THESIS

OCCURRENCE OF CYCLO-SILOXANES IN WASTEWATER TREATMENT PLANTS – QUANTIFICATION AND MONITORING

Submitted by

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ABSTRACT

OCCURRENCE OF CYCLO-SILOXANES IN WASTEWATER TREATMENT PLANTS – QUANTIFICATION AND MONITORING

Siloxanes are persistent, bio-accumulative and toxic emerging contaminants introduced to wastewater from common healthcare and biomedical products, and various industrial processes. They remain unchanged through wastewater treatment and a considerable portion ends up in surface waters through effluent discharge. 30-60 ng/L Decamethylcyclopentasiloxane (D5) was detected in two UK Rivers, while ~400 ng/L of D5 may be found in wastewater effluents. Hence, siloxanes are under consideration by Canadian Environmental Assessment Agency and UK Environment Agency for drinking water regulations. Siloxanes are hydrophobic and also accumulate in activated sludge and biogas, causing mechanical problems due to scaling. This research aims: to quantify the siloxanes in sludge samples obtained from Loveland, CO wastewater treatment plant (WWTP); and to study their removal. A method was developed to effectively extract siloxanes from activated sludge samples using liquid extraction followed by quantification with gas chromatography/mass spectrometry. Results for Loveland Wastewater Treatment Plant samples indicated that Octamethylcyclotetrasiloxane (D4) and Decamethylcyclopentasiloxane D5 are present up to 17.11 µg/g dried-sludge. The effectiveness of H_2O_2 in siloxane removal was investigated. Sludge samples were spiked with D4 and D5 at 12 mg/g and were treated with 1ml, 3ml, and 5ml of 30% H_2O_2 for 1hr, 2hr, and 3hr reaction time each. Results indicated a 72% reduction in D4 and D5 levels after 3 hrs.

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DEDICATION

To my parents, Vijay and Juee

Without their support, understanding, encouragement, and love this work would not have been possible.

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CHAPTER 1. INTRODUCTION

In the last few decades, due to the raise in fuel costs and the scarcity of conventional fuel, an urgent need for an alternative was created. Also it became evident that the fuels contribute to emission of large amounts of green house gases. Recently, the wastewater utilities came up with an alternative way of generating energy from waste. The amount of sludge produced from biological wastewater treatment processes is very high, hence as a sludge treatment, anaerobic digestion was used in most of the plants. The process of anaerobic digestion also has a favorable by-product: biogas that can be used for energy generation. Anaerobic digestion reduces the organic content by anaerobic microbial activities and produces methane as a major output. Methane can be utilized to generate electricity by burning it in gas turbines or steam boilers. However, it was very important to ensure that use of methane for electricity generation was economically feasible (Bullard et al., 2001). Anaerobic digesters are usually used when wastewater flow was greater than 3 MGD. The heating value of the gas produced at wastewater treatment plants was nominally 60 percent that of natural gas which was 1000 BTU per cubic foot. However, maximum digestion and proper purification of gas can increase its value as much as 95 percent (Abbuehi et al., 2009). The quality of digester gas depends on the presence or absence of any organic or inorganic pollutants present in the wastewater stream, their physical, chemical and biological properties and their behaviour in wastewater stream, during anaerobic digestion and the gas. Over the last decades, use of consumer products has increased tremendously due to growing population and availability of various personal care products. One of the most common elements found in a variety of products consumed on a daily basis ranging from personal care products, food, drinks to highly modified commercial and industrial substances was silicon and silicon based compounds. Silicon by itself is not used in many applications however, siloxanes is a very common form used in manufacturing. Siloxanes were started being used in many applications over the last few decades as it was concluded that they do not cause health related issues to humans. Siloxanes in the consumer products ultimately get washed down the drains and end up in the wastewater stream. Siloxanes did not gain any attention until the wastewater treatment plants started using anaerobic digestion followed by methane generation and utilization. Because of the inherent properties of siloxanes, they have the affinity to attach to the organic matter rather than to stay in water. Additionally they are very volatile and easily get into gaseous phase even if a little energy is applied. So because of such properties, siloxanes occur in high concentrations in the sludge produced at the wastewater treatment plants. During the anaerobic digestion, siloxanes are released from the sludge particles and get into gaseous phase where they remain as impurity in the digester gas. When contaminated biogas is burnt, siloxanes form silicon oxides and deposit on the surface of burners causing scaling and fouling issues. This results in elevated operational and maintenance costs. Ultimately, it results in replacement of the entire unit Biogas may be treated to remove siloxanes however it is an expensive method. Also as the concentration of siloxanes spikes in the sludge rather than in the biogas it is essential to understand the levels and study the removal of siloxanes from sludge itself.

1.1. MOTIVATION

This research project was developed based on the problems faced by the local wastewater treatment utilities' operators. City of Loveland and City of Fort Collins in Northern Colorado have always been progressive in trying out new technologies for generation and utilizaiton of digester gases. During a field trip to these wastewater treatment plants, the operators pointed out the issues of having white depositions on the gas handling equipment. Research of literature and case studies indicated that this is due to the siloxanes in the biogas.

1.2. CONTRIBUTIONS

Over the past few years, several cases of damages due to siloxanes have been observed. Many researchers studied this issue with respect to biogas oeprations, environmental significance, health issues and ecological significance of siloxanes. This thesis presents the occurrence of two cyclic siloxane compounds in the waste activated sludge obtained from City of Loveland, CO wastewater treatment plant. An new method has been developed to extract and accurately measure siloxane concentrations using gas chromatography and mass spectrometry.

1.3. OUTLINE

This thesis is organized as follows: Chapter 2 provides the background information on the phsyical nature of siloxanes, engineering properties of siloxanes, their use in commerical products, their ocurrence in the environment and the techniques for analysis and removal of siloxanes from various matrices. Chapter 3 presents the problem statement for the thesis. Chapter 4 is prepared in a manuscript format to include the method develoment for siloxanes analysis and occurrence of siloxanes in waste activated sludge. The appendix includes further details of materials and methods used and the original data processed in Mass Lynx v4.0 and Microsoft Excel.

CHAPTER 2. BACKGROUND INFORMATION

2.1. Nature of Siloxanes: Physical and Chemical

Siloxanes represent a large group of chemicals with a wide range of molecular weights from few hundred to several thousands. The word “Siloxanes” is derived from “Silicon, Oxygen and Alkanes”. Siloxanes are composed of units of the form R_2SiO, where R is a hydrogen atom or a hydrocarbon group. This class of Siloxanes is also termed as organo siloxanes. Siloxanes are present in two types, they can either have branched or un-branched backbones consisting of alternate Silicon and Oxygen atoms –Si-O-Si-O-. These Silicon and Oxygen atoms are connected by an σ-bond with a length of 1.64 +/- 0.03 A^0. The hydrogen or hydrocarbon R is attached on side chains to the silicon atoms. There are more complicated structures present which has eight silicon atoms at the corner of a cube which is connected by twelve oxygen atoms as the cube edges.

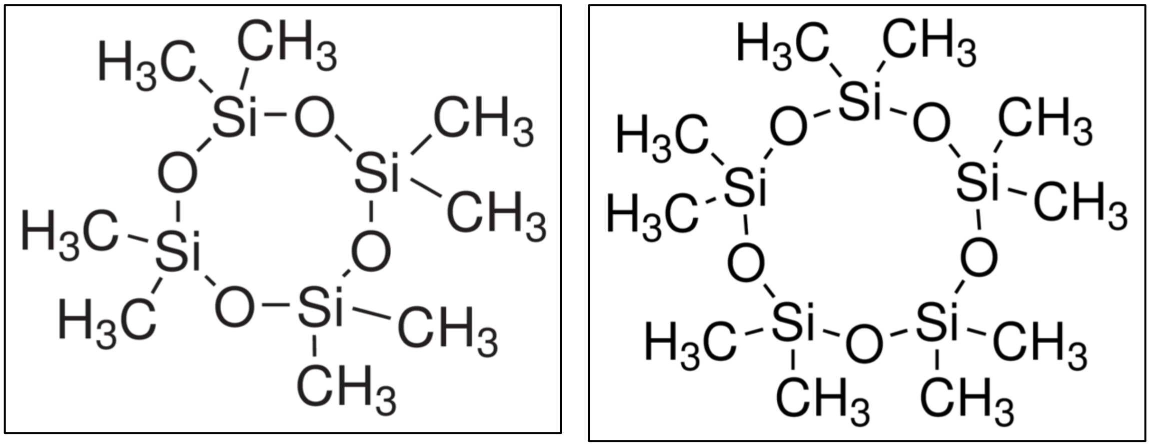


Figure 2-1Structure of D4 and D5

Polymerized Siloxanes having organic chains on side are termed as silicones or as polysiloxanes. These compounds are categorized as a hybrid of both organic and inorganic compounds. Generally Siloxanes are categorized in cyclic and linear Siloxanes. Following table provides a list of some common Siloxanes. Two cyclo-siloxanes studied here are

Octamethylcyclotetrasiloxane (D4) and Decamethylcyclopentasiloxane (D5) has molecular weights of 296.6 g/mol and 370.8 g/mol respectively. Octamethylcyclotetrasiloxane (D4) with molecular formulae $C_8H_{24}O_4Si_4$ and CAS No. 556-67-2.

This siloxane appears as colorless liquid form. Average melting point/freezing point of D4 is within range of 17-18^{0}C (63-64^{0}F). Octamethylcyclotetrasiloxane D4 possess boiling point in a range of 175-176^{0}C (347-349 ^{0}F). Flash point of D4 is 56 ^{0}C (133 ^{0}F) calculated in closed cup. There is no data available on pH, ignition temperature, auto ignition temperature, lower and upper explosion limit, vapor pressure, odor, and odor threshold and evaporation rate with respect to D4. Decamethylcyclopentasiloxane (D5) with molecular formula $C10H30O5Si_5$ and CAS No. 541-02-6. Average melting point / freezing point of D5 are unknown. Boiling point of D5 is 90 ^{0}C (194 ^{0}F) at 13 hPa (10mm Hg). Flash point of D5 is 73 ^{0}C (163 ^{0}F).

Table 2-1 Description of Common Siloxanes

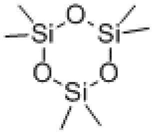
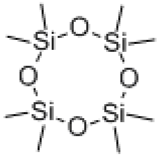
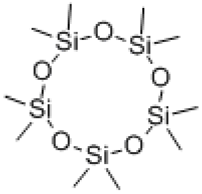
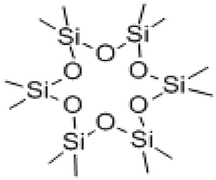
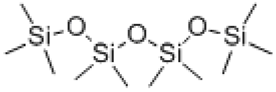
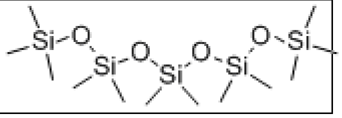
Abbreviation	**Name**	**CAS #**	**Structure**
D3	Hexamethylcyclotrisiloxane	541-05-9	
D4	Octamethylcyclotetrasiloxane	556-67-2	
D5	Decamethylcyclopentasiloxane	541-02-6	
D6	Dodecamethylcyclohexasiloxane	540-97-6	
MM (HMDS)	Hexamethyldisiloxane	107-46-0	
MDM	Octamethyltrisiloxane	107-51-7	
MD2M	Decamethyltetrasiloxane	141-62-8	
MD3M	Dodecamethylpentasiloxane	141-63-9	

Table 2-2 Physical Properties of Common Siloxanes

Compound	**Abbreviation**	**Molecular Weight (g/mol)**	**Boiling Point (^{0}C)**	**Melting Point (^{0}C)**	**Vapor Pressure (kPa)**
Hexamethylcyclotrisiloxane $C_{12}H_{18}O_3Si_3$	D3	222.46	133.8	63.88	1.14 @ 25^{0}C
Octamethylcyclotetrasiloxane $C_8H_{24}O_4Si_4$	D4	296.61	175	17.22	0.13 @ 25^{0}C
Decamethylcyclopentasiloxane $C_{10}H_3O_5Si_5$	D5	370.77	210	-43.88	0.05 @ 25^{0}C
Dodecamethylcyclohexasiloxane $C_{10}H_{36}O_6Si_6$	D6	445.00	245	-3	0.003 @ 25^{0}C
Hexamethyldisiloxane $C_6H_{18}Si_2O$	L2	162.4	100	-67	4.12 @ 25^{0}C
Octamethyltrisiloxane $C_8H_{24}Si_3O_2$	L3	236.5	152.7	-82	0.52 @ 25^{0}C
Decamethyltetrasiloxane $C_{10}H_{30}Si_4O_3$	L4	310.7	193.8	-68	0.073 @ 25^{0}C
Dodecamethylpentasiloxane $C_{12}H_{36}Si_5O_4$	L5	384.8	230	-81	0.009 @ 25^{0}C

2.2. Engineering Properties of Siloxanes

Siloxanes are widely used in various commercial applications because of their favorable properties. Siloxanes commonly are a viscoelastic in nature which means that at long flow times (or high temperatures); it acts as a viscous liquid similar to honey. However, at short flow times (or at lower temperatures); it acts like an elastic solid similar to rubber. This property enables Siloxanes to cover the surface and mold to any surface imperfections. They provide tough, long lasting motor insulation and lubricants for bearings. Siloxanes stay affixed and absorb stress and movement and keep the structure strong and safe. It helps to reduce damage and physical harm from small to medium scale earthquakes due to its elastic nature. Silicones help material against water decay, corrosion and deterioration. Due to efficient insulating properties, Siloxanes enhance energy efficiency. Siloxanes have unique adhesive and durability properties. Siloxanes bond with most of materials whether very porous, non-porous, sensitive materials or hard materials. Siloxanes adhere to materials like concrete, glass, granite, marble, aluminum, steel and plastics. Siloxanes are able to restore strength and permeability to crumbling facades, weakened structures and deteriorating joints without any loss of the integrity of original material. Siloxanes produce air-tight seals and can provide protection to any assemblies that are vulnerable to weather. Siloxanes are non-corrosive, non-pyrophoric in nature. Siloxanes exhibit high and low temperature stability, excellent electrical and thermal insulation, strength, flexibility and pliability, moisture resistance, chemical stability, ultraviolet resistance and other environmental protection and also adhesion to and protection for a broad range of materials. Siloxanes are known as biocompatible material. Human body doesn’t react strongly to the presence of Siloxanes. Siloxanes do not host bacteria and can easily be sterilized. Siloxanes soften and smooth lotions and creams. Siloxanes shows the same properties as latex as allergic agents.

Siloxanes withstand many damaging conditions at once like freeze / thaw cycles, chemical attack such as oils, gasoline, salt spray and acid rain. It also manages to be stable in adverse conditions such as pollution, foot traffic, accidents and natural conditions such as moisture and sunlight. Siloxanes possess water repellent properties and breathability. They also have anticratering; mar resistance, antiflooding and anticarking properties. Siloxanes based substances provide improved spreadability. Siloxanes have volatile and non-cooling properties.

2.3. Siloxanes in commercial products

They are long been recognized by the medical world as efficient, versatile and biocompatible materials and hence used in healthcare products. Some of the typical applications are medical care, dental care, infant care, pharmaceuticals, treatment of wounds, prosthetics etc. Silicones and siloxanes play an important role in personal care business today. They offer superior aesthetic and technical characteristics to formulations, delivering high performance sensory benefits like softness, luxurious texture and longer-lasting, protecting effects. Silicone-based personal care products make excellent moisturizers, keeping actives present for longer and returning softness and vitality of the skin surface. Use of silicon compounds is very popular in personal care products due to their non-stinging, non-staining properties, effectiveness over wide range of temperature, persistence of all properties in water, versatility, and chemical stability. A survey was done to determine concentration of cyclic and linear siloxanes in personal care and household products. It was found that among all siloxanes occurrence of D5 was the highest. Exposure profiles to cyclic and linear siloxanes from personal care and consumer products for women of age 19-65 in United States is given in following table (Horri et al., 2008).

Table 2-3 Exposure Profile of Siloxanes from Personal Care Products

Product Type	Usage (g/day)	D4 (μg/day)	D5 (μg/day)	D6 (μg/day)	D7 (μg/day)	L4-L14 (μg/day)
Shampoo	12.8	198	335	333	214	0.87
Hair conditioners	13.8	712	162000	1310	104	22
Body washes	14.5	0	0	0	0	22
Body lotions	8.7	7.4	4.0	1.1	0	0.40
Face creams	2.1	75	43400	6100	53	49900
Lipsticks	0.024	0.13	0.17	0.098	0.039	14
Liquid foundations	0.67	91	27400	14400	100	3.3
Total		1080	233000	22200	471	50000

Siloxanes are effectively used as engineering sealants and adhesives, building sealants and adhesives, masonry coatings, industrial coatings and maintenance, water repellent adhesives. Use of these products in construction is increasing because of the high consumer benefit by high cost-saving, durability and flexibility. Silicone provides the protection to construction materials against excessive stress, structural movement. Silicone compounds played critical role in developing transportation industries. They withstand extremely high temperatures, exposure to moisture, salts and various fuels. They retain their strength and adhesive properties and ensure the vehicle operates safely for the long haul. Airbags, aviation and aerospace materials, airflow sensors, automotive coatings, automotive wind shields and sunroofs, electronic parts contains siloxanes. They are also used as foam insulation, in car seats/backs in the form of polyurethane foam, ignition parts, radiators, sealants, tires and transmissions. With increasing trend of electronic industry, demand for products containing high levels of siloxanes is increasing. Cell phones, the internet, wireless computers and smart cards are all manufactured with silicones. Silicones seal and protect highly sensitive circuits, semiconductors and devices from heat, contamination and accidental damage and help ensure the continuity of electrical supply. Rubber industry is major consumer of silicone and siloxane compounds due to favorable properties such as temperature stability, flexibility, tear strength, long term tensile strength, elongation, inertness. “There is barely an application in the kitchen where silicones cannot play a supporting role” said the European Silicones Center. This is the truth since silicones is used in making cookware flexible, non-sticky, non-porous surface (which can be cleaned thoroughly). The silicone product surface doesn’t affect the flavor of food or leave behind any taste or odor. Since silicones resist extreme temperatures, they can go from oven to table to freezer without any impact on quality of food. Modified siloxanes are precious additives in the formulation of paints. Silicones are used as the basis for water repellent paints. They are also used in water repellent thick-coat renderings that are applied to protect building facades. Silicone sealants and adhesives have proved to be powerful and flexible products. Silicones enhance the performance of other material. They are also used in power and utilities, agriculture and food, household cleaning solutions like laundry detergents, fabric softeners, polishes and surface cleaners, many domestic appliances like iron, cookers and ovens, solar collectors, toys manufacturing, earplugs, spacesuits. Silicones and siloxanes have unending list of applications.

