (6)$$

Where;

AOC : annualized operating cost, dollars
 C_R : component replacement cost, dollars
 i : annual discrete interest rate
 n : replacement interval, years

8.2.2.2 Operating costs for adsorption systems

Direct operating costs for the carbon adsorption systems included labor hours, supervision, maintenance utilities (electricity, steam, cooling water). For systems requiring periodic replacement, annual costs are included in direct operating costs. **Table 8.2** summarizes the assumptions used for estimating O&M costs.

According to the salary outlook, methane/landfill gas collection system operators earn between \$72,000 and \$108,000 annually (Recruiter, 2015). In the data collected, seven facilities estimated maintenance hours applied for siloxane removal. The cost of steam was estimated as 120% of the fuel cost. Natural gas delivered to consumers in the state of Florida was reported as \$18.46 per thousand cubic feet (US EIA, 2014). The amount of steam required typically ranges between 3 and 4 lbs per pound of VOCs

adsorbed. The cost of cooling water ranges between \$0.15 to \$0.30 per thousand gallons (Vatavuk et al., 1999). Electric power costs can be estimated from the average horsepower requirement of 6 to 8 hp/1000 scfm of gas throughput. The average retail price of electricity to ultimate customers by end use in all sectors was reported as \$10.86 (US EIA, 2014). The average values provided herein were used to estimate the cost of utilities related to operational costs, which include electricity, steam and cooling water.

Since the flue gas flow information was available as standard cubic feet per minute (scfm), conversions to acfm were necessary. The scfm provides the flow in terms of a reference pressure temperature and RH. The most commonly used references are the Compressed Air and Gas Institute (CAGI) and the American Society of Mechanical Engineers (ASME) whereby the pressure, temperature and relative humidity are noted as 14.7 psia, 68°F and 36%, respectively. The conversions account for differences in actual temperature, relative humidity and pressure differences related to elevations change. Equation 7 (White, 2007) provides the conversion.

$$ACFM = SCFM \times \frac{P_S - (RH_S \times PV_S)}{P_b - (RH_a \times PV_a)} \times \frac{T_a}{T_S} \times \frac{P_b}{P_a} \quad (7)$$

where,

P_S : standard pressure (psia) is this 1 atm

P_b : atmospheric pressure – barometer (psia)

R_a : actual pressure (psia)

RH_S : standard relative humidity

RH_a : actual relative humidity

PV_S : saturated vapor pressure of water at standard temperature (psi)

PV_a : saturated vapor pressure of water at actual temperature (psi)

T_S : standard temperature (°R), where °R = °F + 460 is this 460 F

T_a : actual temperature (°R)

Table 8.2 Assumptions for estimation of operating and maintenance costs for carbon adsorption system

Item	Values
Salary for landfill gas technician/operator	\$72,000-\$108,000 per yr
Indirect costs (overhead multiplier for maintenance)	4
Annual maintenance for adsorption system	5% of total installed cost
Operating labor hours	8 hr/d, 5 d/wk
Supervision hours	15% of labor hrs
Taxes and Insurance	2% of TIC
Depreciation	10% of TIC
Mass of carbon	2,400 lbs
Carbon replacement	every 4 months \$2 per lb
HP requirement	6-8 hp/1000 scfm
Cooling water cost	\$0.15-\$0.30 per 1,000 gal
Natural gas	\$18.46 per 1,000 ft ³

For annual operating costs, it was assumed that carbon replacement will occur every 4 months, mass of carbon in a typical adsorption system to be 2,400 pounds, conservatively as indicated in **Table 8.2**. Regeneration of carbon is not considered in this study. For siloxane removal exclusively, a relatively small mass of carbon would be required, typically less than 25 pounds under the specified flow rates. However, the design of adsorption systems relies on other contaminants present in the gas stream including hydrogen sulfide.

8.2.3 Periodic maintenance for removal of siloxane deposits from engine components

Operational data were compiled by survey of seven gas-to-energy facilities for removal/management costs associated with siloxane deposits on engine components. Data obtained from the facilities evaluated did not have a treatment system installed specifically for siloxane removal and did not monitor siloxane emissions. However, many facilities reported that they did routine maintenance for removal of siloxane deposits. Maintenance costs were estimated from a product of hours and typical salary range.