Table 2-4 Application – Consumption of Siloxanes

Application Area	**Consumption Tons/year**	**Percentage**	**Type of Siloxanes**
Sealants used for Construction	920	29	Elastomers
Paints , inks and coatings	200	6	Resins, elastomers
Cosmetics and toiletries	240	8	Fluids, volatile fluid
Wax, polishes and cleaning agents	100	3	Fluids
Mechanical fluids and heat transfer fluids	50	1.6	Fluids, elastomers
Textile applications	380	12	Fluids, elastomers
Processing aids	470	15	Fluids
Paper coating	210	7	Fluids
Health care	110	4	Elastomers, fluids
Other uses of silicone elastomers	390	13	Elastomers
Other uses of silicone fluids	50	1.6	Fluids
Total	3120	100	NA

2.4. Environmental Significance

Octamethylcyclotetrasiloxane (D4) and Decamethylcyclopentasiloxanes (D5) are two lower molecular weight cyclic siloxanes from the broad range of cyclic and linear siloxanes. They occur as clear viscous liquids at room temperature and have varying physical and chemical properties. Physical properties of the siloxanes enable them to become a widely used element in commercial products. The chemical properties of siloxanes are the reason of them being persistent in the environment. In the atmosphere, siloxanes may exist in vapor as well as in particulate form. Following table provides information on the chemical properties of some of the commonly found cyclic and linear siloxanes.

Table 2-5 Chemical and Biochemical Properties of Siloxanes

Compound	**MW (g/mol)**	**W_{sol} (mg/l) (25 ^{0}C)**	**V_P (mm Hg) (25 ^{0}C)**	**H (Atm m^3 /mol)**	**Log K_{OW}**	**BCF (L/Kg)**	**K_{OC}**
D3	225.5	-	-	-	-	-	-
D4[a]	296.6	0.9	1	0.42	-	12400	2.85×10^4
D5[b]	370.8	0.24[b],0.017[c]	0.2[b,c]	0.4[b],0.3[c]	5.7[b],5.2[c]	5300[a]	1.6×10^{4}[b]
D6[a]	444.9	-	-	-	-	-	-
MM[a]	162.4	2	42	4.5	4.2	900	4.6×10^3
MDM[a]	236.5	-	-	-	-	-	-
MD2M[a]	310.7	-	-	-	-	-	-
MD3M[a]	384.8	3.1×10^{-4}[c]	0.102[c]	0.79[c]	6[c]	-	-

(HSDB, 2004[a]; ECB, 2005[b]; SRC, 2005[c])

When the siloxanes in the atmosphere are in vapor phase, they may also react with hydroxyl radicals (HSDB, 2004). Hazardous Substances Data Bank has investigated the half-life periods for reaction with hydroxyl radicals in air. One linear siloxane Hexamethyldisiloxane (MM) and two cyclic, Octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) are present in vapor phase in the air. The half-life period for their reaction with hydroxyl radicals are given in following table.

Table 2-6 Half-Life Period for Atmospheric Reactions

Compound	Half Life (Days)	References
MM	12	HSDB, 2004
D4	16	HSDB, 2004
D5	10	HSDB, 2004

These three siloxanes have high vapor pressures and high Henry's law constants and hence they readily volatilize both from wet and dry soils as well as from water. Siloxanes with high K_{OC} (Table 2-5) are expected to be immobile in soil. It is likely to be adsorbed to the particles in water and sediments (HSDB, 2004). It was observed that the chemical reactions like oxidation, reduction and photo- degradation do not affect siloxanes (HSDB, 2004). It is generally considered that siloxanes do not undergo hydrolysis. However it was shown in a study of hydrolysis kinetics of Octamethylcyclotetrasiloxane (D4) that within the pH range of 5-9 at 25 ^{0}C, D4 undergoes degradation with an environmentally significant rate. However no data is available on intermediate and final hydrolysis products during the reaction (Durham et al., 2004). Results from an equilibrium criterion model (EQC) by Mackay et al. (1996) emphasized the high volatile nature of siloxanes showing that the significant partitioning to air when it is emitted to air or soil. However, when it is emitted to water, which is the focus of this study, a large amount is also expected to deposit onto sediments because of relatively higher K_{OW} value. A considerable amount of D5 is predicted to remain in water. For this study, the sludge in the wastewater is functionally analogous to sediments in surface water with regards to higher K_{OW} value of D5. So it is expected that, whether siloxanes are emitted in soil, water or air, because of volatile nature and relatively higher K_{OW} values, their persistence can be observed in all the environmental matrices.

2.5. Ecological Significance

Generally higher molecular weight siloxanes possess higher while lower molecular weight siloxanes possess lower bio concentration factors calculated from apparent octanol/water partitioning coefficient. However in practice, absorbance of large molecular weight siloxanes through cell membranes can be restricted the due to large size. Also due to the volatile nature of siloxanes, concentration in water or soil is reduced and less concentration is available for uptake in biota (HSDB, 2004). It was observed that MM is irritant to skin and D4 was classified as R62 “possible risk of impaired fertility” and as R53 “may cause long term adverse effects in the aquatic environment” in Europe (Keml, 2004). USEPA in 2003 found some evidences of the potential carcinogenicity of siloxane D5. An ecological toxicity study was carried out for D4 (US EPA 2003) which demonstrated the concentrations of D4 and effects on various organisms. The effect studied were immobilization, growth, mortality, reproduction, intoxication, multiple effects recorded as one result. Following table shows the eco-toxicological data for D4.

Table 2-7 Toxicological Data for D4

Common Name / Scientific Name	**Endpoint**	**Effect**	**Duration (Days)**	**Conc. (µg/l)**
Opposum Shrimp / Americamysis bahia	NOEC	IMBL	14	9.1
Midge/ Chironomus tentans	NOEC	GRO	14	>15
Midge/ Chironomus tentans	NOEC	MOR	14	?15
Sheepshead minnow / Cyprinodon variegatus	NOEC	MOR	14	6.3
Water Flea (Daphnia magna)	NOEC	IMBL	48	>15
Water Flea (Daphnia magna)	NOEC	REP	21	1.7-15
Rainbow trout, Donaldson trout / (Oncorhynchus mykiss)	LC50	MOR	14	10, 8.5-13
Rainbow trout, Donaldson trout / (Oncorhynchus mykiss)	LOEC	MOR	14	6.9
Rainbow trout, Donaldson trout / (Oncorhynchus mykiss)	NOEC	MOR	14	<=4.4
Rainbow trout, Donaldson trout / (Oncorhynchus mykiss)	NOEC	NOC, MULT	93	4.4
Water Flea (Daphnia magna)	-	ITX, IMBL	21	1.7-15

OEC: No Observed Effect Concentrations; IMBL: Immobilization; GRO: Growth; MOR: Mortality; REP: Reproduction; ITX: Intoxication; NOC, MULT: Multiple effects recorded as one result.

It can be seen that the lowest NOEC was found 1.7µg/l for Water Flea (Daphnia magna) which is a commonly found zooplankton which is representative of healthy limnic ecosystems. In support of this study, using US EPA’s PBT Profiler software, chronic values for fish for three siloxanes were derived to understand long term impact of siloxanes in aquatic environment (Lassen et al., 2005). The table below shows the data.

Table 2-8 Chronic Values for fish (Lassen et al., 2005)

Compound	**Fish ChV (mg/L)**
D4	0.058
D5	0.021
MM	0.062
MDM	0.028

2.6. Regulatory Status

US EPA has received results of a cancer study on Siloxane D5 in rodents submitted under TSCA section 8 (e). The results of the study indicate that there may be a cancer risk associated with D5. However, EPA hasn't yet conducted a risk assessment for D5 and hence is not in a position to characterize potential risks to human health or the environment. (Siloxane D5 Fact Sheet, USEPA). Polymethyldisiloxane, one of the linear siloxanes, has been approved by FDA as a food additive as long as the levels do not exceed 10 ppm except for gelatin desserts which may contain up to 16 ppm per serving. (FDA. 1969). Polymethylsiloxanes (100 cSt) and /or polymethyl-phenylsiloxanes (not more than 2% cyclosiloxanes of up to 4 siloxy units) have been approved for use on metal surfaces which come in contact with food (F.D.A., 1972). The department of transportation does not require a special label on siloxane products except when the formulation contains other active ingredients such as toluene (Union Carbide, 1973). US EPA Combined Heat and Power Partnership program supported Biomass CHP Catalog of NREL, (2003) that siloxanes may damage the prime mover (a machine that transforms energy) during electricity generation using biogas and need to be treated. Siloxanes are included as a general category of emerging chemicals in US EPA's Strategic Surveillance Plan (March 2009). In December 2010, US EPA updated chemical action plans, siloxanes were targeted under Potential Future US Chemical Actions. A study in Nordic countries in 2005(Siloxanes in Nordic Environment, 2005, ISBN 92-893-1268-8) showed that, up to 100 tons of total siloxanes are used every year. Siloxanes enter the environment via point and non-point sources. They were declared as Persistent, Bio-accumulative and Toxic (PB&T) by US Environmental Protection Agency after an intense study in 1974. Danish Ministry of Environment published a document regarding some significant information on siloxanes in 2002. This document sheds light on the increasing consumption of siloxanes and their fate in the environment (Lassen et al., 2002). Canada Government – Ministry of Environment expanded the analysis of priority substances in selected media and sites which included siloxanes in selected fish, air, landfill gas and wastewater. They also initiated an international inter-laboratory study on volatile methyl siloxanes in fish, in corporation with company DOW Chemical. Environmental Penalty orders were introduced through the Environmental Enforcement Statute Law Amendment Act (Bill 133, June 2005). This legislation amended the Environmental Protection Act (EPA) and the Ontario Water Resources Act (OWRA), establishing the overall framework of EP orders. Two regulations (one under each Act) provide details of how, when and to which types of violations EPs will be applied. The enabling provisions in the Acts and the EP regulations come into force on August 1, 2007. The criteria are set out in CEPA regulations as follows.

Table 2-9 Criteria for Persistence

Criteria for Persistence		
Medium	Half-life	Half-life of D5
Water	>=6 months	38 days
Sediments	>= 1year	340 days
Soil	>= 6 months	340 days

Persistence is related to the length of time that a substance resides in the natural environment. The most common measure of persistence is a substance’s half-life or time it takes for the concentration of substance to be reduced to half of its original concentration in a specific media (air, water, sediment, soil). Persistence is based on a consideration of all environmental media. A substance is considered persistent if the transformation of half-life is met in any one medium. Degradation processes that are taken into consideration by Environment Canada when determining half-life of a substance are limited to substance, biochemical and photochemical processes.

Table 2-10 Criteria for Bioaccumulation

Criteria for Bioaccumulation			
Parameter	Limit	Actual (D4)	Actual (D5)
BAF	>= 5000	-	-
BCF	>= 5000	1700	5300
log K_{ow}	>= 5	5.1	5.7

Bioaccumulation indicates the uptake of substances by biota through consumption of food sources which are contaminated with the substance and / or directly from the surrounding media (Ex. Water, sediments). Three characteristics (as listed in Table 2-10 above) are considered that can be referred to determine the bio accumulative property of a substance. Most important is Bioaccumulation Factor (BAF), BAF is the amount of a substance within an organism (in its tissue) that has been taken up either via exposure to the surrounding media or through ingestion of contaminated organisms on which it feeds. Bio concentration Factor (BCF), BCF is the amount of a substance within an organism that has been taken up following exposure to contaminated media in which it resides. And the log of the octanol-water partitioning coefficient (log K_{OW}) of specific substance, which is a laboratory derived value that provides indication of bioaccumulation potential of a substance based on how much of it enters into the octanol phase (lipid surrogate) compared to water phase. Based on above criteria, siloxanes were included in the list of toxic substances prepared by Canada Ministry of Environment and are subject to Environmental Penalty upon violation under Environmental Protection Act and Ontario Water Resources Act.

2.7. Health Issues

It is evident that humans are exposed to siloxanes through use of personal and health care products. However, discussing human exposure to the siloxanes must be an attempt to assess their environmental safety rather than their apparent harmlessness to human being. Controlled studies on animals indicated that siloxanes are not responsible for fatigue, or irritation on human skin on repeated insult patch tests (Barry, 1973). In another study four human volunteers were fed a 7530 mg mixture of 6% silicon dioxide and 94% polydimethylsiloxane (1000cSt) for 10 days and neither adverse nor intestinal absorption were noted. On the other hand, during the occupational studies, certain compounds used in the manufacture of various siloxanes were found to be highly toxic. However, commonly used siloxanes themselves are not considered hazardous under occupational exposure conditions. (Hobbs, 1973). In epidemiological studies, siloxanes have resulted in no documented wide-spread syndrome of adverse effects and thus have no warranted epidemiological investigations in the strictest sense of the term. Studies failed to show the correlation between mammoplasty and breast cancer (Bowers and Radlauer, 1969; Hoopes et al., 1967). An interesting study was reported by Talbot and Meade in 1971, during the course of routine clinical anticoagulant procedure, some patients under treatment with warfarin or phenindione had elevated thrombotest percentages indicating either insufficient dosage or some interfering agent. After the investigation all patients indicated that they consumed potato chips cooked in an oil containing additives “allied” to the polydimethylsiloxane. After eliminating this product from diet for 7 days, thrombotest percentage returned to normal without alteration of anticoagulant (Talbot and Meade, 1971). These results indicate a possible adverse health effect of siloxanes consumed by ingestion on human body.

2.8. Operational Issues

Currently the real problem with siloxanes regards the operations of various instruments, equipment which is used in utilities, facilities and industries. Recently, legislation has encouraged the dry cleaning industry to change from using chlorofluoro solvents to more environmentally friendly products such as siloxanes. Due to widespread usage of siloxanes in all the applications, it is obvious to have higher concentrations of siloxanes in wastewater streams. As mentioned earlier, siloxanes have relatively higher K_{OW} values and hence have higher affinity to attach onto the particles, such as organic solids in wastewater. This causes the accumulation of siloxanes in sludge generated during the wastewater treatment. Today, most wastewater treatment facilities are inclined to digest the waste activated sludge anaerobically, produce biogas and utilize this gas for heat and electricity generation in house. Since the siloxanes accumulated in the sludge are volatile, they are detached from sludge particle during the anaerobic digestion and remain as an impurity in the biogas. While burning the biogas or utilizing it for any beneficial purpose, siloxanes are transformed into silicon oxide and stable solid amorphous compounds. The layer of siloxanes is formed on every equipment that is handling the gas, instruments like motor, boilers. Siloxanes are thermal and electrical insulators and hence it reduces the heat transferring efficiency of boilers and fire tubes. Usually generated biogas is utilized to heat the digester during winter and the deposition of siloxanes increases the demand of biogas and hence the heating costs. When the siloxane rich gas is used in engines, efficiency of engine falls dramatically because of silicone oxides deposition in combustion chamber. Frequent monitoring and repair of engines is required in such cases to avoid any bigger damages to valves, pistons, piston rings, liners, cylinder heads, and spark plugs and turbocharges. The operational issues with siloxanes have been observed among large and medium scale wastewater treatment plants where biogas is utilized for beneficial purpose (Robinson Group LLC., Siloxane Removal Technology, and SAGPack). Figure 2-2 shows the reported damages due to siloxanes in United States (red dots indicate the location where problems with boilers are observed). Wastewater treatment facilities on West coast, east coast and some places in north east have reported severe damage due to siloxanes. Some of the places around world have also reported similar damage. More studies have been conducted in Nordic countries, China and Japan. The figure 2-3 below shows the siloxane damages around the world. Typical concentration of siloxanes found in landfill gas is reported as 0.5 to 50ppm (v/v) and that in digesters gas is about 0.5 to 140 ppm (v/v). It is estimated that removal of siloxanes can save a 5 MGD Wastewater Treatment Plant $60,000 to $130,000 per year in operating costs. Following picture shows the deposition of siloxanes in a boiler (Bullard et al., 2009).

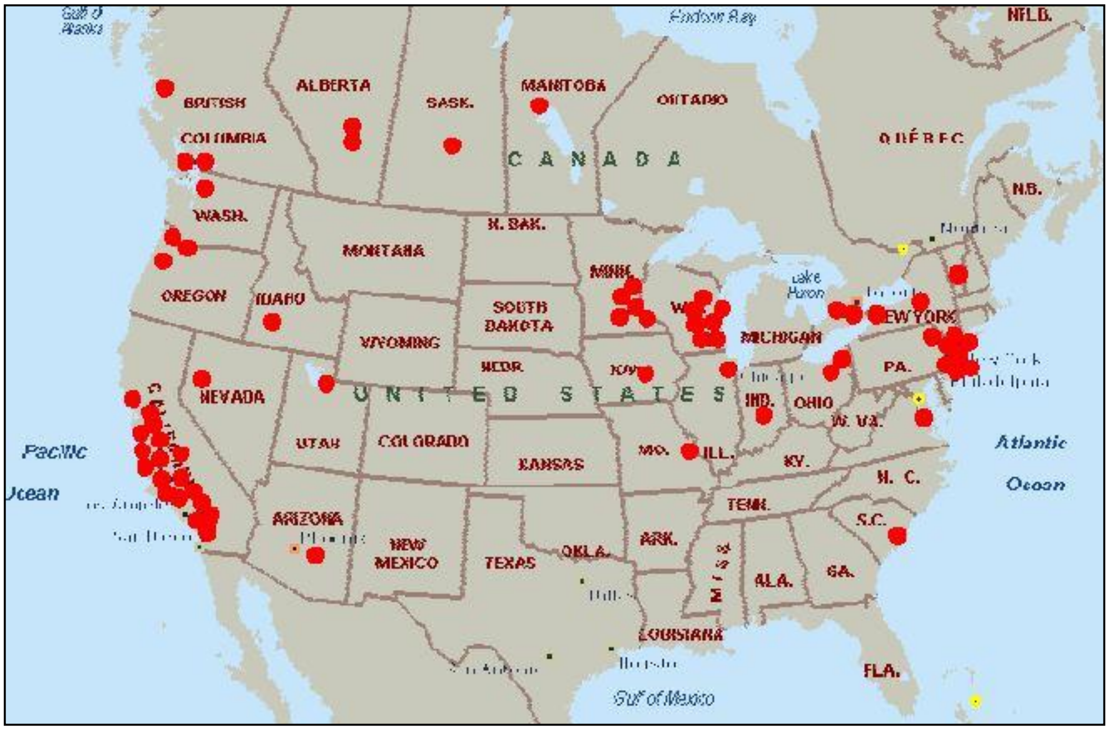


Figure 2-2 Damage due to Siloxanes: United States of America (Applied Filter Technology)

Figure 2-3 Damage due to Siloxanes: World

Figure 2-4 Siloxane Deposition in a boiler

When the deposits on the surface of equipment were analyzed it was found that silicon is the major contributing element that comes from siloxanes. Below is the summary of analysis (Dewil et al., 2006).