8.3 Results and Discussion

Table 8.3 provides annualized cost estimates for fixed-bed carbon adsorption systems (FBCASs) for facilities 1 through 7 respectively, all of which are located in the continental United States. The additional 6 facilities were not included in this study as the data obtained for comparison purposes were incomplete. Variations in elevation, barometric pressures, temperatures and relative humidity were accounted for at each facility. The conversions demonstrate change from standard to actual flow rates ranging from zero to 2.8 percent. Trends for annualized capital costs of installation of FBCAS are illustrated in **Fig. 8.2**.

Table 8.4 presents the estimated gross operating costs for average technician wage range between \$34.60 per hour (low) and \$51.90 per hour (high). Credit for recovered gases has been excluded in this study.

Table 8.3 Estimated capital cost of fixed-bed carbon adsorption system (FBCAS)

Facility	LFG utilized (acfm)	Cost/LFG utilized (\$/acfm)	Annualized cost (\$/yr)	Annualized cost (\$/acfm-yr)
1	10	76,667	31,200	2,600
2	140	7,279	22,500	170
3	340	2,558	20,000	60
4	560	1,464	18,600	30
5	710	1,128	18,100	30
6	1,100	680	17,100	20
7	2,880	868	18,300	10

Table 8.4 Estimated annual maintenance costs for siloxane removal

Biogas utilized (acfm)	Estimated maintenance hours ^a (hr/year)	Annual maintenance cost ^b (\$/yr)
10	120	20,800 ± 4,200
140	120	20,800 ± 4,200
340	408	70,600 ± 14,100
560	768	132,900 ± 26,600
700	160	27,700 ± 5,500
1,100	1,100	190,400 ± 38,100
2,900	100	17,300 ± 3,500

^a Based on survey results.

^b Based on hourly wages ranging from \$34.60 to \$51.90

Fig. 8.2 Estimated capital costs of fixed bed carbon adsorption system: a. cost per cubic foot of LFG utilized, b. annualized cost per cubic foot of LFG utilized

The maintenance needs for most facilities surveyed ranged between 100 and 800 man-hours per year as presented in **Table 8.4**. Facility 6 provided an extremely high maintenance hours between 8,000 and 11,000 hours annually; however, the maintenance practices included additional maintenance activities which were not related with the siloxane management. Therefore, maintenance hours were scaled down to 10% for this facility in view of the allocated hours for removal of deposits from engine components. **Table 8.4** provides the estimated maintenance cost associated with siloxane removal from engine components based on the aforementioned assumptions. **Fig. 8.2** presents the range of maintenance dollars at each facility surveyed per cubic foot of LFG utilized. From approximately 100 acfm to the highest value of 2,900 acfm, the estimated capital cost remained consistent, ranging from 100 to 1,000 dollars per cubic foot of LFG utilized.

In practice, modifications are made to sorbents to enhance the adsorption and retention of specific compounds. The critical parameters are loading rate of contaminant to be removed and saturation point of the adsorbent (i.e., sorption capacity). Additional treatment such as chilling/drying may become necessary prior to adsorption (EA, 2010). There are no standard methods for treating and monitoring siloxanes in biogas; however, manufacturers of gas engines are implementing stringent requirements for equipment maintenance warranties (Niemann et al., 1997; Sevimoglu and Tansel, 20013a). Another concern arising from the use of adsorption units is the disposal or regeneration of spent media (Huppermann et al., 1996, Stoddart et al., 1999; Lyn et al., 2002), which incurs additional costs or regeneration. In landfill gas, VOC and hydrogen sulphide

concentrations are higher than the levels in digester gas and therefore will exhaust adsorption capabilities at a faster rate (Schneider, 2001).

Fig. 8.3 compares the annual operating costs under previously outlined assumptions and the maintenance costs associated with siloxane deposit removal sans adsorption system. According to the data obtained from the facility surveys, it is not deemed feasible to install FBCAs as the maintenance hours for removal of siloxane deposits exceeded in all instances. In Facilities 4 and 6 (560 and 1,100 acfm respectively), the costs associated with siloxane deposit removal were 84% and 62% of the total annualized capital and operational costs therefore these facilities may benefit from the investment of the FBCAS.

The facility with biogas utilization rates of 2,900 acfm reported only 100 hours of maintenance for siloxane removal which is grossly underestimated. **Fig 8.3.** demonstrates the biogas utilization rates in which installation of carbon adsorption systems would benefit the facility with respect to cost of siloxane deposit removal. It is indicated that total annualized capital and operational costs exceed maintenance costs; however at a range approximating 1,200 and 1,400 acfm, the cost difference would not be significant.

Fig. 8.3 Comparison of annualized FBCAS costs and maintenance costs for siloxane removal 1) \$/yr and b) \$/acf-yr

8.4 Conclusions

The cost for carbon adsorption systems were estimated based on data available from seven facilities located in the United States (under varying conditions including temperature, relative humidity, pressure, and gas flow rates). The evaluation also included considerations for hourly salary and horsepower inputs. Total installed costs ranged from approximately \$168,000 to \$306,000 for 1,100 and 10 acfm LFG generating facilities respectively. From approximately 100 acfm to the highest value of 2,900 acfm, the estimated annualized capital cost of FBCAS remained consistent, between \$100 and \$1,000 per cubic foot of LFG utilized. Annualized capital and operational costs associated with the FBCAS averaged \$212,800 to \$263,000. Maintenance costs for siloxane deposit removal ranged from \$20,800 to \$190,400 annually. The estimated

installation and operational costs of carbon adsorption system for siloxane removal far exceeded the maintenance costs associated with the maintenance procedures for siloxane deposit removal. On the basis of siloxane removal costs alone, it is not economically feasible to install a carbon adsorption system for siloxane removal prior to combustion for small facilities that are processing less than 1,400 acfm of biogas. However, fixed bed carbon adsorption systems may be beneficial for removing other contaminants present in LFG as well as siloxanes, hence, improving the overall performance of the gas engines.

Acknowledgments

Partial funding for this research has been provided by the Hinkley Center for Solid and Hazardous Waste Management of University of Florida and Florida International University Dissertation Year Fellowship.

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9. Conclusions

This dissertation aimed to discuss the emergence and fate of siloxanes in waste streams, both wastewater management facilities and landfills. The release mechanisms, partitioning and persistence in three environmental compartments (air, water and solids) relative to siloxane use was investigated.

In order to evaluate persistence of siloxanes, it was first necessary to develop predictive models for product manufacture, usage and disposal. **Chapter 2** provided an estimation based on silicone-based material patents generated. A saturated growth trend was established for the generation which included the lag time between first patent developed and the exponential growth experienced. From here, the two sectors of waste emphasized were the paper/paperboard industry and the construction industry due to the prevalent use of siloxanes in those industries. Fractions of silicone within the products and estimated degradation times were used to quantify the expected emissions from landfills. These projections indicate that the siloxane content of landfill gas is likely to increase by 29% during the next 10 years and by 78% during the next 25 years based on the assumption that 5% of the siloxanes entering the landfills will partition to the landfill gas.

The primary concern with siloxane use is the accumulation of silicone dioxides on engine components at biogas or LFG to energy plants. . Silicone dioxides are the byproduct of incineration of materials containing siloxanes. However some concerns have arisen due to potential health impacts Chapter 3 of this dissertation focuses on the oxidation and nanotoxicity of Si-based particles as they are released into the atmosphere. Based on the temperature of combustion, particle sizes are expected to range from 50 to

100 nm. This particle size range tends to enter the body via inhalation, may deposit into the lungs and cause respiratory problems and potentially lead to silicosis.

The analysis of particle size ranges led to an examination of the deposits that are formed during combustion of biogas from anaerobic digesters and LFG. Deposits were scraped from engine heads and valves from one WWTP and 2 LFs. Morphological characteristics were determined with the use of SEM and EDS. Carbon-oxygen-silicon ratios in the deposits were about 5:7:1 in the deposits obtained from the engines operated with biogas from the anaerobic digesters and 2:3.5:1 in the deposits from the engines operated with landfill gas. It was determined that the carbon present in the deposits was not in carbonate form but in bound form to the crystal structure of the silicates. Typically, silicon content found in the deposits of facilities operated with biogas from anaerobic digesters was lower than those of landfills.