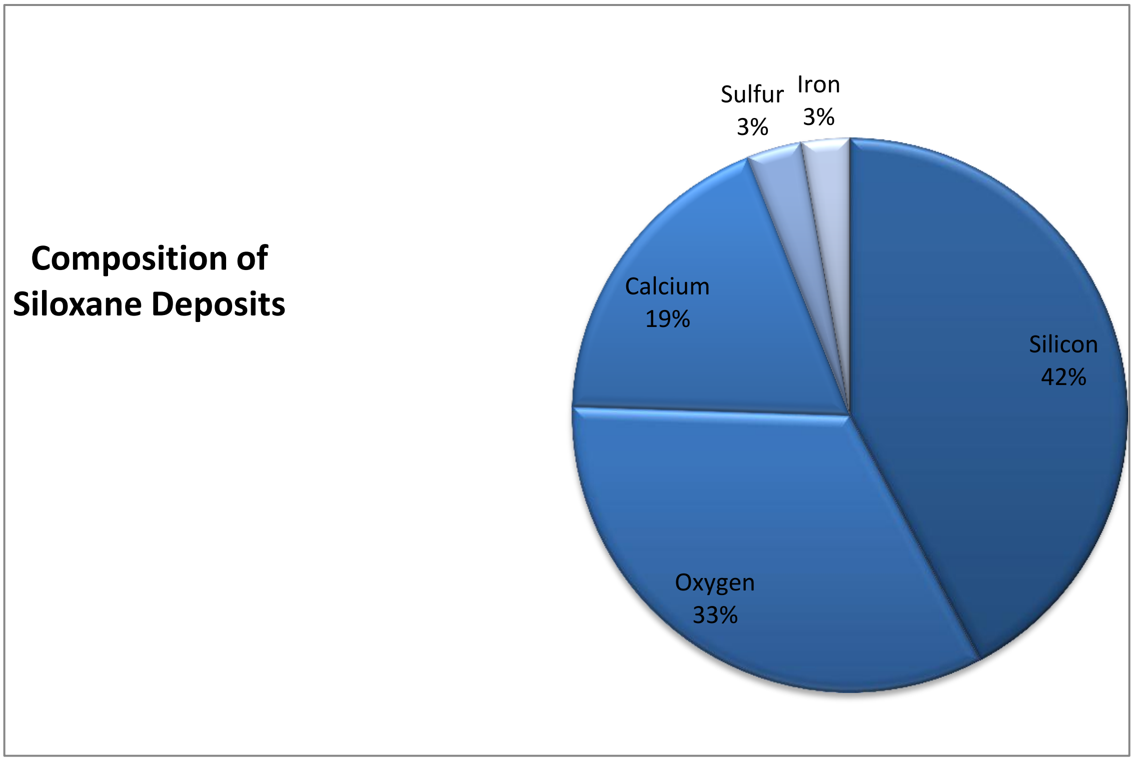


Figure 2-5 Composition of Siloxanes Deposits

A study was conducted to understand the role of siloxanes to evaluate beneficial use of digester gas. It was concluded that the siloxane deposition has considerable adverse effect on the efficiency of boilers. Typical digester gas constituents are given in the table 2-11. (Bullard et al., 2009)

Table 2-11 Constituents of Digester Gas

Constituent	Units	Typical Digester
Methane	% Volume	58-73
Carbon Dioxide	% Volume	35-41
Nitrogen	% Volume	0.1-2.5
Oxygen	% Volume	0.0 – 1.5
Heat Content	BTU /CFT	580 – 730
Total Siloxanes	Ppbv	2500 -7500

Table 2-12 provides the different species of siloxanes observed in digester gas and their concentration.

Table 2-12 Species of Siloxanes in Typical Digester Gas (PPBV) (Bullard et al., 2009).

Constituent	Digester Concentration
Octamethyltrisiloxane (MDM)	5
Hexamethylcyclotrisiloxane (D3)	2
Octamethylcyclotetrasiloxane (D4)	600
Decamethylcyclopentasiloxane (D5)	850
Total Siloxanes and Organosilicons	1457

2.9. Occurrence of Siloxanes in environment

Siloxanes are found in all environmental matrices. Although siloxanes do not exhibit any health related issues, their presence in environmental matrices is definitely anthropogenic and not natural. There are various issues related to siloxanes in their respective forms in different environmental matrices.

Siloxanes in Ambient Air

The study conducted in Nordic countries on siloxanes in natural environment reported the data regarding siloxanes in ambient air at different locations. The findings indicated that the highest concentrations of cyclo-siloxanes were found in ambient air near sewage treatment plants. The concentrations ranged from 0.1 – 18 µg /m^3 for D4, 0.1 – 21 µg /m^3 for D5 and 0.1 – 0.5 µg /m^3 for D6 in ambient air near sewage treatment plants. Concentrations up to 0.1 – 2 µg /m^3 were found in urban area ambient air. Surprisingly, air above landfills weren’t determined to contain considerable amounts of siloxanes. Except sewage treatment plant air samples, all other samples ranged from 0.1 to 5 µg /m^3. The concentration of linear siloxanes in air was below the detection limit in all samples analyzed. The atmospheric dispersion pattern of siloxanes in air is still unknown. But it was shown that sewage treatment plants and several other point sources generate the elevated concentrations of siloxanes in air. The study concluded that more extensive air monitoring along urban-rural transects or with increasing distance from sewage treatment plants would be required to understand behavior of siloxanes in air (Siloxanes in Nordic Environment, 2005, ISBN 92-893-1268-8). It is generally assumed that siloxanes do not undergo any chemical reactions such as oxidation or photo degradation. It means that the reaction rate of siloxanes in atmosphere is very low. Following table gives the information on reaction rate of different siloxanes in atmosphere.

Table 2-13 Reaction Rates and Reactants in atmosphere (Dewil et al., 2005)

Compound	**O_3**	**$^{\cdot}NO_3$**	**$^{\cdot}OH$**
HMDS	$< 7 x 10^{-21}$	$< 8 x 10^{-17}$	$< 1.4 x 10^{-12}$
D3	$< 3 x 10^{-20}$	$< 2 x 10^{-16}$	$< 5.2 x 10^{-11}$
D4	$< 3 x 10^{-20}$	$< 2 x 10^{-16}$	$< 1.0 x 10^{-12}$
D5	$< 3 x 10^{-20}$	$< 3 x 10^{-16}$	$< 1.5 x 10^{-12}$

There is a complex path for oxidation of siloxanes in atmosphere. It starts with the initial attachment of methyl group of siloxanes forming a silico-methyl radical ($Si – CH_2^{\cdot}$). This radical then reacts with atmospheric O_2 to peroxide radical ($Si – CH_2OO^{\cdot}$). Since Si and O have affinity towards each other, the peroxide is further transformed into an oxycarbon ($Si – O – CH_2 – O^{\cdot}$) and (Si – O – CH2 = O). Both of these intermediates are unstable and hence easily hydrolyzed into a silanol (Si –OH) and are further degraded. The same process repeats until all methyl groups have been removed from Si atom which ultimately leads to silicates and CO_2 as the reaction products (Dewil et al., 2006). Cyclo siloxanes are resistant to environmental decomposition process. Siloxanes in gas phase undergo oxidative degradation through photolytic chemical change, by reaction with hydroxyl or nitrate radical or by reaction with ozone. Experiments were done to understand life time of cyclo siloxanes in the environment and results showed that the calculated life time of Decamethylcyclopentasiloxane (D5) is 10 days and that for Octamethylcyclotetrasiloxane (D4) is 30 days. It is observed that the life time in environment increases with decrease in molecular weight (Grumping 1998).

Siloxanes in Digester Gas

Quality of digester gas is an important parameter for combined heat and power projects, which are adopted by most of the wastewater treatment utilities. Digester gas samples have been analyzed for major gas constituents, siloxanes and organosilicons, sulfur species and volatile organic compounds. Major constituents in the biogas stream include methane, carbon dioxide; nitrogen and oxygen (Table 2-11). Total siloxanes content in the biogas from both a volumetric and fuel content standpoint is important since this is the indication of fouling potential associated with siloxanes on relative basis between streams. Following table indicates the fouling potential concentrations of siloxanes in digester gas.

Table 2-14 Fouling Potential of Siloxanes

Constituent	Units	Typical Digester
Total Siloxanes	Ppbv	2500 -7500
Silicon in Fuel	µg Si / CFT	150 – 1500
Silicon in Fuel	µg Si / BTU	0.10 – 1.80

The list of siloxanes species found in digester gas is given in Table 2-12. It is clearly seen that among the siloxanes found in digester gas, Decamethylcyclopentasiloxane (D5) is the dominating siloxanes species among all other. Octamethylcyclotetrasiloxane (D4) stands second in significant amount. Most of other linear and cyclic siloxanes species do not have significant concentration in the digester gas. The following equation expresses the formation of oxides of silicones during combustion of the biogas.

$$\begin{array}{lllllllll} C_{10}Si_5H_{30}O_5 & + & 15\,O_2 & \rightarrow & 5SiO_2 & + & 10CO_2 & + & 15\,H_2O \\ 370.8 & & 479.7 & & 300.35 & & 440 & & 270 \end{array}$$

The scales on two of the engines damaged due to siloxanes were analyzed in Germany; it was observed that 34 % and 32 % Silicon, 66% and 60% Oxygen, 5% Aluminum and 4 % Calcium by weight were the constituents of residues in the engine. It confirms the fact that the damaging agent is siloxanes which comes from biogas (Dewil et al., 2006). The analysis of digester gas from Fort Collins Water Treatment Plant, CO indicated that D5 contributes to about 81% of total siloxanes in digester gas. D4 was the second largest concentration after D5. All other linear and cyclic siloxanes were negligible. Fig. 2-6 below shows the average values of siloxanes concentrations of two digesters at wastewater treatment facility.

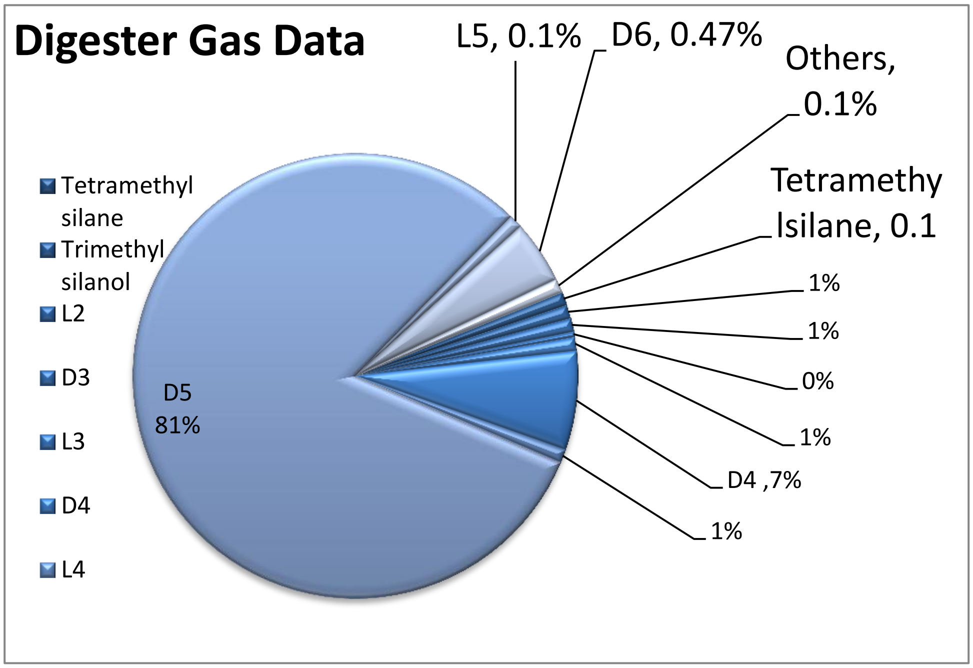


Figure 2-6 Siloxanes in Digester Gas (Data: Drake WWTP, Fort Collins, CO)

Siloxanes in surface water sources

As we have seen earlier, siloxanes possess very low water solubility and very high K_{oc} (10000 to 600000). Because of this property, Siloxanes have high tendency to attach very tightly to organic matter in aquatic environment including surface water. Lot of work has been done. A lot of research has been conducted to study concentrations of siloxanes in river systems in China and Nordic countries. Some work also has been done in United States to study concentrations of siloxanes and organo-silicones in great lakes. Decamethylcyclopentasiloxane (D5) concentrations were measured in the samples from River Nene, United Kingdom at various distances away from the sewage treatment plant effluent discharge point.

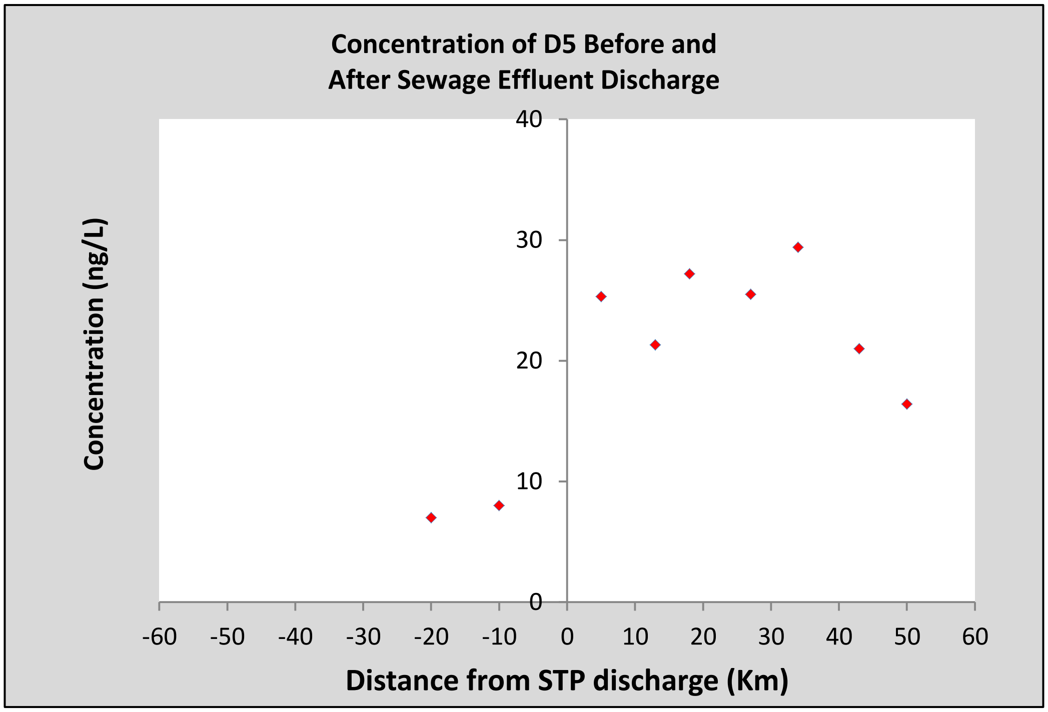


Figure 2-7 Siloxanes concentration in River System (Data: Sparham et al., 2008)

It is clearly seen from Fig 2-7 that the concentration of siloxanes in the River Nene increased drastically after the sewage treatment plant effluent discharge point. Hence, although the concentrations are low, siloxanes end up in surface waters through wastewater effluent discharges (Sparham et al., 2008). Another study in UK reported that considering estimated D5 flux into wastewater of about 11.6 mg per capita per day, 95.2% removal rate in sewage treatment plants and dilution factor of 10 resulted in modeled surface water concentrations up to an order of magnitude higher than those observed downstream of sewage treatment plants in two UK Rivers. This study suggested that looking at the modeled concentrations in river systems, an exposure assessment is required. Concentrations of D5 have been reported in the range of 12.9 to 151 ng/L in River Nene and River Ouse (Price et al., 2010). Substantial amounts of both cyclic and linear siloxanes were observed in wastewater, which indicates the use of personal care products and discharge of siloxanes in used water. The concentration of cyclic siloxanes is about 100 times greater than concentration of linear siloxanes. Again, water samples shows that the Decamethylcyclopentasiloxane (D5) is the dominating siloxanes amongst all cyclic and linear siloxanes. However, this ratios and concentrations varied for different locations. However physical and chemical properties of MM indicate that it was more soluble in water than other siloxanes, but was also more volatile (Kaj et al., 2007, Siloxanes in Nordic Environment, 2005, ISBN 92-893-1268-8). In another laboratory study by Hamelink et al. (1996), the Henry's law constant was determined for Octamethylcyclotetrasiloxane in aquatic matrix. At 20^0C, it is determined as 3.4. The calculated half-life for Octamethylcyclotetrasiloxane volatilization from river water would fall within the range of 3 – 138 hours and the half-life for lakes and ponds would be 138 – 345 hours. These results suggest that under typical environmental conditions, inorganic and organic co-solutes will increase the Henry's law constant for Octamethylcyclotetrasiloxane and reduce any potential hazard to aquatic organisms. This study concluded that the siloxanes are expected to rapidly partition into atmosphere from water bodies and once in the atmosphere they are expected to undergo oxidative decomposition in the troposphere (Hamelink et al., 1996). Distributions of silicones in waters of Japanese rivers were studied and siloxanes concentrations ranged from 2 to 54.2 ppb. The correlation between BOD / COD and the siloxanes was established and it was reported that siloxanes concentrations are higher in waters of higher BOD / COD concentrations. This fact supports that siloxanes in the aquatic environment come from anthropogenic sources (Watanabe et al., 1988).

Siloxanes in sediments

Since siloxanes have higher K_{OW} values, they have affinity to attach to sediments. A study was conducted in Northeastern China and reported concentrations of cyclic and linear siloxanes in sediments of Songhua River. Four cyclic siloxanes namely Octamethylcyclotetrasiloxane (D4), Decamethylcyclopentasiloxane (D5), Dodecamethylcyclohexasiloxane (D6) and tetradecamethylcycloheptasiloxane (D7) as well as thirteen linear siloxanes (L4 to L16) were detected in sediment samples from Songhua River in northeastern China. All sediment samples showed concentration of total siloxanes as high as 2050 ng /g dry weight. Concentration of cyclic siloxanes was greater than the linear siloxanes in sediment samples. D5 and D7 were the dominant compounds amongst cyclic siloxanes. Among linear siloxanes L6 contributed about 30% of all. Total concentration of cyclic and linear siloxanes totaled up to 7.94 to 2040 ng/g dry weight for sediment samples tested. (Zhang et al., 2011). Another study was carried out in United Kingdom to determine Decamethylcyclopentasiloxane (D5) concentrations in river and estuarine sediments. In sediment samples from river Great Ouse (UK), Decamethylcyclopentasiloxanes concentration was detected within the range of 186 to 1450 ng/g of dry weight while Octamethylcyclotetrasiloxane (D4) was 12 to 24 ng/g of dry weight. Hydrophobic nature of D5 confirms that it is likely to attach to sediments. During Nordic monitoring program, marine sediments in urban areas were found to contain siloxanes at concentrations within the range of 1.8 to 130 ng/g dry weight with only one sample of 2000 ng/g dry weight concentration. Lake Ontario sediment samples were analyzed by Dow Corning (Brookes et al., 2007) and determined the concentration of D5 of 780 ng/g of dry weight. The propensity of D5 to sorb to organic carbon in sediment has been confirmed in this study (Sparham et al., 2011). Polydimethyl Siloxanes which are widely used in healthcare industries accumulates in soil, sediments. The natural degradation of PDMS results in cyclo siloxanes of lower molecular weight such as Octamethylcyclotetrasiloxane (D4), Decamethylcyclopentasiloxane (D5) as end products. The rate of natural degradation depends upon the soil moisture conditions. (Steven et al., 1998).