Initial research was directed towards analyzing two particular siloxane compounds known as D4 and D5, cyclic compounds that are encountered at the highest concentrations at most wastewater and landfill facilities globally. Compound characteristics including high Henry's constant and low solubility, a majority of the compounds are expected to end up in biogas during decomposition. However they have relatively high octanol water partition coefficients and are therefore also expected to sorb onto solids. From a practical engineering perspective, the first order kinetics is used to estimate the fate of chemicals in complex systems. This approach provides a simple method for comparing the relative persistence of different compounds. The first order reaction rate constant includes (by definition) the uncertainties associated with the complex nature of the phenomena without specifying the individual contributions of each

and every factor involved in reaction. It is well understood that the fate of D4 and D5 in the environment are strongly dependent on temperature, humidity, and wind effects among other environmental factors (e.g. presence of other chemicals, pH). It was theoretically determined that D5 is approximately 10 times more likely to partition into biosolids than D4. Additionally, the D5 concentrations are anticipated to be in 15 and 18 times higher in wastewater influent and biogas respectively when compared to D4.

Continued research in the area of persistence and fate of siloxane compounds aimed to analyze multiphase partitioning of commonly encountered siloxanes in biosolids and to develop a hazard index based on three categories: initial concentrations encountered, persistence and partitioning characteristics. The hazard rating was based on taking the product of a scale of 1 to 5 for each category. Linear siloxane (L3) as well as D3, D4, D6 and D6 were analyzed as they were the compounds found in highest concentrations consistently in a local wastewater treatment facility. It was determined that D4 posed the highest hazard potential in liquid and biosolids, whereas D6 posed the highest risk in gaseous phase.

Even though siloxanes are most prevalent in two of the three environmental compartments (air and solids), contribution of siloxanes to COD loading in the waste water stream was considered. The fate and removal of cyclic siloxanes D4, D5 and D6 was studied to determine removal efficiencies in three separate treatment tracks. Track 1 included oxidation; track 2 included aeration, clarification and primary settling; and track 3 consisted of trickling filter, final clarifier and sand filter. The COD levels were estimated based on each compounds theoretical oxygen demand. Siloxane-based COD loading has been determined to be negligible in active wastewater treatment systems.

Oxidation systems tend to eliminate more siloxane –based COD loading as compared to aeration tanks and filtration systems. However in cases where a bypass to primary settled sludge exists, cyclic siloxanes (D4, D5 and D6) are anticipated to bioaccumulate due to sorption of approximately 50% of the influent siloxanes onto biosolids.

Because of increased patent development of silicone-based materials and no federal or state mandates existing to regulate siloxane use, it is becoming essential to provide additional treatment systems such carbon adsorption to remove siloxanes prior to combustion. Removal of these siloxanes will prevent the deposition of the byproduct silicon dioxide which can cause increased maintenance practices and in some instances, complete engine overhauls.

The final chapter of this dissertation preliminarily compares the cost of continued maintenance practices related to siloxane removal to the costs of adsorption system installation and operation. The estimated annualized capital cost of FBCAS remained consistent at approximately 10^2 to 10^3 dollars per cubic foot of landfill gas utilized. Operational and maintenance costs ranged from \$212,000 to \$263,000 million annually, whereas maintenance costs associated to siloxane deposition removal only ranged from \$20,800 to \$190,400. Under the specified conditions found in Chapter 8, the estimated installation and operational costs of carbon adsorption systems far exceed the maintenance cost for physical deposition removal and are not deemed economically feasible on the basis of siloxane removal alone up until a biogas generation rate of 1,400 acfm.

Further research is necessary to specify removal efficiency for target compounds and would become instrumental for design aspects in both wastewater treatment systems

and landfills utilizing biogas for energy and the synergistic effects of a myriad of contaminants in the waste stream. Additionally, breakthrough studies of common activated carbons used in association to siloxane concentrations will be evaluated in future studies.

APPENDICES

Appendix 1 - Evaluation of a Full-Scale Water-Based Scrubber for Removing Siloxanes from Digester Gas: A Case Study (Accepted for publication in Water Environment Research)

Introduction

Digester gas is produced during the reduction of organic matter under anaerobic conditions. Its primary constituents are methane and carbon dioxide but increasing quantities of hydrogen sulfide, nitrogen, water vapor and volatile organic compounds have been observed. Synthetic volatile methylsiloxanes (VMS) are among those compounds becoming more prominent in landfill and digester gasses. Many of the siloxanes encountered volatilize; however some sorb onto biosolids (Dewil et al., 2006). During anaerobic digestion, siloxanes are typically released from sludge flocs due to decomposition of organic matter and temperature increases causing compartmentalization into gas phase (Appels et al., 2008). Hydrogen sulfide and siloxanes are at the top of the list of undesirable digester gas components (Barhost and Gupta, 2011).