Siloxanes in Wastewater and Sludge

A study by Dewil et al. (2007) demonstrated that linear and cyclo siloxanes preferentially adsorb on to Extracellular polymeric substances (EPMS) of sludge flocks. Smaller molecules such as hexamethy-lcyclotrisiloxane (D3) volatilizes rapidly and are present in wastewater in small amounts, whereas large molecules such as Dodecamethylcyclohexasiloxane (D6) do not volatilize during sludge digestion due to low vapor pressure and remain in waste activated sludge. The fate of Octamethylcyclotetrasiloxane (D4) and Decamethylcyclopentasiloxane (D5) at Activated Sludge pilot wastewater treatment plant was investigated by continuously dosing the influent with exaggerated amounts of the compounds and measuring emissions in various matrices such as gas, effluent, sludge. Fig. 2-8 below shows the removal tendency of D4 and D5 in pilot wastewater treatment plant. It is clear from Fig 2-8 that siloxanes concentrations are higher in the waste activated sludge. This is due to the fact that siloxanes are hydrophobic and have high affinity to attach with sludge during wastewater treatment. Very low concentrations measured in the air samples above primary clarifier, aeration basin and secondary clarifier are representative of amount of volatilization that occurs in the treatment train. It has been observed that siloxanes concentration up to 300- 500 mg /kg is observed in sludge at some sewage treatment plants.

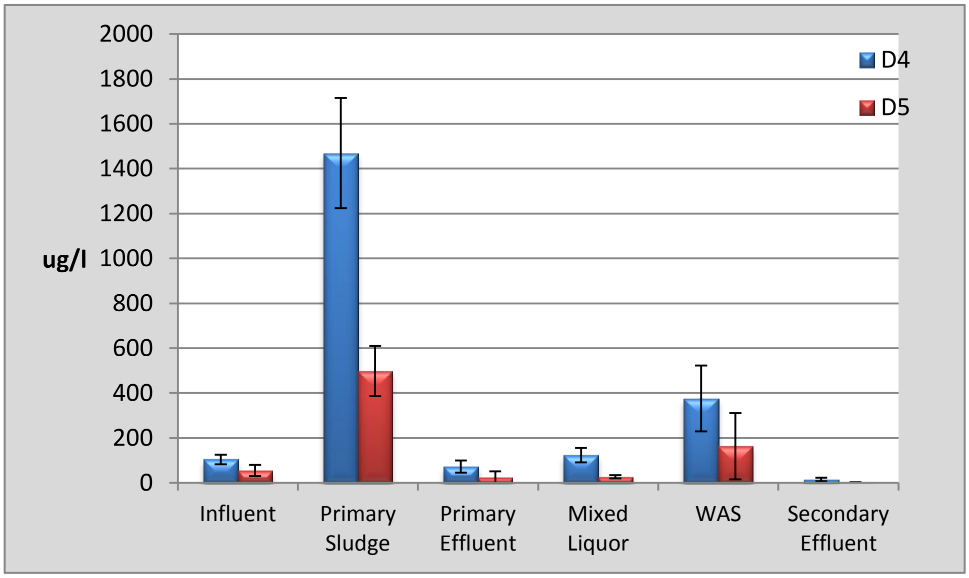


Figure 2-8 Removal Tendency of Siloxanes (Data Courtesy: Parker et al., 1999)

It has been observed by Parker et al. (1999) that out of total Siloxanes entering in environment, 33% of Octamethylcyclotetrasiloxane (D4) enters in wastewater stream. As this travels through the treatment plant, 95% of Octamethylcyclotetrasiloxane (D4) is removed in conventional activated sludge process via process of sorption to solids and volatilization by aeration. Adsorption to sludge contributes 49% of removal of Siloxanes while 38% is removed by volatilization. 2008). A study at wastewater treatment plant showed that the estimated wastewater load for Decamethylcyclopentasiloxane (D5) is about 11.6 mg per capita per day. Use of cosmetic products, healthcare products brings around 8500 tons per year into the environment. This is usage is increasing day by day. The study assumed average D5 content of 30% and 10% loss of D5 to wastewater during and after use. The predicted environmental concentration (PEC) of Siloxanes from personal healthcare products was determined as 330 ng/l (Price 2010). Siloxanes enter the soil compartment through direct and indirect routes including spreading of treated sludge, spills and landfills (Consuelo 2010). The concentration ranges in sewage sludge samples from 602 to 2360 ng/g dry sludge. Cyclic siloxanes were always found to be in higher concentrations than linear siloxanes. Among cyclic siloxanes, D5 was the dominant compound in both sediments and sludge samples. Siloxanes show very low water solubility about 0.002 to 0.056 mg/l at 25^0C. The low water solubility suggests that these compounds will be partially removed from aqueous phase during wastewater treatment by adsorption onto sludge (extra-cellular polymeric substances). Chinese siloxanes monomer production capacity was expanded to 1 million tons/year and very less information is available on concentrations of siloxanes in the environment (Zhang et al., 2011).

Others

A study done in China demonstrated the potential of D4 and D5 exposures from indoor dust. This study showed that there is considerable amount of Siloxanes attached to indoor dust and can affect adversely the human health. Floor dust collected from vacuum cleaner was tested for siloxanes. Frequency of detection was observed as 63.6% for L5 and 55.7% for L6 for floor dust while it was 50% and 58.3% for the dust collected from inside electrical devices. Linear siloxanes were higher in concentration than cyclic siloxanes. This pattern has proved that high molecular weight linear siloxanes are widely present in products used indoors in China. The highest concentrations of L9-L14 measured in indoor dust were within the range from151 to 924 ng/g. L10 was the most common siloxanes found. A relationship between concentration of siloxanes and number of electrical / electronic devices has been established. It is observed that the concentration of D4, L8, L9 and L10 were significantly higher in dust samples from the room where more electrical /electronic devices are used. Electronic components are coated in siloxanes to increase stability against mechanical and electrical shock, radiation and vibration. These compounds can volatilize and accumulate in dust. Another relationship between siloxanes concentrations and the number of occupants and smokers has also been established. The general trend suggests that greater use of siloxanes containing products occurs when there is more number of occupants. Higher concentrations of total cyclic and linear siloxanes were observed in dust samples from houses with smokers than that in nonsmokers. However this difference was not statistically significant. Additional statistical approach suggested by (Kersten and Reich) using 75th percentile of the category was used and found that smoking is a source for some linear siloxanes in indoor dust (Yan Lu, 2010).

2.10. Analysis of Siloxanes: Available Techniques

It is realized that presences of siloxanes adversely affect the operations of mechanical equipment.

Analysis of siloxanes in Gas Phase

A method was described by Kierkegaard et al., 2010 to determine Decamethylcyclopentasiloxane (D5) in gas phase using commercial solid phase extraction cartridges. This method is based on the high trapping efficiency of sorbent Isolute ENV+, combined with a comparably high sampling rate. A small amount of sorbent (10mg) is eluted in a small volume of n-hexane (0.1 – 0.6 ml), which is injected onto a GC/MS system without further processing. The limit of quantification provided by this method is low (~0.3 ng/m^3), good repeatability and limited breakthrough (~1%). The concentration measured by this method is reliable. Concentrations measured in Swedish air ranged from 0.7 – 8 ng/m^3 over a period of 4 months. The sampling is done using two 10mg ENV+ cartridges assembled in series. The air is pulled using a diaphragm pump (GASTMAA-V109-HD, Gas Manufacturing, Inc., MI, USA). The flow rates vary from 0.9 – 3.0 L/min. ENV+ cartridges are rinsed with 6ml of hexane prior to sampling. Prior to extraction, 35 ul of a 2 ng/ul ^{13}C-D5 solution is spiked and then cartridges are subsequently eluted with 0.6ml n-hexane directly into a GC vial. Analysis was done on a Trace GC Ultra (Thermo Electron Corp.) coupled to a MD800 MS detector (Fisons Instruments

SpA) using electron ionization (EI). The GC was equipped with a large volume splitles injector (Thermo Electron Corp.) with a Merlin microseal ® septum. 5 ul of the extract injected at an injector temperature of 220^0C. 13C-D5 is used as internal standard. The calibration curve included 9-11 standards with a concentration range of 0.53 – 180 pg/ul. In order to control quality, each sample and backup is accompanied by a field blank. The field blank and samples were treated in identical manner except pumping air through blank cartridges for few second. The sample, backup and field blank are prepared and extracted in parallel. The recovery of 96% was observed. (Kierkegaard et al., 2010). Using GC-MS and Fourier Transform Infrared (FT-IR) spectroscopy, mixture of linear and cyclic organic siloxanes were analyzed. Dimethyldichlorosilane when undergoes various controlled conditions during technical applications, it gets hydrolyzed and siloxanes structures are formed. GC-MS provides the information on molecular mass of these compounds however do not identify isomeric structures which are also formed in lower quantities. Hence GC is coupled with FT-IR to identify these isomeric compounds. Using this combination complex cyclo siloxanes compounds were elucidated. Results showed that the cryo-GC-FT-IR system combined with GC-MS is a powerful tool in elucidating complex siloxanes structures (Wachholz et al., 1994). In another method Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) technology is used for characterization of siloxanes residues. The hydrophobic properties of polydimethylsiloxane elastomers after environmental degradation arises from the migration of low molecular weight siloxanes form the bulk to the surface (Hunt et al., 2000). For the adsorption of cyclic siloxanes from gas phase XAD-2, XAD-4 resin, activated carbon or polyurethane foam were placed in a glass tube (155 x 5 mm I.D. or 190 x 14 mm I.D.) and fixed with glass wool on both sides. For complete adsorption the gas mixture stored in the gas bag has to be pumped once through this material with 0.5 L/min. Then 10 ml of the desorption solvent are dosed into this adsorbing tube passing it against the direction of loading. About 1 drop /min of the eluent is added this way. Alternatively, the material from the adsorbing tube was transferred to a test tube with screw neck, 5 ml of hexane is added and the tube is closed. Desorption is aided by 10 min ultrasonification (P=200W). The solutions of desorbed siloxanes obtained with both methods are spiked with 300 ul of tetradecane solution in hexane (100mg/ml) and diluted with hexane to 25 ml. This solution is used for GC separation using flame ionization detector or mass spectrometric detection. A Varian (Darmstadt / Germany) Model 3700 GC system with a fused-silica capillary column and an FID was used and programmed as follows: 60^0C min isothermal, 10^0C / min to 240^0C, 10 min isothermal at 240^0C. Helium is used as carrier gas with 33 cm/s linear velocity. Injector temperature was set up at 240^0C. Injection volume is 1ul and split ratio is 1:20. The column used is SE-54 with film thickness 0.25um, 50m x 0.32 I.D. Mass detection is done using TSQ 70 from Finnigan MAT combined with a PDP 11/73 data station. Electron impact ionization is applied with energy of 70eV. The electron multiplier is operated at 1200V with a dynode voltage of 5kV. Source temperature is maintained at 150^0C (Huppmann et al., 1995). Another method demonstrates the use of Low Temperature Gas Chromatography coupled on line with Inductive Coupled Plasma Optical Emission Spectroscopy (LT-GC/ICP-OES) and Gas Chromatography –Mass Spectrometry (GC-MS). Gas samples are collected into PE-bottles and stored in the dark at 4^0C. Biogas samples are collected in gas sampling bags (Grumping et al., 1998). Quantitative analysis of volatile methyl siloxanes in landfill biogases is done using Atmospheric Pressure Chemical Ionization / tandem Mass Spectrometry (APCI-MS/MS) in another study. HMDS-d18 is used as internal standard. The limit of detection is achieved as 2 µg /m^3. The method is successfully applied for determination of D4 and D5 contents in biogas samples. The diluent gas is sampled directly into the ion source, the headspace vapors are dynamically diluted into the gas stream via a 500 ul gastight syringe mounted in a syringe pump model 22. Flow rate of the headspace samples is controlled by the speed of syringe pump to provide analyte concentrations ranging from 70 – 6500 µg/m^3 (Badjagbo et al., 2009). In another method, the biogas is collected in a gas bag. The flow of siloxanes is adjusted to 1 l/min using a suction pump and approximately 15L of biogas is circulated through the wet sampling equipment for 15 min for each measurement. In the wet sampling equipment, three 150 ml impingers were connected in series. The first impinger is empty, while the second and third impingers are filled with a total of 200 ml of n-hexane. All three impingers are chilled with ice. The integrated gas volume is measured using a dry gas meter. After sampling, concentrations of the seven types of siloxanes present in the gas are measured by GC/MS without pretreatment of collected liquid sample. In addition, real time measurement of the concentration of siloxanes is performed by bifurcating a sampling line of biogas and circulating the biogas at a rate of 0.5 – 0.8. L/min through a siloxanes continuous analyzer. In GC/MS, carrier gas used is Helium, HP-5MS capillary column with 60m length, 0.25 mm internal diameter and 0.25um film thickness is used. Selected ion monitoring mode is used and the molecular ion of each compound is scanned at a rate of 1.5 – 2 scans /s. The inlet and interface temperatures are maintained at 230^{0}C and 280^{0}C respectively. The column temperature is initially held at 40^{0}C for 4 min and is then increased to 100^{0}C at a rate of 6^{0}C/min and then to 200^{0}C at 4^{0}C/min. Finally the column is heated to 280^{0}C at a rate of 30^{0}C/min, and its temperature is maintained at 280^{0}C for 3 min (Oshita et al., 2003). Another research has compared impinger method and canister method for analysis of siloxanes in air. Sample collection is complicated, required active sampling and slow in impinger method while canister method is simple, passive sampling and is fast. Standard preparation is simple and fast for impinger method while it's complicated and slow for canister method. Impinger method can analyze MM, MDM, D4, D5 and D6 with good efficiency while canister method can analyze only pentamethyldisiloxane, MM, MDM and D3. Reporting limits in impinger method are 1µg/ml for all compounds other than D6 and 2µg/ml for D6, or ~50ppb assuming 6ml methanol and 20L air volume. For canister method limit of reporting is 0.5 ppmv (Saeed, Kao and Graening, 2002). Apart from these research based methods, some commercial application methods and instrumentation is available for analysis of siloxanes in gas or air phase. Some of the methods are Air Toxics, Jet Care, OSB, AtmAA, AnSol, Deutz and Jenbacher method. Of these, Air Toxic method is the impinger method described above. Jet Care method is an oil sampling method. The sample is bubbled through three oil bottles in series. Siloxanes are absorbed into the oil and then analyzed on GC/ICP. This method does not differentiate if the silicon is from VOSCs or from particulates. Concentration of siloxanes is back calculated based on gas volume processed. Siloxanes are reported as mg Si /m^3 at 100% methane equivalent by this method. Currently this method has limited use in biogas industry, but it is gaining traction due to solar turbine's identification of Jet Care as preferred test method. Mineral oil used may not capture 100% of the siloxanes. Composite sample rather than grab sample is preferred. Detection limits are similar to Air Toxics impinger method. This method captures all silicon, including silica. Silica may be less problematic though than siloxanes. The results from this method do not give speciation. OSB method includes collecting grab samples in bags. This method can analyze twenty two siloxanes using GC/MS. This is direct determination of concentration of siloxanes in gas. Results are reported in mg/m^3, mg Si/m^3 and ppmv. This method does provide speciation of siloxanes. This method is widely used in ultra-low siloxanes levels in high –Btu plant product gases. This method allows very low limits of detection. The method requires using bags with non-silicon based valve lubricants for collection of sample. Broad siloxanes scans few such siloxanes where are not analyzed by any other method. Deutz method uses bags for collection of sample and shipped to Germany for analysis. This method test for 8 siloxanes namely L2, L3, L4, D3, D4, D5, MOH and tetramethylsilane. Very low limits of detection are obtained. Results can be reported in mg/m^3 and $mg\ Si / m^3$ at methane content collected and at 100% methane content equivalent. Limited data about this method is available. Jenbacher method requires gas passed through a sample tube containing activated carbon and tube is then shipped to lab. Sample draw time is 30 min. The mass of siloxanes on activated carbon is determined by GC/MS and concentration of siloxanes in gas is back calculated. This method tests for L2, L3, L4, D3, D4, D5, MOH and four silanes. Results are reported as mg/m^3, $mg\ Si/m^3$ and ppmv (as Si equivalent). This is a private method. Very limited comparative database is available. Activated carbon may not capture 100% siloxanes but probably does. Units are conveniently expressed and lower limits of detection are obtained. AtmAA method is moderately used in LFGE industry. Gas is sampled by bag or canister and analyzed on GC/MS. L2, L3, L4, D3, D4 and D5 are tested. Moderately low limit of detection is available. Ansol method requires bag samples or canisters. More than ten siloxanes are analyzed on GC/AED. This reports siloxanes on a speciated basis as ppmv (as Si) and as $mg\ Si/m^3$ in total. The Table 2-15 below summarizes the available techniques for analysis of siloxanes in air / gas phase and their usefulness.

Table 2-15 Comparison of Air / Gas sample collection methods

Performance Criteria	Canister	Impinger	Sorbent Tube
Ease of Sampling	Excellent	Poor	Fail
Representative Sample	Fair /Poor	Excellent	Fair
D4 / D5 siloxanes recovery	Fair	Excellent	Fair / Poor

Table 2-16 Comparison of Analytical Techniques for Quantification

Performance Criteria	FID	AED	MS
Detector selectivity	Poor	Fair	Excellent
Availability	Excellent	Poor	Fair / Excellent
Cost	Excellent	Poor	Fair
Reporting Limit	< 0.50 ppmv possible	< 0.50 ppmv possible	< 0.50 ppmv possible

Liquid Phase Analysis

Although siloxanes are hydrophobic in nature, they are present in aqueous matrices up to some extent. A method by Sparham et al., (2008) describes the analysis of Decamethylcyclopentasiloxane (D5) in river water and wastewater treatment plant effluent using headspace gas chromatography and mass spectrometry. Internal standard addition to samples and field blanks were carried out in the field to provide measure of recovery and prevent any exposure of samples to laboratory air which might contain background D5 levels. Acetone was used for preparation of spiking solutions with high performance liquid chromatography grade. Ultrapure water is used. 20ml headspace glass vials with 20 mm butyl/PTFE crimp caps are used. Both vials and caps are used without any pretreatment. Method development and validation were carried out on HP 7694 headspace auto sampler. Each vial is moved to the heated zone and allowed to equilibrate at 80^0C for 10 min. Other parameters include : transfer line 120^0C, loop 100^0C, cycle time 30 min, injection time 1 min, loop equilibrium time 0.01 min, loop fill 0.2 min, pressurization time 0.15 min, vial equilibration time 10 min and vial pressure 10psi. During the heating phase sample is mixed by mechanical vibration. The vial is then pressurized with helium which forced a portion of headspace (3ml) through the inlet held at 220^0C onto a 6890 gas chromatography equipped with a 5973 mass spectrometric detector from Agilent Technologies. The column used is J&W DB-FFAP (30m, 0.25mm inner diameter, 0.25um film thickness, helium flow 1.5ml/min) and is programmed at 50^0C for 4 min, increased to 200^0C at 20^0C/min and held for 5 min) which is then detected by MS. The concentration determined by relating the MS response for the D5 quantification ion to the MS response of the internal standard. A calibration relationship is established for 0-1 x 10^4 ng/l and using internal standardization concentration of blank water, river water, sewage effluent (diluted 1 in 5 with ultrapure water), spiked and un-spiked with D5 is quantified. Performance testing of the headspace GC/MS method consists of analysis of five batches of duplicate samples of un-spiked, low concentration spiked (LS) and high concentration spiked (HS) samples. All samples were fortified with mass labeled internal standard (^{13}C-D5). The LS and HS samples were spiked at 20 and 1000 ng/l, respectively. Calibration standards are prepared by spiking ultrapure water with D5 standard solution in acetone. A headspace GC/MS method for the analysis of cyclic volatile methyl siloxanes D5 in river water and sewage effluent is straightforward to use and has limit of quantification of 10ng/l. Internal standard recovery was observed in the range of 71 – 125% for all sample types analyzed. The variability in recovery study was believed to be due to instrumental drift rather than a true matrix effect. Recovery of the internal standard was excellent (~90%) even for sewage effluents (Sparham et al., 2008).

Sludge /Sediment Analysis

Siloxanes possess higher affinity to attach sediments in surface water and sludge in wastewater. They are accumulated in this matrix at very high concentrations and hence it is convenient to measure their concentration in sludge or sediments. Method by Zhang et al., (2011) outlines the steps for extraction and detection of siloxanes from solid matrices as follows: Five grams of sediments or 1 gram of sludge (previously freeze dried and homogenized) was taken in a 50ml polypropylene tube, and 500 ng of M4Q was spiked as a surrogate standard. After 1 h of equilibration, 25 ml of a mixture of ethyl acetate / n-hexane (1:1 v/v) was added. After shaking for 30 min and centrifugation at 3000 rpm for 5 min, the solvent layer was transferred into a round bottom flask. The extraction was repeated two more times, and the extracts were combined into the round bottom flask. The extract was concentrated by rotary evaporation to approximately 2-3 ml and 5 ml isooctane was added and evaporated under a gentle stream of nitrogen to approximately 1 ml. The extract was further purified by passage through a silica gel packed glass column, which was eluted with 12 ml dichloromethane / n-hexane (1:4 v/v). The elute was concentrated and 10 ng PCB-30 was spiked as an internal standard for gas chromatography mass spectrometry analysis. Since siloxanes are found in components of GC and in the stationary phase of the capillary chromatography column, steps were taken to decrease the instrumental background. Concentration of linear and cyclic siloxanes was determined by Agilent 6890 GC interfaced with an Agilent 5973 MSD. GC separation was accomplished by use of 30m Rxi-5MS fused silica capillary column with 0.25 mm inner diameter and 0.25 um film thickness. One microliter of the aliquot was injected in splitles mode at 200^0C. The column oven temperature was programmed from 40^0C for 2 min, to 220^0C at a rate of 20^0C /min and to 280^0C at 5^0C/min and held for 10 min. Post run time at 300^0C was 5 min. The MS was operated in an electron impact selected ion monitoring mode. The ions were monitored at m/z 281 for D4, m/z 255 and 267 for D5, m/z 341 and 429 for D6, m/z 281, 147 and 341 for D7, m/z 207 and 295 for L4, m/z 281, 147 and 369 for L5, m/z 221, 281 and 355 for L6, m/z 221, 147 and 295 for L7 to L16, m/z 281, 369 and 147 for M4Q and m/z 256 for PCB-30 (Zhang et al., 2011). Siloxanes are analyzed from soil samples as well. Soil samples were air dried, sieved with 2mm sieve and stored frozen at -18^0C in glass containers. The characteristics of soil tested are pH of 7.69, TOC of 0.97%, sand 44.34%, silt of 37.44% and clay of 18.22%. Surface soil is sampled from agricultural fields in Spain. Soil is amended with sewage sludge at 12 ton / ha and industrial soil is also sampled.

The extraction method adapted is similar to that for pesticides analysis based on sonication assisted extraction in small columns. Two filter paper circles of 2 cm diameter are placed at the end of glass column and anhydrous sodium sulfate (2g) is added as a layer over the paper filter. Then sieved soil is weighed 5 g and placed in the column. For recovery study, soil samples were previous spiked with the mixture of siloxanes and M4Q as IS to reach final concentrations of 10, 20 and 50 ng/g and left at room temperature for 2 h to allow solvent evaporation. Soil samples are extracted with 5 ml of n-hexane for 15 min in an ultrasonic water bath at room temperature. The water level in bath is adjusted to equal the extraction solvent level inside the columns, which were supported upright in a tube rack and closed with 1-way stopcocks. After extraction the columns are placed on a multiport vacuum manifold and the solvent is collected in graduated tubes. Soil samples are extracted again with another 5ml of hexane. The extracting solvent is collected and soil samples washed with 1 ml of additional solvent. The total extract collected in 10ml graduate tubes is concentrated with a gentle stream of nitrogen to an approximate volume 1ml. The extract is then analyzed by GC/MS. Prior to each analysis, inlet is flushed by heating at 300^0C for 30 min and procedural blanks are analyzed after every four samples. No siloxanes are detected in these blanks. In addition, quality controls of standards and n-hexane are analyzed after four sample runs to check for instrumental background and stability. A selected ion monitoring mode is used (Sanchez-Brunete et al., 2010). House dust in China is analyzed for siloxanes. Dust is collected from vacuum cleaners. Prior to analysis non dust particles such as hair, pet fur are removed. The sample is then sieved through a 500 um mesh sieve. Three hundred to five hundred milligrams of dust sample is weighed accurately and spiked with 100ul of 1ppm M4Q as an internal standard. The extraction procedure included sieved dust particles are shaken with 5 ml of n-hexane for 15 min. After shaking samples are centrifuged at 4000 rpm for 5 min and the solvent layer is transferred into a flat bottom flask. The samples are re-extracted three times with ethyl acetate / n-hexane mixture (1:1). To confirm extraction efficiency after first two extractions, samples are soaked in 5 ml of solvent mixture overnight. Each extraction is concentrated to 1-2 ml using a rotary evaporator and then purified by passage through a solid phase extraction cartridge topped with 0.2g of sodium sulfate and 0.5 g of silica gel. Six milliliters of n-hexane and 5 ml of dichloromethane / n-hexane (1:1) mixture are diluted through the cartridge. The fraction is collected in a polypropylene tube and concentrated to 500 ul under a gentle stream of nitrogen for GC/MS analysis. Cyclic and linear siloxanes are identified and quantified by GC-MS and separation is achieved by a 30 m DB- 5 MS column with 0.25 mm internal diameter, 0.25 um film thickness. Two microliters of sample extract is injected in splitles mode at 200^0C. The oven temperature is programed at 40^0C for 2 min to 220^0C at rate of 20^0C/min and to 280^0C at 5^0C/min with a hold for 10 min. A post run included 300^0C for 5 min. The MS is operated in electron impact – selected ion monitoring mode. The ions monitored for individual siloxanes are mentioned earlier. For quality control, analyst has taken care to not to use any hand lotions that might contain siloxanes (Lu and Kannan, 2010). It has been observed that the increasing presence of siloxanes in waste activated sludge hampers the energy usage of biogas generated in the anaerobic digestion process. Dewil et al., (2007) outlined the method for the extraction and quantification of siloxanes using n-hexane and a subsequent analysis of the extract using gas chromatography/flame ionization detection. Activated sludge samples were obtained from a full scale wastewater treatment plant located in Belgium. Dry solid content of the sludge was determined according to standard method. The sludge was then spiked with known amounts of D4 and D5 for the experiment. The mixture of sludge and siloxanes was gently stirred for 10 min. Then it was stored at 4^0C for 24 hours in order to achieve a complete adsorption of the siloxanes onto the sludge flocs. After homogenizing sludge samples, 50 ml of sludge was introduced in a calibrated flask and 10 ml of n-hexane was added for extraction. The sludge-hexane mixture was vortex mixed at high speed for 10 min. The extracts were subsequently centrifuged at 4400 rpm (approximately 8900 x g) for 5 min. Since n-hexane and water are immiscible, a phase separation was obtained during centrifugation. The top phase of n-hexane containing extracted siloxanes was removed by suction pipette. The analysis of siloxanes extracts was performed using a Varian 3400 GC with an 8200 auto sampler coupled with FI detector. The separation was carried out in a Varian FactorFour VF-1MS capillary column. The injector port temperature was set at 125^0C. The initial oven temperature was 60^0C. This temperature was maintained for 4 min. After this, temperature was linearly increased to 250^0C at a rate of 8^0C/min. This temperature was held for another 15 min. The detector temperature was set up at 250^0C. The high end temperature and extended elution time per sample was applied to confirm all extracted compounds leave the column before next injection. A calibration curve was prepared by injecting known concentrations of D4 and D5 in n-hexane solution. Retention time of 5.539 min and 9.034 min was observed for D4 and D5 respectively. This method provides probably the best approach to determine siloxanes from waste activated sludge, the focus of our research (Dewil et al., 2007). Table 2-17 below summarizes some other common methods used for siloxanes analysis in sludge matrix.

Table 2-17 Summary of Analytical Methods

Reference	Solvent	Type	Column	Temperature Profile
Horri and Kannan, 2008	Ethyl acetate: n-hexane (1:1)	GC/MS Selected Ion Monitoring	30-m Rxi-5MS fused silica capillary column; 0.25 mm inner diameter; 0.25 micrometer film thickness; Restek.	40^0C (2 min) to 220^0C at a rate of 20^0C/ min and to 280^0C at 5^0C / min, which was held for 10 min. Post run at 300^0C for 5 min.
Dewil et al., 2007	n-hexane	GC/ Flame Ionization Detector	Varian FactorFour VF-1MS capillary column.	The injector pore temperature was set at 125^0C. The initial oven temperature was 60^0C for 4 min. Temperature was then linearly increased to 250^0C at a rate of 8 C/min and was held for 15 min. The detector temperature was set at 250^0C.
Sparham et al., 2008	Acetone	GC/MS	J&W DB-FFAP (30 m, 0.25 mm inner diameter, 0.25 micrometer film thickness, helium flow 1.5 ml /min) / itroterephthalic acid modified poly-ethylene glycol column.	50^0C for 4 min, increased to 200^0C at 20 C/min and held for 5 min.
Sánchez-Brunete et al., 2010	n-hexane + ultrasonic water bath	GC/MS Electron impact ionization	Fused silica capillary column ZB-5MS, 5% phenyl polysiloxane as nonpolar stationary phase, 30 m x 0.25mm and 0.10 micrometer film thickness.	40^0C for 2 min, then 10^0C/min to 220^0C and held for 1 min., the total analysis time was 21 min and the equilibration time 2 min.
Zhang et al.,	n-hexane +acetone	GC/MS	Fused silica capillary 30-m Rxi-5ms column with 0.25 um film thickness, 0.25 mm inner diameter	40^0C for 2 min, to 220^0C at 20^0C/min, to 280^0C at 5^0C/min, hold for 10min, post run at 300^0C for 5 min

2.11. Removal of Siloxanes: Available Techniques

As mentioned in previous sections, siloxanes in environmental matrices cause very little health, ecological issues but tremendous operational issues. Biogas with higher concentration of siloxanes, when utilized for heat and power generation, silicates is formed during the combustion or engine run which ultimately reduces the efficiency of engine or that gas handling equipment. This reduction in efficiency leads to adverse impact on operation and maintenance cost of the equipment directly. It also impacts directly the power production or heat production depending upon the application. It also impacts on emissions, poison to SCR, OCR catalysts. Hence, siloxanes have to be removed before the gas is utilized. This section explains available techniques for removal of siloxanes from various matrices. However, so far, siloxanes are commonly removed from the gas phase using the expensive treatment. Only few studies have shown the potential of removing siloxanes before it gets into the gas phases.

Removal of siloxanes from Gas

A laboratory study by Popat et al., 2008 was carried out to test various adsorption matrices, to evaluate their siloxanes removal efficiencies. Concentrated nitric acid and sulfuric acid were found to be especially potent siloxane removing agents at elevated temperatures. Solid adsorbents tested were activated charcoal, carbopack B, Texax TA, XAD II resins, molecular sieve 13X and silica gel. Except for the activated charcoal, silica gel showed especially high adsorption capacities of more than 100 mg/g for siloxanes. Efficiency of silica gel in removing gaseous siloxanes was verified at sewage treatment plant where adsorption bed with silica gel was used for biogas drying. During liquid adsorbents study, it was observed that 33% nitric acid at temperature of 60^0C eliminates siloxanes at rate of 70 – 75% (Popat et al., 2008). Concentrated phosphoric acid was determined to be ineffective in removing siloxanes even at temperatures of 60^0C since elimination was only at 44 – 48% for D5 and 53 – 60% for L2. Another study by (Popat et al., 2008) reported that removal of siloxanes from digester and landfill gases is possible by biological means. The study looked at the feasibility of using biological treatment to control volatile methyl siloxanes. Bio trickling filters were tested for removal of D4. The removal of D4 in aerobic bio trickling filter followed a linear trend reaching 43% at a gas empty bed residence time of 19.5 min. The estimated maximum mass transfer of D4 in bio trickling filter was within the range of 30 – 100 mg / m^3 / h. The laboratory tests with culture showed the low biomass growth in D4 rich environment. This indicates the low biodegradability of D4 (Popat et al., 2008). Another study supported the biological removal of siloxanes saying bio filtration can be a cost effective and environment friendly alternative. The researchers presented the results of biodegradation studies on siloxanes aimed to investigate the possibility of using bio filtration to treat biogas. Bacteria was isolated from activated sludge and kept with Octamethylcyclotetrasiloxane (D4) as the only carbon source and the growth was observed. It was determined by 16S-rDNA sequencing that the mixed population mainly contained Pseudomonas as dominating genus. It determined that that D4 can be biodegraded by community of microorganisms isolated from activated sludge. Other microorganisms include Rhodanobacter, Zooglea, Mesorhizobium and Xanthomonadacea. Removal of D4 up to 10 – 20% is obtained while similar system in abiotic conditions reports no removal at all which confirms the biodegradability of D4 (Accettola et al., 2008). Based on the research, many companies have developed techniques and instrumentation to remove siloxanes from biogas as practical applications. AFT has developed the SAGTM Filter System to remove siloxanes. The technology consists of porous pelletized or granular media contained in a vessel sized by the gas flow, pressure, temperature, siloxane flux and organic species. There are around 270 types of media available that can be loaded into these vessels. This technology claims and has proven longer maintenance time intervals for boilers and heat transfer equipment, longer "up" time for generator engines, longer life for emission control catalysts, lower abrasion of generator engine components such as doubling of spark plug life, extending engine oil life from 500 hours to 3000 hours, doubling or even tripling engine heads, cylinder linings, piston, impellers and heat recovery component life, increasing engine run time up to 40000 hours before maintenance is required (Paul Tower, Applied Filter Technology, 2003 WEFTEC). SCS Energy suggested refrigeration to 40^0F, subzero refrigeration, activated carbon adsorption, silica gel adsorption, liquid scrubbing as the possible ways to remove siloxanes from biogas (Pierce, SCS Energy). PROFACTOR suggested adsorption on activated carbon combined with cooling down to -30^0C helps bringing siloxanes concentration less than 1 mg / m^3. Adsorption on polymorphous graphite helps to reduce siloxanes down to 0.3 mg /m^3. Absorption in solvents like polyethylene glycol is also an alternative. However there is high cost involved in regeneration and material disposal with these technologies. Biological treatments using bio filter are much more cost effective. Following Fig 2-9 shows the picture of Bio trickling filter modified for siloxane removal with culture from activated sludge that contains Pseudomonas citronellosis and Pseudomonas putida as dominating bacteria (Ahrer, PROFACTOR, 2005).