Siloxanes are widely used in personal care products due to their soft texture, low inflammability, low surface tension, thermal stability, high compressibility, low toxicity, ability to breakdown in environment and low allergenicity (Siefers and Mary, 2010).

Table 1 provides a comparison of characteristics of siloxanes detected in digester gas with H_2S and CH_4 . Siloxanes degrade to silicates and SiO_2 at high temperatures, resulting in crystalline particle formation that becomes impermeable. These particles bond onto metal surfaces with heat. Without proper maintenance, severe damage can occur to engine components including valves, pistons, and cylinder heads, thereby imposing downtime and costly repairs. Lack of maintenance can cause damage from

Table 1 Comparison of selected properties of siloxanes detected in digester gas with H₂S and CH₄.

Compound	Abbreviation	Chemical formula	Molecular weight (g/mol)	Henry's Constant (Pa·m ³ /mole)	Vapor pressure (at 25°C) (kPa)	Water solubility (at 20°C) (mg/L)
Trimethylsilanol	TMS MOH	C ₃ H ₁₀ OSi	90.2	5.13 ^a	2.13 ^j	35,000 ^j
Hexamethyldisiloxane	L2	C ₆ H ₁₈ OSi ₂	162.4	4,559,625 ^b	4.12 5.626 ^k	0.93 ^k
Octamethyltrisiloxane	L3	C ₈ H ₂₄ O ₂ Si ₃	236.5	323,346 ^c	0.52	0.05 ^l 0.034 ^m
Decamethyltetrasiloxane	L4	C ₁₀ H ₃₀ O ₃ Si ₄	310.7	0.609 ^d	0.073	0.007 ^m
Dodecamethylpentasiloxane	L5	C ₁₂ H ₃₆ Si ₅ O ₄	384.8	-	0.009	3.1x10 ⁻⁴ⁿ
Hexamethylcyclotrisiloxane	D3	C ₆ H ₁₈ O ₃ Si ₃	222.5	6,485 ^e	1.14 1.147 ^k	1.56 ^k
Octamethylcyclotetrasiloxane	D4	C ₈ H ₂₄ O ₄ Si ₄	296.6	1,214,000 ^f 22,177–83,310 ^g	0.13 0.132 ^k	0.056 ^k
Decamethylcyclopentasiloxane	D5	C ₁₀ H ₃₀ O ₅ Si ₅	370.8	3,342,000 ^f	0.050 0.023 ^k	0.017 ^k
Dodecamethylcyclohexasiloxane	D6	C ₁₂ H ₃₆ O ₆ Si ₆	444.9	14,667 ^f	0.003 0.004 ^k	0.005 ^k
Methane (for comparison)	-	CH ₄	16.0	46.437 ^h	-	22.7 ^o
Hydrogen sulfide (for comparison)	-	H ₂ S	34.1	867 ⁱ	1740 ^a	2900-3980 ⁱ

^aChemSpider, The free chemical database (2013)

^bCalifornia Environmental Protection Agency (2013a)

^cChemDplus Advanced. United States National Library of Medicine (2013a)

^dCalifornia Environmental Protection Agency (2013b)

^eChemDplus Advanced. United States National Library of Medicine (2013b)

^fEuropean Silicones Centre. (2013)

^gEnvironment Agency (2013)

^hNanoscale Research Facility, University of Florida (2013)

ⁱCanadian Centre for Occupational Health and Safety(2013)

^jSchweigkofler and Niessner(2001)

^kSchweigkofler (2001); in biogas

^lPierce (2011); in biogas

^mKochetkov et al., (2001), (L2-L5 at 298K, D4-D6 at 296K)

ⁿArnold and Kajolinna (2010)

^oThe Engineering Toolbox (2013)

siloxanes and can account for a cost of approximately \$60,000 annually for a 5 million gallon per day (MGD) water resource recovery facility with generator (Tower, 2006).