Figure 2-9 Bio trickling Filter for Siloxanes Removal (Ahrer, PROFACTOR, 2005)

Removal of siloxanes from Sludge

A study by Appels et al, (2008) presented some peroxidation methods for the reduction of siloxane content from waste activated sludge. The method aimed to break down the siloxanes into lower molecular weight siloxanes, silicones and silica and to degrade the extracellular polymeric substance to which siloxanes are bound, thus improving their volatilization before digestion. An effective reduction rate was observed. The studied peroxidants included Fenton reactants, with peroxymonosulphate (POMS) and with dimethyldioxirane (DMDO). Hydrogen peroxide (H_2O_2) is widely used in wastewater treatment. With a strong oxidative strength it can oxidize variety of organic and inorganic pollutants. A POMS (H_2SO_5) is used in numerous industrial processes because of its oxidative capacity. Dioxiranes are very powerful oxidizing agents which can be used for the transfer of oxygen and for the oxidation of persistent organic molecules. The sludge samples were obtained from secondary clarifier of a full scale wastewater treatment plant in Belgium. Collected sludge was settled in the laboratory for 4 h prior to treatment. Sludge was spiked with known amounts of D4 and D5. Sludge siloxane mixture was gently stirred for 10 min and stored at 4^0C for 24 h in order to obtain complete adsorption of siloxanes to sludge flocs. Fenton treatment was performed in a batch reactor, containing 2 L of sludge at ambient temperature and pressure. The pH of sludge was firstly adjusted to 3 using H_2SO_4. The Fe^{2+} catalyst was added in the form of $FeSO_4$. A ratio of 0.07 g Fe^{2+} / g of H_2O_2 was added. The mixture was stirred gently during the reaction. The oxidation released reaction gases and the time of reaction was considered as the time until gas production stopped. This time was about 60 min. After the reaction sludge was neutralized using $Ca(OH)_2$. For using POMS, 2 L of sludge was treated in the reactor with 10 grams of solid peroxymonosulphate dissolved in 100 ml of deionized water. No adjustment of pH was done. For DMDO 4.2 g of sodium bicarbonate was added to 100 ml of deionized water and then 10 g of peroxymonosulphate triple salt (Oxone ©). Siloxane concentrations were measured by the method given by Dewil et al 2007)

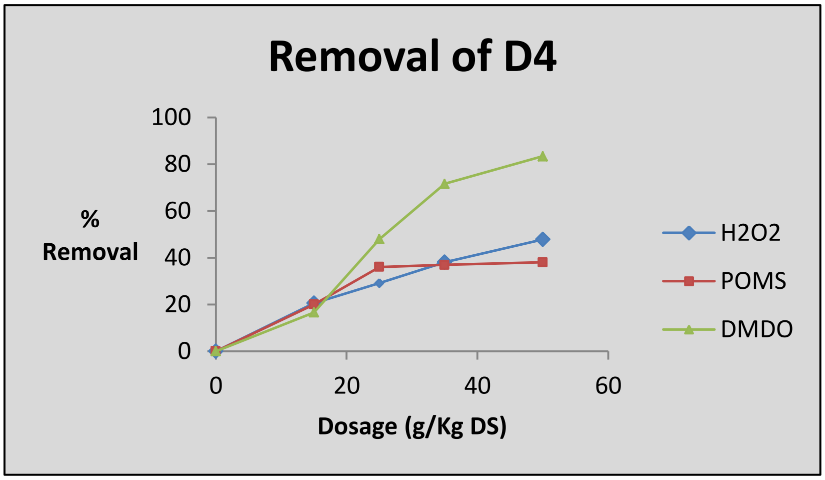


Figure 2-10 Removal of D4 (Appels et al., 2008)

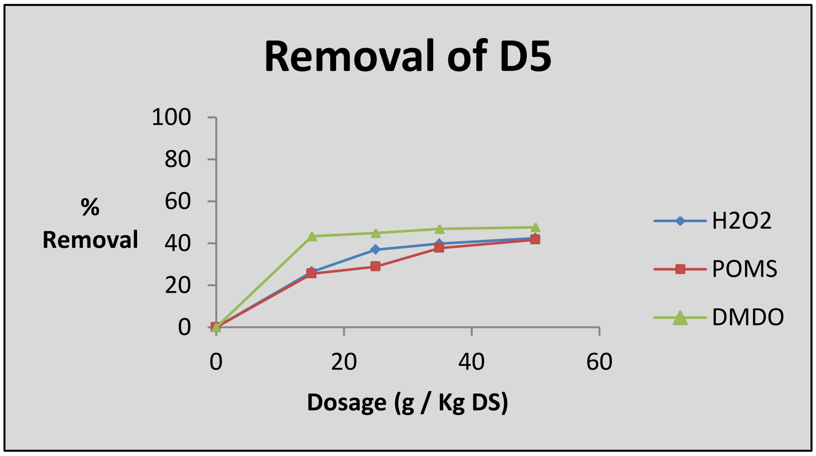


Figure 2-11 Removal of D5 (Appels et al., 2008)

Fig 2-10 and Fig. 2-11 above shows the % recovery obtained during the removal study tests by Appels et al. (2008). It can be seen that 85 % removal of D4 was achieved with DMDO the general removal rate for D4 was about 40 – 50%. Removal rates for D5 were stable at 40 – 50 % for all the oxidants used.

CHAPTER 3. PROBLEM STATEMENT

In recent years, most of wastewater treatment utilities have started biogas generation projects. So far utilizing the biogas has been limited for fulfilling heating requirements in the facility itself and to some extent for electricity generation. The cost of conventional fuel is increasing and the biogas produced may be the best alternative. However, this can only be valid when the cost of biogas can be brought nearly equal to that of conventional fuel. At present, the cost of utilization of biogas is higher because of the impurities, pretreatment required and its incompatibility with most of the engines. Siloxanes are one of the greatest reasons why the cost of biogas is higher. Along with this, operational issues associated with siloxanes increases the cost of operation even more. The techniques available for the treatment of gas to remove siloxanes are expensive and contribute toward the higher cost of biogas for commercial utilization. Hence it is necessary to find a way to remove the siloxanes before they enter into the gaseous phase. This research is the outcome of discussions with wastewater treatment utilities in Northern Colorado regarding the issues pointed by them regarding siloxanes depositions at their facilities. City of Loveland, CO has a conventional wastewater treatment plant that serves 24,706 customers. The deposition of siloxanes was observed on the fire tubes at this plant and the heating system had to be shut down.

3.1. City of Loveland Wastewater Treatment Plant

City of Loveland is located about 15 miles south of Fort Collins. This is a small town in northern Colorado. The wastewater treatment plant was built in 1902. This plant serves about 29 square miles of geographical area which includes 17 lift stations (14 public and 3 private), 334 miles of sewer lines and 8291 wastewater manholes. The plant runs at an average flow of 6.9 MGD during wet season of April – September. The actual average flow in dry season of January – March to October- December is 5.8 MGD. This plant treats about 20,236 lb of organic matter (BOD) per day. The raw wastewater is collected in a sump tank and equalized. Then the grit chamber removes the coarser and larger particles. The initial BOD of raw wastewater is around 275 mg /L. About 41% of BOD is removed by the primary clarifiers. Wastewater is then treated further with a step feed activated sludge system flows through secondary biological treatment. Wastewater is passed in aeration basin. Aeration basin is divided into three separate tanks and each tank is divided into two trains where the wastewater flows in parallel. The flow diagram prepared in BioWin model is attached as Appendix F. This is a step feed activated sludge process. The primary effluent is fed to anoxic zone followed by an aerated zone created in each of three aeration tanks. Average MLSS of 1935 mg / l is maintained in all the anoxic and aeration basins. After the secondary treatment, wastewater is passed through three after the secondary clarifiers BOD is reduced to ~ 5 mg/L. The waste activated sludge collected by the secondary clarifiers is sent to a sludge thickener and then sent to anaerobic digesters for bio solids processing. The volume of primary sludge produced was 48,078 gallons/day in 2011 while that of thickened sludge was 7,456 gallons/day. Average of 5953810 units of biogas is produced per day. This gas is used for in house heating. For boiler heating, 35,148 units of biogas are used and waste gas usage is 62330 units. It was observed that after utilization of biogas produced in the plant, the inner sides of the fire tubes were covered with white/silver colored residues. This was due to the higher siloxanes concentrations in the wastewater stream. Just within the 14 months of biogas utilization for heating the digester, fire tubes had severe siloxane deposition issue and had to be shut down. Use of natural gas increased. Fig. 3.1 below shows the picture of fire tubes before and after siloxane deposition. Similar issues were addressed during a visit to the Mulberry and Drake Wastewater Treatment facilities in Fort Collins, CO.

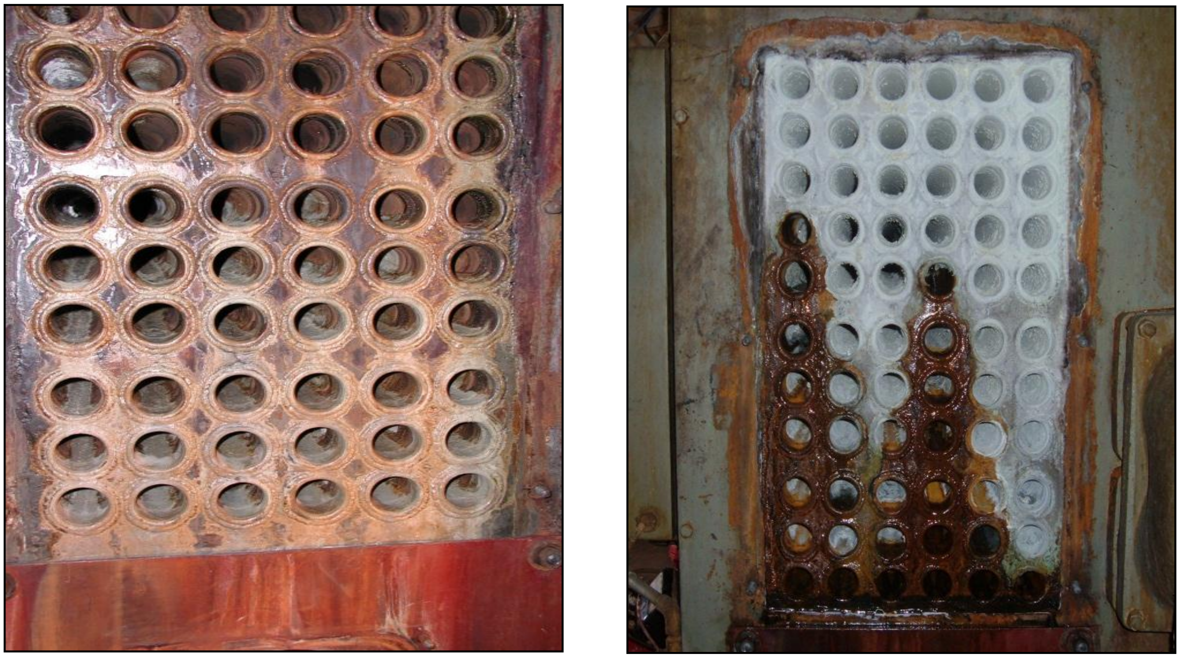


Figure 3-1 Picture of the Fire Tube in June 2010 (to left) and in March 2011 (to right)

3.2. Goal of this Study

The goal of this research was to study the occurrence of cyclic siloxanes in a conventional activated sludge wastewater treatment plant and removal of siloxanes from waste activated sludge using bench scale tests. The first objective of this research was to develop and validate a method to analyze cyclic siloxanes in waste activated sludge by solid-liquid extraction and by gas chromatography/mass spectrometry The second objective of this research was to test for cyclic siloxanes in waste activated sludge samples collected over six months from the City of Loveland Wastewater Treatment Plant and to study the trend in their occurrence. Not much data is available about the levels of siloxanes and the related operational issues The third objective of this research was to conduct an electronic survey to collect data on siloxanes issues, status of remedial measures and awareness.

CHAPTER 4. EXTRACTION,DETECTION AND MONITORING OF CYCLIC SILOXANES IN WASTE ACTIVATED SLUDGE USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

4.1. Introduction

Siloxanes are expected to be present at higher concentrations in wastewater, surface waters and biogas due to increased use of personal care products containing them (Siloxanes in Nordic Environment, 2005). However, very little information was available on the occurrence of siloxanes in the environment as the issues related to their presence were realized only over the last decade. Siloxanes can create a significant problem for the wastewater treatment plants that generate and utilize biogas (Dewil et al., 2007). It has been shown that linear and cyclo siloxanes adsorb onto extracellular polymeric substances (EPMS) of sludge flocks (Dewil et al., 2007) and concentrate in the activated sludge (Parker et al., 1999). The most commonly observed siloxanes in wastewater sludge are Decamethylcyclopentasiloxane (D5) and Octamethylcyclotetrasiloxane (D4) (Horri, 2008; Zhang et al., 2011), with water solubility of 0.24 mg/l and 0.9 mg/l respectively. When waste activated sludge is digested to produce biogas, siloxanes are released into the gas phase and form scales on the boilers or fire tubes (City of Loveland data, 2011). Several studies have measured siloxanes in landfill gas, biogas and in ambient air using established techniques such as gas chromatography with mass spectrometry (GC-MS) or flame ionization detection (GC-FID) (Kierkegaard et al., 2010; Wachholz et al., 1994). Apart from these research based methods, some commercial application methods and instrumentation are available for analysis of siloxanes in gas phase. Although siloxanes are hydrophobic in nature, they are present in the aquatic environment (Price et al., 2010) and several studies show that siloxanes in aquatic environment might affect the biota (US EPA 2003). Siloxanes were detected in fish tissues investigated under controlled environment by US EPA in 2003. It was observed that Trout fish died within 14 days when exposed to cyclic siloxanes at a concentration of 10 µg/l. Water flea failed to reproduce with 1.7 to 15 µg/l of D4 exposure for 21 days (US EPA 2003 D4 Toxicological Data). Adverse effects on reproductive capacity of fish were observed in a bioassay study under controlled environment with D5 at 700ppm (US EPA, 2003). Currently there is not much information about the adverse effects of siloxanes on human health. Sparham et al. (2008) reported D_5 concentrations in river water and wastewater treatment plant effluent as 30.6 ng/L and 10 ng/L, respectively, using headspace GC-MS with a recovery up to 85%. $^{13}C_5$ labeled D5 was used as the internal standard. Siloxanes tend to attach to sediments in surface waters and sludge in wastewater (Sparham et al., 2008). They accumulate in solids, so measuring their concentration in sludge or sediment samples may give a better representation of occurrence. A recent study by Zhang et al. (2011) outlined a method to analyze siloxanes in sediments and sludge by extraction with ethyl acetate/n-hexane (1:1 v/v), PCB-30 as internal standard and detection with GC-MS. Cyclic and linear siloxanes were found in all sediment and sludge samples analyzed in northwestern China. Concentration of D5 as high as 3310 ng/g dry solids was observed (Zhang et al., 2011). In another study, sonication assisted extraction in small columns and subsequent quantification and identification by GC-MS was used for determination of cyclic and linear siloxanes and n-hexane was used as solvent. Recovery of cyclic and linear siloxanes ranged from 87.7% to 108% and 84.9% to 107.6% respectively (Sanchez-Bruntete et al., 2010). Dewil et al. (2007) provided a comprehensive method to extract siloxanes using n-hexane from the activated sludge samples from a wastewater treatment plant in Belgium, and to quantify using GC-FID. Even though the method was thorough, it lacked an internal standard to ensure the recovery of siloxanes detected. The activated sludge sample is a very complex matrix of organic and inorganic compounds that could alter the extraction efficiency of siloxanes. To reduce this effect in our study, PCB-30 (2, 4, 6-Trichlorobiphenyl, $C_{12}H_7Cl_3C_{12}H_7Cl_3$ - CAS No. 35693-92-6) was used as internal (surrogate) standard since other deuterated siloxanes standards were commercially unavailable. PCB-30 has been used in past as internal standard to determine siloxanes from wastewater sludge (Zhang et al., 2011) in China. This paper proposes a novel analytical method for the analysis of two cyclic siloxanes D4 and D5 in waste activated sludge, using PCB-30 as an internal standard.

4.2. Materials and Methods

Materials

GC grade n-hexane was obtained from the Fisher Scientific (Pittsburgh, PA). Standards of Octamethylcyclotetrasiloxane (D4) and Decamethylcyclopentasiloxane (D5) were purchased from TCI-America (Portland, OR) at 98.0% and 97.0% purity respectively and were stored at room temperature in dark. Internal standard PCB-30 (2, 4, 6-Trichlorobiphenyl) was obtained from Fisher Scientific (Pittsburgh, PA) at 1000µg/ml in isooctane and was refrigerated at 4^0C. 2 mL amber glass GC vials with Teflon line screw caps were obtained from Fisher Scientific (Pittsburgh, PA). Glass syringes at 50 uL, 250 uL, and 1 mL obtained from Fisher Scientific (Pittsburgh, PA) were used for stock solution preparation. For phase separation of sludge 50 mL heavy duty round bottom Pyrex glass centrifuge tubes with 24-410 screw caps were purchased from Fisher Scientific (Pittsburgh, PA). An Analog Vortex Mixer (Fisher Scientific) was used for homogenizing the sludge samples and dispersion of the solvent. For centrifuging Thermo IEC Centra GP8R model electronically operated centrifuge was used.

Sample Collection

Majority of the activated sludge samples were collected from City of Loveland Wastewater Treatment plant. This plant is operated at an average flow of 6.9 MGD and 5.8 MGD during wet and dry seasons, respectively. This plant treats about 20236 lb. of organic matter (BOD) per day.

Wastewater is treated with a step feed activated sludge system. City of Loveland has anaerobic sludge digesters and utilizes the produced gas for heating. Three samples, each of primary and waste activated sludge were collected from Drake Wastewater Treatment Facility, Fort Collins. Wastewater is treated by primary settling followed by activated sludge process, combination of biological and chemical process. Bio solids are dewatered and used for beneficial purpose. Three samples, each of primary and waste activated sludge, were collected from City of Boulder wastewater treatment plant. This plant approximately treats 15MGD wastewater using primary settling followed by waste activated sludge process, combination of biological and chemical processes. Anaerobic digesters are used for bio solids stabilization. Three samples were collected from City of Greeley wastewater treatment plant. This plant treats around 8-9 MGD. Activated sludge process is used for wastewater treatment and anaerobic digester is used to digest the sludge. Process flow diagrams for all the plants are in Appendix F. Sludge samples, from the waste activated sludge line of the secondary clarifier at the wastewater treatment plants were collected in 500 mL wide mouth amber glass bottles with Teflon lined caps purchased from Fisher Scientific (Pittsburgh, PA). The sludge sample bottles were immediately refrigerated and stored in dark.

Methods

Stock solutions of D4 and D5 were used to prepare a calibration curve to quantify the concentration of siloxanes in the sludge samples. The original concentrations of D4 and D5 were 0.956 g / mL and 0.958 g / mL, respectively. Stock solutions were prepared fresh at 10mg/ml, 100µg/ml, 1µg/ml and 100ng/ml with GC grade n-hexane before running samples. Stock solution of internal standard PCB-30 was also prepared as 10ug/ml from the original stock concentration of 1000 ug/ml. The concentrations of 1000, 250, 125, 62.5, 15.625 and 7.8 ng /mL of both D4 and D5 were prepared for calibration curve in 2ml GC vials by dilution. 25ul of 10ug/ml of PCB-30 is added to 1ml of each standard to achieve final concentration of 250 ng/ml. The sludge bottles were brought to room temperature within 2 hours. About 300 - 400 mL of sludge from each bottle was transferred to flat bottom graduated conical flasks and covered with parafilm. The flasks were vortexed for 5 minutes at the highest speed until sludge samples were homogenized. After homogenizing, 40 mL of the sludge was weighed and transferred to another clean graduated conical flask. 200 ul of PCB-30 (at 10 µg/ml) was spiked into each sample and samples were vortexed for 3 minutes at highest speed for ensured homogenization. The flasks were then kept at room temperature in dark for 30 minutes to improve transfer of siloxanes from sludge matrix into the solvent. The flasks were vortexed for a final time for 3 minutes and the sludge/solvent mixtures were transferred to clean glass centrifuge tubes using a glass funnel. The samples were centrifuged at 1500 rpm for 10 minutes using Thermo IEC Centra GP8R model electronically operated centrifuge, and 0.5 mL of the separated hexane phase was transferred into GC vials using a 1 mL glass syringe. All of the GC vials then received 0.5 mL of n-hexane for a 1:2 dilution.

Gas Chromatography – Mass Spectrometry Analysis

Siloxanes were measured with a Waters Quattro Micro GC-MS system operated in the electron ionization (EI) positive mode. The carrier gas was ultra-high purity helium at a head column pressure of 79 kPa. Injections were made using an Agilent 7683B autosampler in the splitless mode onto a SLB-5ms capillary column (30mm X 0.25mm I.D., 0.25um film thickness) (Supelco, Bellefonte, Pennsylvania). The oven temperature profile used to separate siloxanes was initially 40^{0}C for 5 mins, then raised to 200^{0}C at 20^{0}C/min and held for 4 mins, then to 300^{0}C at 80^{0}C/min and held for 4 mins. The inlet temperature was 250^{0}C and the GC-mass spectrometer interface temperature was set at 280^{0}C. The mass spectrometer was operated in selected ion monitoring for each analyte and internal standard, ions monitored were as follows: D4 281 and 93 m/z, D5 355 and 267 m/z, and PCB-30 256 and 186 m/z. Fig 4-1 shows elution of D4, D5 and PCB-30 at 8.59 min, 10.09 min and 15.49 min respectively. A full scan mass spectrum of sludge samples spiked with D4 (Fig 4-2), D5 (Fig 4-3) and PCB30 (Fig 4-4) was used to select quantification ions for the compounds. Standard calibration curves for each compound were prepared by plotting the ratio of peak for each quantification ion to the PCB-30 ion peak area against the amount (ng/ml) of standard. A linear regression was performed to determine siloxane concentrations in the hexane extract. The actual sample concentrations of D4 and D5 were then calculated with the following equation.

$$Actual\ Concentration\left(\frac{ug}{g\ of\ dry\ sludge}\right) = \frac{\left(\frac{ng}{mL}\ in\ hexane\ extract\right) * (8mL\ of\ hexane) * Dilution\ Factor}{(40\ g\ of\ sludge) * (\%TS) * 1000}$$

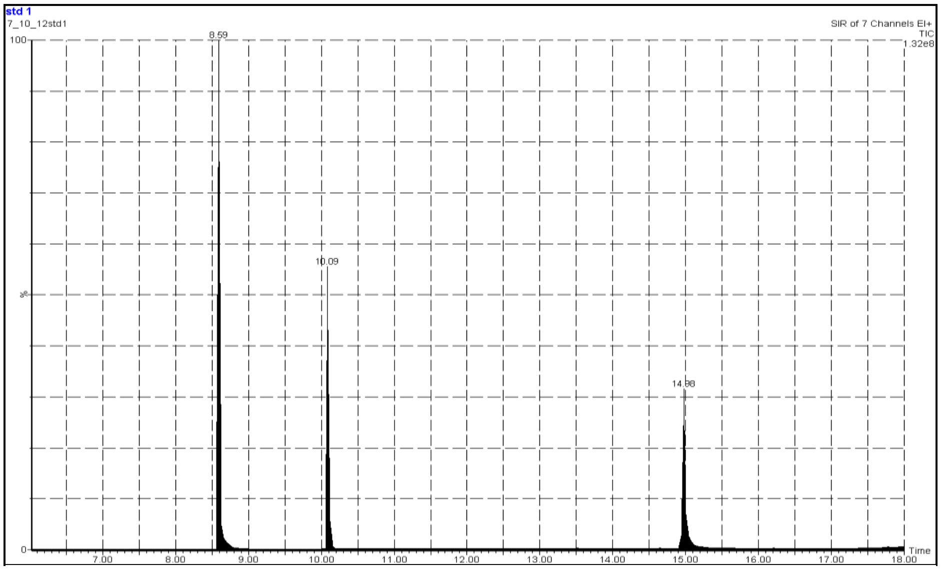


Figure 4-1 Gas Chromatogram of D4, D5 and PCB-30

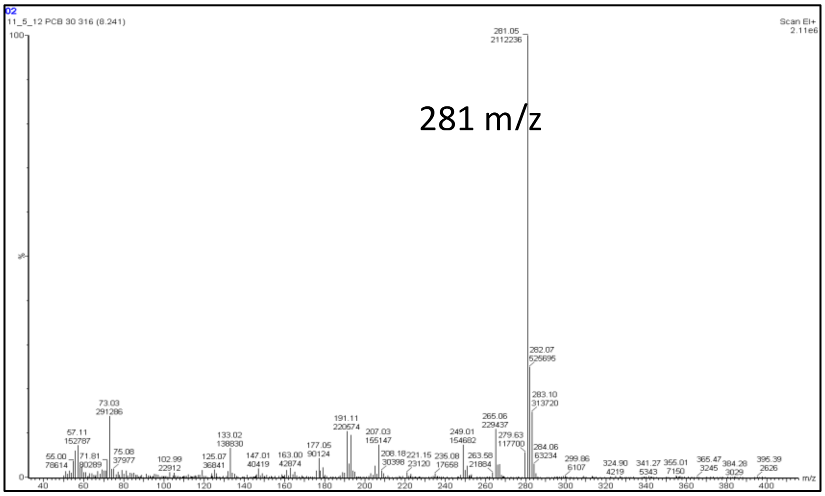


Figure 4-2 Full scan mass spectrum of sludge sample spiked with D4

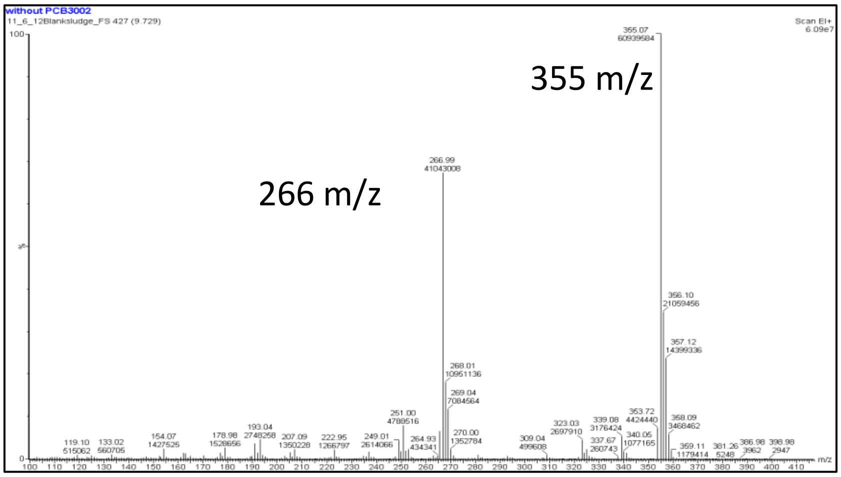


Figure 4-3 Full scan mass spectrum of sludge sample spiked with D5

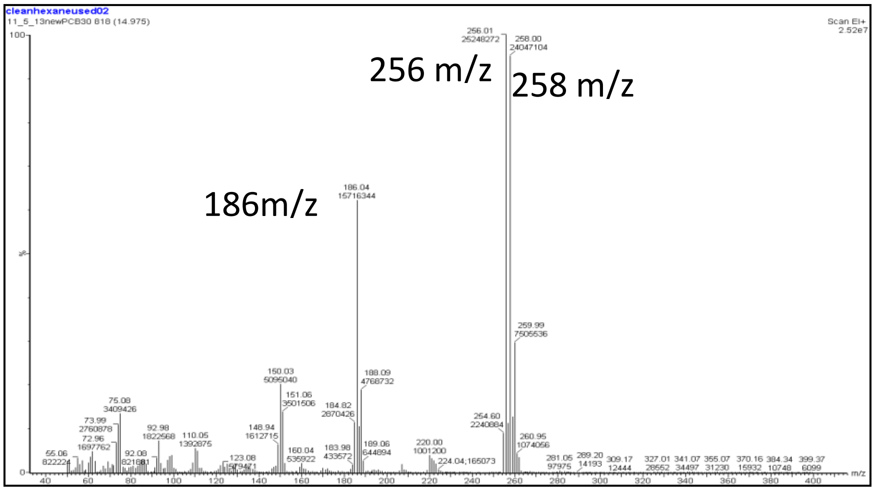


Figure 4-4 Full scan mass spectrum of sludge sample spiked with PCB30

Characteristics of Sludge Samples

It was necessary to determine the percentage of total volatile substances (TVS) in the sludge in order to correctly report siloxanes per gram of dry solids. It was proved that siloxanes have affinity to attach with organic matter present in the wastewater (Dewil et al., 2007). Fig 4-5 below shows the ratio of % total volatile solids (TVS) to % total non volatile solids in 135 waste activated sludge samples of Loveland WWTP over the period of September 2011 to October 2012. 12-13 samples per month were obtained and analyzed. The average TVS/TNVS ratio of 7.08, standard deviation of 1.2, maximum ratio of 10 and minimum ratio of 2.71 was observed. Sludge samples possessed overall constant characteristics.

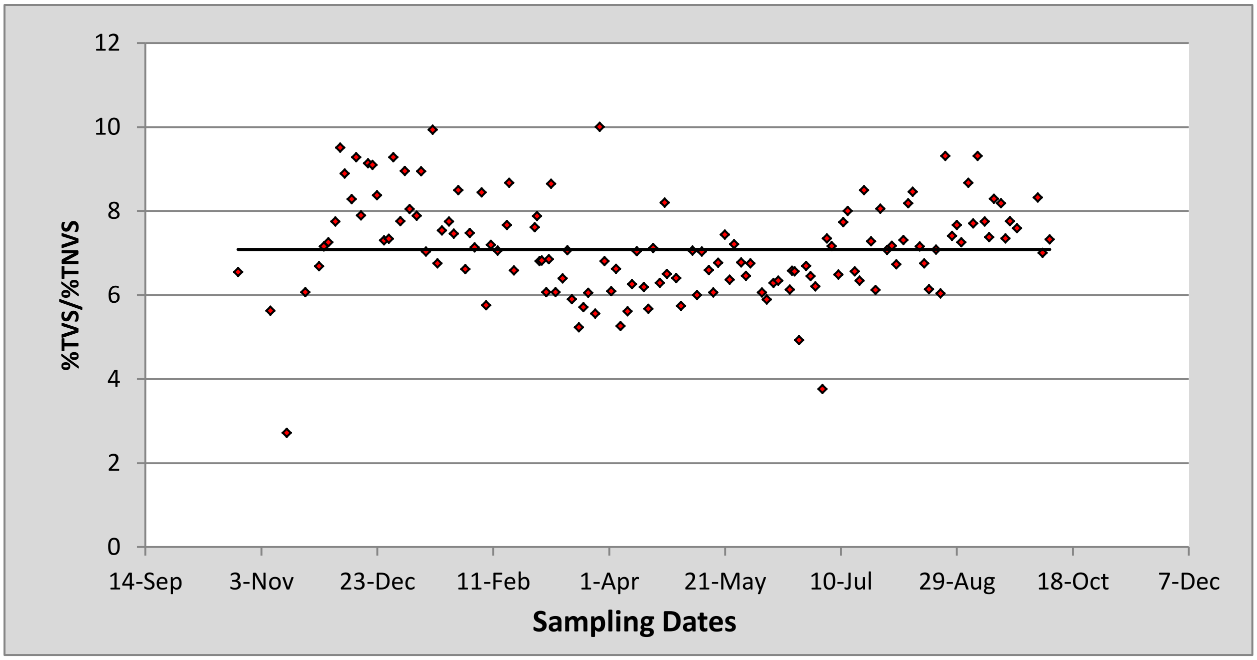


Figure 4-5 Sludge Characteristics showing fraction of volatile to nonvolatile solids

Siloxanes recovery study

To test the efficiency of extraction, i.e. siloxanes recovery from samples, three replicates of D4 and D5 were spiked in n-hexane and sludge samples. Six D4 and D5 concentrations (1000, 250, 125, 62.5, 15.625 and 7.8 ng/ml) were analyzed along with a calibration curve with same concentrations. Recovery was determined for D4 and D5 by comparing average response factors for triplicates of spiked hexane samples and triplicates of spiked sludge samples. Coefficient of variance was calculated by comparing set of six standards in hexane and sludge with replicates and reproducibility was determined. A procedural blank and sludge blank was analyzed. A pure hexane blank was run after every six samples.

4.3. RESULTS AND DISCUSSIONS

A calibration curve was obtained for D4 and D5 before every analysis. The R^2 values obtained for both D4 and D5 were >0.98 for all analyses. Since it was known that siloxanes are present in components of GC and in the stationary phase of capillary chromatograph column, additional precautions were required while developing the method for siloxanes analysis. Multiple blanks were run in between the sludge samples to determine the bleeding from column and results were compared to standards. It was proved that the siloxanes bleed was negligible as compared to concentrations of siloxanes in the standards and in sludge samples. While calculating actual concentrations, concentration of D4 and D5 in blanks were subtracted from consecutive sludge sample’s peak area. Percent recovery of D4, D5 and PCB-30 was determined by spiking 500 ng/ml in n-hexane, sludge samples and five sludge samples with only PCB30 at 500ng/ml. It was observed that the coefficient of variation was less than 7.5% in each set of samples which was a good indication of reproducibility of the method. Maximum limit of 10% is conventionally accepted for good repeatability of the method. Per cent recovery was calculated by comparing the integrated peak area of compound in sludge samples to that in standards. Three replicates were used and average of 84.84% (+/-5.7%), 92.66 %(+/-1.5%) and 98.04% (+/- 8.4%) recovery of D4, D5 and PCB-30 respectively was obtained.

Concentration of Siloxanes

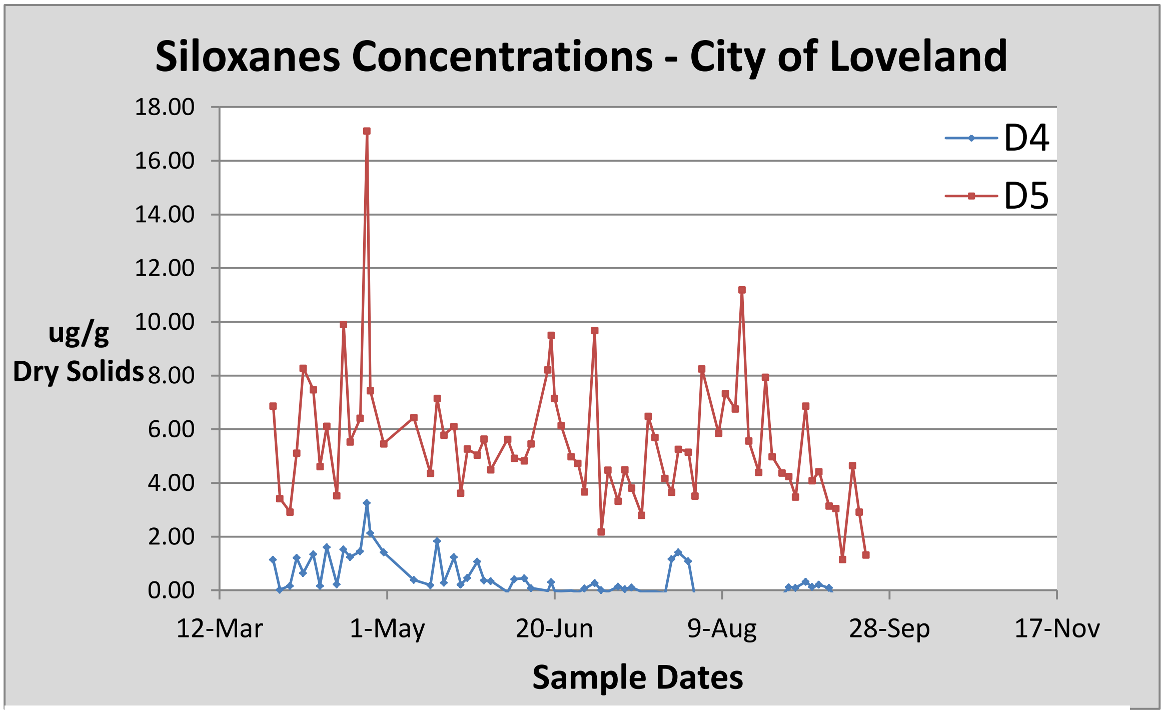


Figure 4-6 Concentration of Siloxanes in WAS from City of Loveland Wastewater Treatment Plant

The sludge samples obtained from City of Loveland Wastewater Treatment plant were monitoring over six months. For the 71 sludge samples obtained during the study period, it was found that D5 occurs at much higher concentrations than D4 in waste activated sludge. Average concentration of D4 was determined to be 0.43 µg/g of dry solids (+/-0.6) while that of D5 was 5.50 µg/g of dry solids (+/-2.4). All D4 concentrations were within the range of 0 to 3.25 ug/g dry solids while all D5 concentrations were within the range of 1.15 to 17.11 ug/g dry solids. A similar study done in China by Zhang et al. (2011), indicated that about 20% of sludge samples tested proved to have detectable concentrations of D4 and D5. The average concentrations of siloxanes determined were 280 ng/g dry sludge for D5 and 63 ng/g dry sludge for D4 which was lower than the siloxanes concentrations measured in Loveland WWTP samples. The highest average monthly concentration of D4 and D5 was observed in April as 1.26 and 6.92 ug/g dry solids. The lowest average monthly concentration of D4 was observed in August as 0.02 ug/g dry solids and that of D5 in the month of September as 3.51 ug/g Dry Solids. Fig 4-6 shows the concentrations of D4 and D5 in WAS samples of City of Loveland from March to September 2012 with ~12samples per month for a total of 71 samples.

Siloxanes at Four Northern Colorado Utilities

Waste activated sludge samples were analyzed for D4 and D5 from 3 more utilities in Northern Colorado, including Drake Wastewater Reclamation Facility-Fort Collins, Boulder Wastewater Treatment Facility-Boulder and City of Greeley Wastewater Treatment Plant. The average results of 4 sludge samples from each plant are given in Fig 4-7.