A literature review was conducted to quantify siloxane emissions in water resource recovery facilities located in Austria, Germany, Finland, Greece, Spain and China. **Table 2** provides the mean concentrations for trimethylsilanol, L2, D3, L3, D4, L4 and D5 where available. These compounds occurred most frequently in all locations (Bletsou et al., 2013; Schweigkofler and Niessner, 2001; Accetola and Haberbauer, 2005; Rasi et al., 2010; Cortada et al., 2013; Xu et al., 2013). Approximately 50% of VMS are volatilized from the liquid stream while the remaining VMSs are sorbed onto solids and carried to the digester. The heavier molecular weight siloxanes, referred to as polydimethylsiloxanes are mostly sorbed onto the surface of biosolids (approximately 90%) (Soreanu, G., et al., 2011).

As noted, commonly detected siloxanes in digester gas include hexamethylcyclotrisiloxane (D3) octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) (Surita and Tansel, 2014; Barhost and Gupta, 2011; Rasi et al., 2010; Schweigkofler and Niessner, 2001). The U.S. Environmental Protection Agency (USEPA) has declared D4 to be a compound considered both persistent and bioaccumulative (Bletsou et al., 2013). Target concentrations recommended are less than 100 parts per billion (ppb) for reciprocating engines and boilers and less than 50 ppb for turbines (Barhost and Gupta, 2011).

Table 2 Mean siloxane concentrations in wastewater gases at different sites

Mean Siloxane Concentration (mg/m ³)							Location
TMSOH	L2	D3	L3	D4	L4	D5	
b.d.	0.02	0.04	0.02	0.93	b.d.	6.03	Asten, Austria ^a
0.105	0.03	0.1725	0.025	4.82	0.08	6.043	4 WWTPs in Munich, Germany ^b
0.038	0.038	<0.04	<0.2	0.45	<0.04	0.685	4 WWTPs in Finland ^c
n.a.	n.a.	0.152	b.d.	0.129	0.037	1.79	Athens, Greece ^d
b.d.	1.7	0.9	-	2.53	b.d.	8.95	Spain ^e
n.a.	b.d.	0.284	b.d.	1.862	b.d.	2.738	China ^f

a. Accettola and Haberbauer (2005)

d. Bletsou (2013)

b. Schweigkofler and Niessner (2001)

e. Cortada et al. (2013)

c. Rasi et al. (2010)

f. Xu et al. (2013)

Scrubber Technologies

Scrubber technologies include adsorption (dry scrubbing), wet scrubbing and refrigeration. Wet scrubbing works by contact between target compounds or particulate matter and the scrubbing solution in order to remove one or more undesirable compounds from biogas. Solutions may simply be water or solutions of reagents targeting specific compounds. For improved contact, biogas may be cooled prior to entering scrubbing unit and absorbent (either water, carbohydrate solution, hypochlorite) may be finely sprayed onto the packing filter counter-current to the biogas flow containing siloxane (Soreanu et al., 2011). Water-based scrubbers are generally used at water resource recovery facilities to remove hydrogen sulfide from digester gas. The biogas is mixed with the scrubbing liquid containing (most often sodium hypochlorite (NaOCl)). Unit processes may be used in series. For example, iron sponge adsorption, wet scrubber, chiller and activated carbon may be installed to remove hydrogen sulfide, carbon dioxide, particulates and siloxanes respectively.

Oxidation of siloxanes during combustion requires between 12 and 22 mol O₂/mole of siloxane (Tansel and Surita, 2014). The oxidation reactions are pH dependent, with the optimum scrubber solution pH in the 9.5 – 10.5 range. In this range, hydrogen sulfide is absorbed into the recirculation liquid. As pH decreases below the optimum range, the solubility of hydrogen sulfide decreases.

Multi stage scrubbers reduce chemical consumption as well as control sulfur deposits forming during scrubbing H₂S. The objective of this study was to evaluate the efficiency of a full-scale, water-based scrubber, which is used for removing H₂S from the

digester gas, for siloxane removal at the South District Wastewater Treatment Plant (SDWTP) in Miami, Florida. Digester gas samples were collected before and after treatment via water-based scrubbing, and were analyzed for siloxanes. The results were compared with the theoretically estimated removal based on the characteristics of the siloxanes detected.

The use of scrubbers in conjunction with tire derived rubber particles (TDRP) as media as presented by Siefers (2010), demonstrated in excess of 98% siloxane removal efficiencies. This study was provided only in gas phase. Additionally, Sulfur Oxidation and Siloxanes Adsorption (SOXSIA) acts as a catalyst for absorbing siloxane and hydrogen sulfide removal from the gas stream (DTI, 2012). Energy Solutions' Wet Gas Scrubber (WGS) was designed to eliminate silicon in the form of siloxanes from the biogas stream, but no statistical analysis of removal efficiency (Energy Solutions, 2013) was readily available. The novelty of this work is the evaluation of a full scale water-based scrubber for siloxane removal because siloxanes are becoming a concern for operators of biogas-to-energy plants. This study addresses the need for improving biogas prior to energy recovery in addition to water-based scrubbers.

Methodology

Scrubber facilities at the South District Wastewater Treatment Plant

Wet scrubbing is employed at the SDWWTP for removing H₂S from the biogas generated at the anaerobic digesters. In the SDWWTP, digester gas is passed through a liquid medium that contains sodium hypochlorite to remove particulates and other gases (**Fig. 1**). The typical range of hydrogen sulfide encountered is between 1000 and 5000 ppm.

a. Scrubbers (2) used at the treatment plant.

b. Schematic of the scrubber unit.

Fig. 1 Scrubbers used for H_2S and removal from biogas at the SDWWTP

Two scrubbers are employed at the SDWWTP and receive 200 to 215 cubic feet of water per minute and 5 cubic feet per minute of sodium hypochlorite at a concentration of 0.8 mg/L. Biogas from 12 on-site digesters enters the system at 17 cubic feet per hour prior and are pushed with hot water to the cogeneration plant. Six chambers divided by baffles within each scrubber are operated utilizing two pumps and an additional backup pump. Sulfites settle to the bottom of the scrubber and are drained. The water is subsequently recirculated, while the clean gas is then sent to a compressor for transport to the cogeneration plant.

Digester gas sampling and analyses of siloxanes

Gas samples for siloxane analyses can be collected with different storage media, including Tedlar bags, canisters and sorbent tubes. Tedlar bags are recommended for gas of high humidity (>90%) as overall siloxane recovery may be hindered. Low limits of detection below 10 nm are typically achievable using Tedlar bags with good reproducibility. However, Tedlar bags have a shorter hold time than sorbent tubes; 3 days and 14 days respectively. Gas chromatography/Mass spectrometry is used for identification and quantification of siloxanes.

This study utilized specialized tubing which was secured into both sides of a T-fitting which connected to the gas line and the other to the calibration tube as seen in **Fig 2**. The slip stream, which prevents water build-up into the sample, was located at the lowest elevation of the sampling train. The gas line was turned on and the rotameter was then adjusted to provide a reading of 0.2 L/min with proper calibration for sample collection into thermal desorption sorbent tubes.

Fig. 2 Gas sampling for siloxanes using rotameter (calibration) and sorbent tube

A contracted laboratory, performing siloxane analysis, has developed sampling protocol involving extraction in-house and analysis by thermal desorption. Sorbent tubes were thermally desorbed and injected in GC/MS at a specified temperature and gas flow comparable to the studies conducted by Narros, A. et al. (2009) and Raich-Montiu et al., (2013). Carrier gas helium was used during injection. Quality assurance/quality control (QA/QC) criteria established by the National Environmental Laboratory Accreditation Program was adhered to.

Results/Discussion

Mean concentrations of siloxanes in digester gas from the SDWWTP are summarized in **Table 3** for samples taken before and after treatment via water-based scrubber. Linear siloxanes L2, L4, and L5 were not detected in the gas samples

Table 3 Mean siloxane concentrating in digester gas before and after scrubber

Compound	Abbreviation	Before Scrubber ^a as siloxane (µg/m ³)		After Scrubber as siloxane (µg/m ³)		Siloxane removed	
		mean concentration	Std dev	mean concentration	Std dev	mean removal (%)	Std dev
Trimethylsilanol	TMSOH	75	106.1	36.5	51.6	51.3	36.3
Hexamethyldisiloxane	L2	<46	-	<46	-	-	-
Octamethyltrisiloxane	L3	260	56.6	290	42.4	0.0	0.0
Decamethyltetrasiloxane	L4	<48	-	<48	-	-	-
Dodecamethylpentasiloxane	L5	<48	-	<48	-	-	-
Hexamethylcyclotrisiloxane	D3	285.5	331.6	164	149.9	42.6	34.0
Octamethylcyclotetrasiloxane	D4	4,150	1202.1	4,550	70.7	0.0	7.1
Decamethylcyclopentasiloxane	D5	1,800	0.0	1,450	212.1	19.4	19.6
Dodecamethylcyclohexasiloxane	D6	89.5	12.0	72.5	10.6	19.0	13.0
Total		7,868	1708.4	6,543	28.3	16.8	11.9

collected. D4 and D5 siloxanes were found in significant amounts at 5000 and 1800 $\mu\text{g}/\text{m}^3$ respectively, which was similarly noted in literature (Schweigkofler and Niessner, 2001).

Results have indicated that scrubbers which are used for H_2S removal at the facility do not provide effective removal of gas-phase siloxanes due to their high Henry's Constant and low water solubility. TMSOH had the highest removal by the water-based scrubber (51.3%) followed by D3 (42.6%). However, D4 and D5 were not removed effectively.

The partitioning of siloxanes between vapor and liquid phases was analyzed. The dimensionless Henry's constant was used to estimate the partitioning between the gas and liquid phases as presented by Equations 2 and 3 (Kuo, 1999).

$$H^* = H/RT \times 10,000 \quad (2)$$

$$C = G/ H^* \quad (3)$$

where H^* : Henry's Constant (dimensionless)

H : Henry's constant ($\text{atm}\cdot\text{m}^3/\text{mole}$)

T : Temperature (Kelvin)

C : Concentration in liquid phase (mg/L)

G : Concentration in gas phase (mg/L)

Table 4 presents the estimated siloxane concentrations in the water phase of the scrubber that is in contact with the digester gas in the 1st and last (6th) chamber. Based on the estimated concentrations, only trimethylsilanol and D3 would be expected to have significant removal due to their relatively low Henry's constants and substantially higher

solubilities. The high solubility of trimethylsilanol allows it to be removed by the scrubber. However, the expected removals at the water-based scrubber for D3, D4, D5, and D6 would not be significant.

Table 4 Estimated siloxane concentrations in the water phase of the scrubber that is in contact with the digester gas in the 1st and last (6th) chamber.

Compound	Abbr.	Estimated siloxane concentration in water	
		1 st chamber ($\mu\text{g}/\text{m}^3$)	6 th chamber ($\mu\text{g}/\text{m}^3$)
Trimethylsilanol	TMSOH	72.44	35.25
Hexamethylcyclotrisiloxane	D3	198	103
Octamethyltrisiloxane	L3	2.30	2.30
Octamethylcyclotetrasiloxane	D4	10.20	9.18
Decamethylcyclopentasiloxane	D5	1.33	0.96
Dodecamethylcyclohexasiloxane	D6	16.55	13.51

Additionally, because of initial concentrations and non-uniform compositions at varying locations, removal efficiencies of water-based scrubbers are expected to also vary. Degradation profiles will play a significant role (Surita and Tansel, 2014) and therefore technologies selected for siloxane removal will differ on a case-by-case basis. Peroxidation or the use of sorbent materials such as silica gel, activated alumina or activated carbon may function well for the purposes of siloxane removal. Furthermore, biological methods could become a sustainable option with a detailed investigation of other compounds present in biogas along with determination of the initial siloxane compositions.

Conclusions

The varying composition of initial concentrations may affect the overall removal of specified siloxane compounds. The high Henry's Constant of D4, D5 and D6 indicate that these compounds have a strong tendency to partition from water to gas phase. Hence, the gas phase is the primary phase for D4, D5 and D6. Therefore, the water-based scrubbers, which are used for H₂S removal from the digester gas at the water resource recovery facility, do not provide effective removal for siloxanes. Post scrubber treatment in the form of adsorption or peroxidation is recommended to remove siloxanes prior to combustion.

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Appendix 2 – Estimated contribution of siloxanes from wastewater treatment plants and landfills

Estimated contribution of siloxanes from wastewater treatment plants and landfills

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