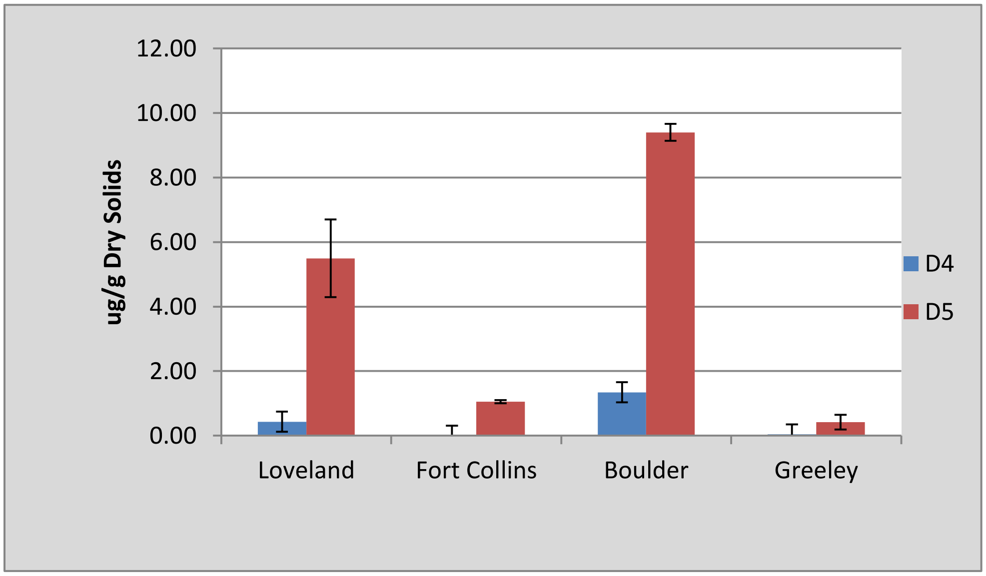


Figure 4-7 Siloxanes in Waste Activated Sludge of Four Wastewater Utilities in Northern Colorado

It was observed that City of Boulder had higher concentrations of D5 in the waste activated sludge samples while Greeley wastewater treatment plant had lowest concentration. And all sludge samples contained less D4 concentrations compared to D5 levels. For further exploration, primary sludge samples were also tested for City of Boulder, Fort Collins and Greeley. Fig4-8 and Fig 4-9 below shows the concentration of D4 and D5 in primary and waste activated sludge samples obtained from four utilities in Northern Colorado. Results for primary sludge samples from Loveland were not analyzed. Fort Collins and Greeley possessed higher siloxanes concentrations in primary sludge while Boulder possessed higher concentrations in waste activated sludge.

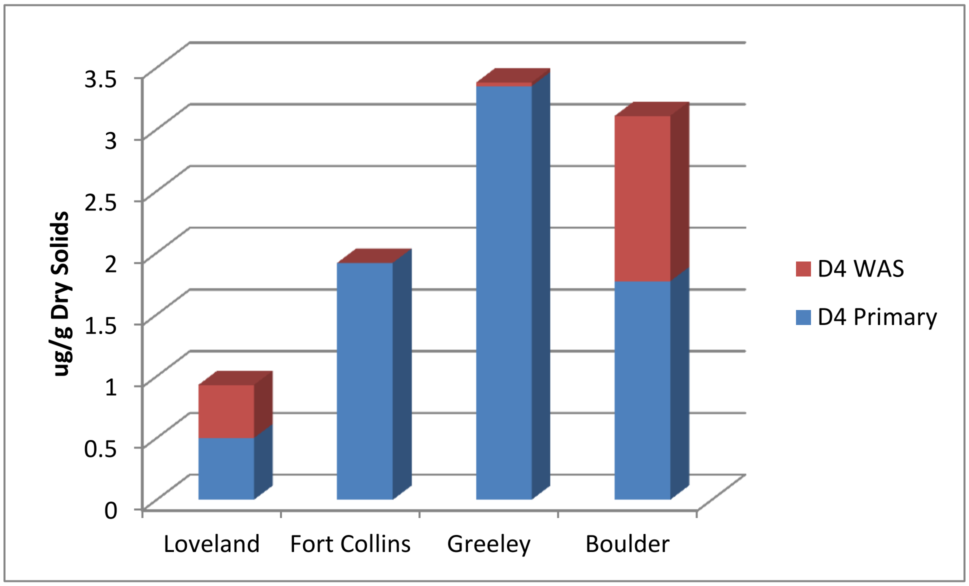


Figure 4-8 D4 in Primary and WAS

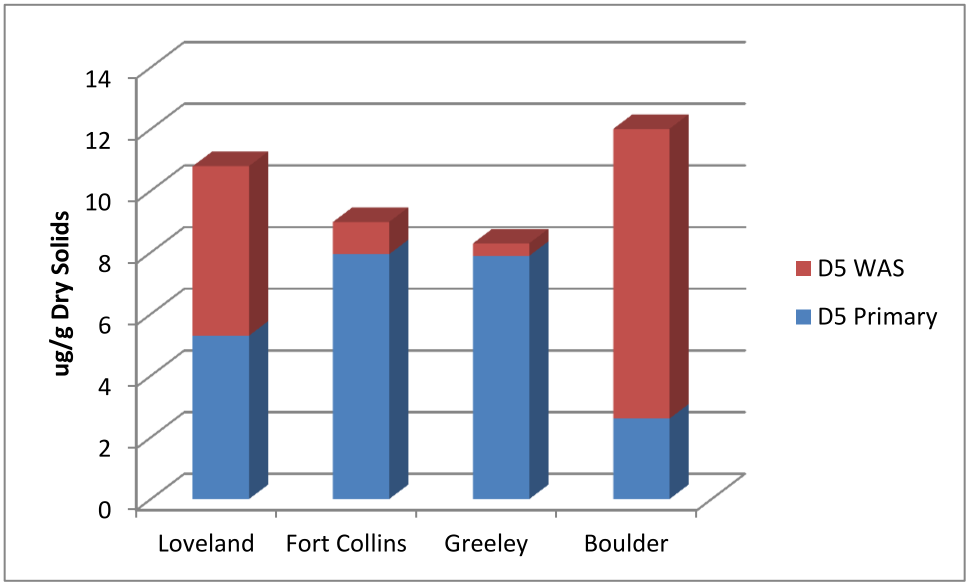


Figure 4-9 D5 in Primary and Waste Activated Sludge

Composition of Siloxanes species

It was observed that in WAS samples, D5 was the dominating siloxanes compared to D4. D5 has higher molecular weight and have higher affinity to stay in the sludge while D4 with lower molecular weight quickly volatilizes by even a small amount of aeration during wastewater treatment. Table 4-1 below shows average composition of total siloxanes measured in WAS samples. Irrespective of the difference in presence of siloxanes in Primary sludge and/or WAS samples, the composition of total siloxanes present in all four utilities were

Table 4-1 % D4 and D5 concentration in WAS samples of four wastewater utilities in Northern Colorado

Sample Collection WWTP	% D4	% D5	Standard Deviation
Loveland WWTP	7.25	92.75	7.4
Fort Collins WWTP	0.01	99.99	0
Boulder WWTP	12.49	87.51	15.23
Greeley WWTP	8.35	91.65	6.17

Zhang et al. (2011) reported concentrations of D4 and D5 in WAS from a wastewater treatment plant in northeastern China as 63.3 ng/g dry solids and 280 ng/g dry solids respectively. It was observed that the concentrations found in City of Loveland wastewater treatment plant are much higher which may be due to higher consumption and discharge of siloxane containing products in the US. Another wastewater treatment plant in China was reported to have total cyclic siloxanes (D4 – D7) concentration of 997 ng/g dry solids in WAS (Zhang et al., 2011). Kaj et al. (2005) reported total cyclic siloxanes concentrations (D4-D7) up to 100000 ng/g dry solids in WAS of wastewater treatment plant in Finland and 6100 ng/g dry solids in a Swedish wastewater treatment plant. City of Fort Collins, digester gas was found to have total 10.18 ppmv Siloxanes, out of which 8.24 ppmv (approximately 81 %) was D5 and 0.73ppmv (approximately 7%) was D4 and remaining other siloxanes. The ratio of D4 and D5 concentrations measured in sludge samples of all utilities (Table 4-1) matches with the concentrations in gas reported by the City of Fort Collins. The concentrations of D4 and D5 measured in sludge samples were in the same ratio as those in gas samples reported by the City of Fort Collins. A study carried out on a pilot wastewater treatment plant in Ontario, Canada reported that when 105 ug/l of D4 and 72 ug/l of D5 was spiked into wastewater influent, primary sludge was found to accumulate about 1470ug/l of D4 and 498 ug/l of D5 while the concentrations measured in waste activated sludge was 377 ug/l of D4 and 165 ug/l of D5, which showed that large portion of Siloxanes was removed in primary sludge (Parker et al., 1999).

4.4. Conclusions

The growing demand and use of health care products leads to increase in siloxanes concentrations in the environment. Siloxanes hamper the operations of wastewater utilities and the cogeneration facilities resulting in significant economic loss. Siloxanes also obstruct utilization of the biogas effectively for producing consumable form of energy. There is no data available on actual measurement of cyclic siloxanes in sludge within United States, and hence this research provides novel information on the occurrence of cyclic siloxanes in four utilities in

Northern Colorado. This research developed a method to identify and quantify D4 and D5 in WAS using GC/MS techniques with PCB-30 as internal standard. The validation procedure confirms the excellent recovery of this method. Also, this research gives an overall idea about the distribution of siloxanes in four significant wastewater utilities in Northern Colorado. This data is helpful for these and other utilities for planning of co-generation facilities for biogas and other operational parameters.

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APPENDIX

A. MATERIALS AND INSTRUMENTATION

Glassware

Glassware of different types was used for sample collection, sample handling, phase separation and final analysis. Waste activated sludge was very complex matrix of organic and inorganic compounds. Many of these contaminants may have effect of light on their properties and may photo-degrade during the period of storage. Hence, for sample collection 250 mL and 500 mL amber color, tight cap, wide mouth glass bottles are used (provided by City of Loveland). Picture of 250 mL and 500 mL bottles used is shown in Fig 5-1 below.

Figure A-1 Sample Collection Bottles

Conical calibrated flasks are used to transfer the samples for further processing. These are 500mL flat bottom, straight neck conical flasks obtained from Sigma – Aldrich. These flasks are made up of transparent polycarbonate. 50 mL amber glass vials with white tight cap with septa are used for standards preparation. These are used for preparing stock solution for various internal and external standards. For GC-MS analysis, 2 mL amber color glass vials with screw thread finish, flat bottom with numbered graduation are used. The Fig 5-2 below shows the picture of vials used. Blue GC vial caps and septa are separated ordered. Glass syringes are used of capacity 250 ul, 50 ul and 1 ml. Fig. 5-2 shows the glass syringes used.

Figure A-2 Sample Preparation Material

For phase separation of sludge , water and n-hexane, 50 mL glass centrifuge tubes are used. These are 50 mL heavy duty round bottom PYREX centrifuge tubes with 24 – 410 screw caps. These are very much useful for the handling of sputum specimens, digestion, shaking, neutralizing and centrifuging. The screw caps resist the effects of temperature and steam. The tubes have a black phenolic cap with a glued-in white rubber liner. Initially, 50 mL non-sterile polypropylene centrifuge conical tubes with graduated caps were used. These were cheap and easier for centrifugation without any risk of breaking. However it was observed that, there was risk of siloxane contamination from these tubes and hence switched to the glass tubes. Fig 5-3 below shows the picture of glass centrifuge tubes.

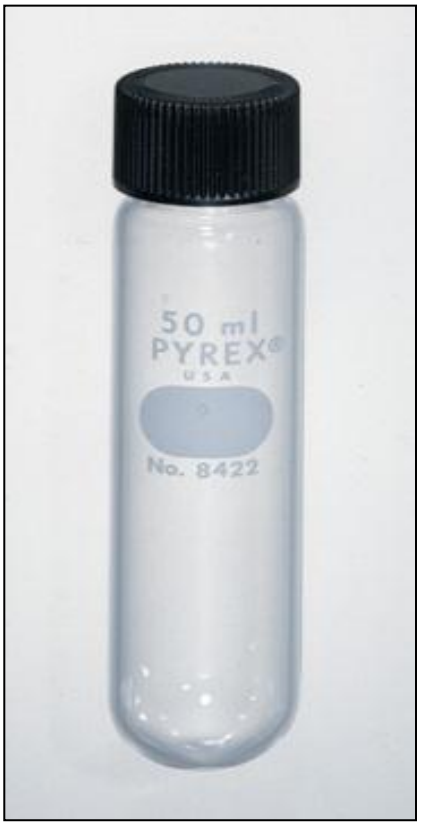

Figure A-3 Glass Centrifuge Tube

5.1.1. Vortex Mixer

An analog Vortex Mixer (Fisher Scientific Catalog # 02215365) was used for mixing and / or shaking the sludge samples for homogenizing and mixing with solvent. This vortex mixer allows 0 to 3000 rpm and have a manual control. A 3 inch head cover was used to facilitate mixing with flat bottom conical flask. The component of this instrument are shown in Fig 5-4 below.

Figure A-4 Analog Vortex Mixer and Head Cover

Centrifuge

For centrifuging Thermo IEC Centra GP8R model electronically operated centrifuge was used.

Fig 5-5 below shows the picture of centrifuge used.

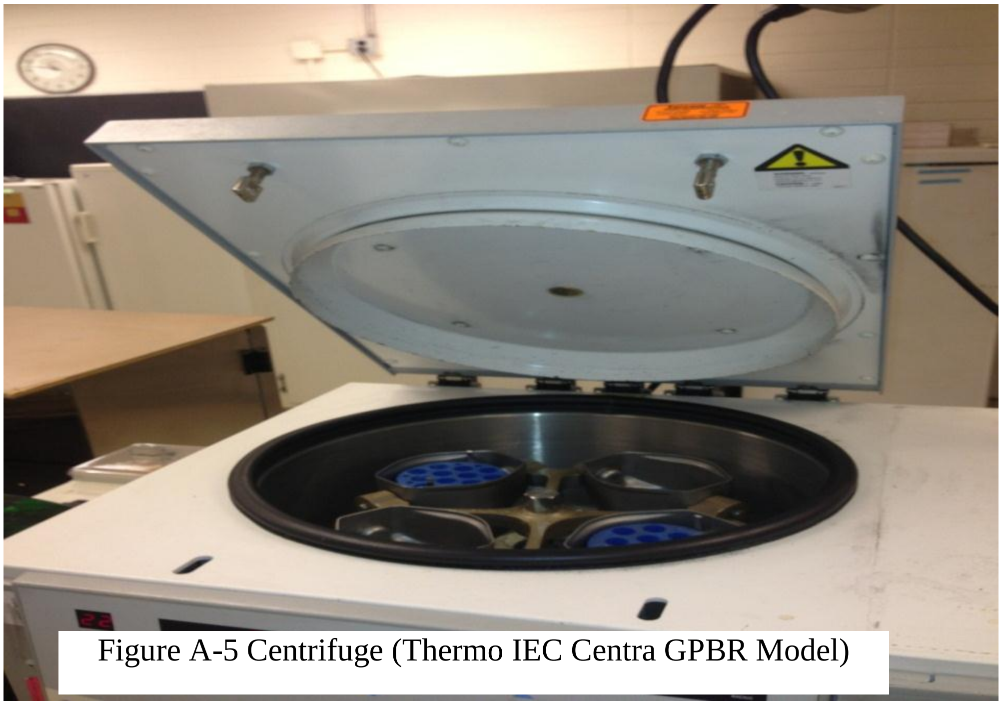

Figure A-5 Centrifuge (Thermo IEC Centra GPBR Model)

GC – MS

Agilent 6890 GC coupled with an auto sampler was used for analysis. Waters Quattro Micro Triple Quad Mass Spectrometer is used for detection. Fig 5-6 below shows the picture of GC-MS assembly used at Physiology department, Colorado State University, Fort Collins.

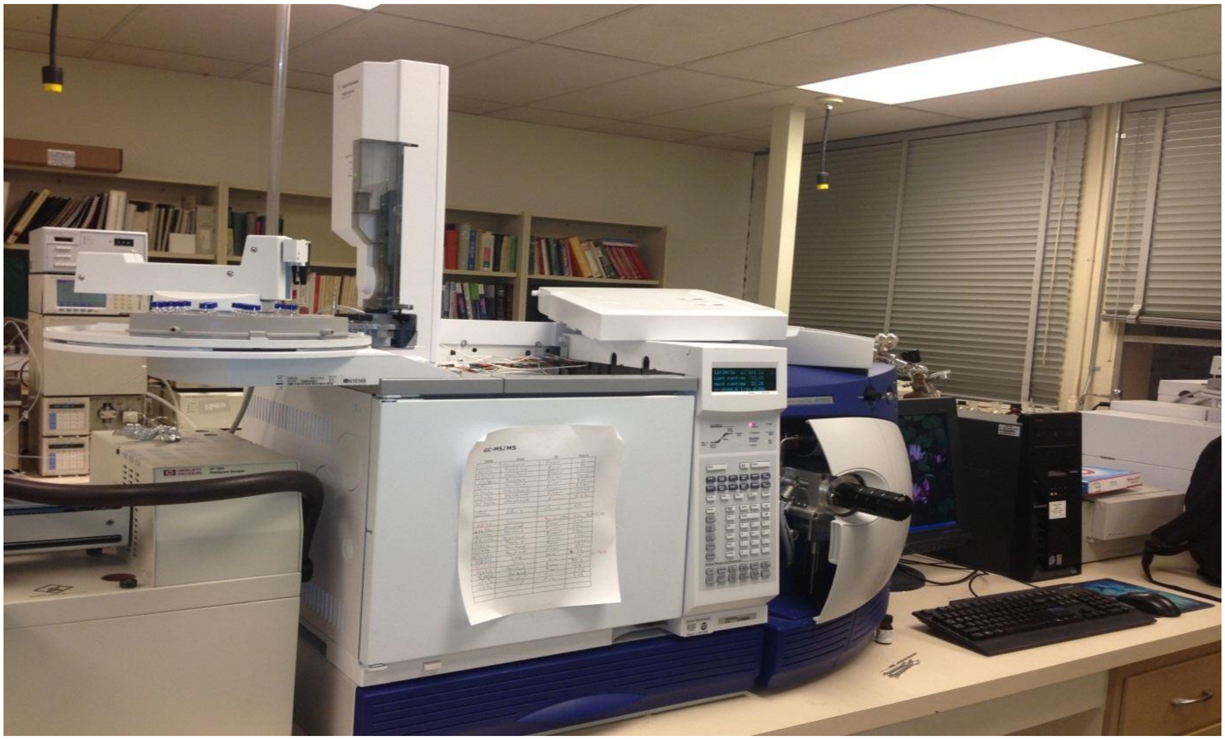

Figure A-6 GC-MS Assembly

Qualtrics Survey Tool

Qualtrics is a survey based reasearch tool. It was used to circulate the eletronic survey to collect information about siloxanes issues nationwide. This software was easier to use, sophisticated and includes lot helpful features. It was possible to customize everything from creating survey to analyzing results. This tool was considered as the cutting edge survey based research tool and has been used for variety of survey applications. This enabled smooth transfer of data in any required format. For international distribution of survey, created survey can be translated and distributed in around 48 international languages automatically. Over 100 different types of questions are available to build the survey which includes multiple choice questions, matrix table, slider, heat map, rak order, text entry, drill down menu, grouping, meta and many more. This enabled user interactive questions to increase response rate. Formatting of the question by changing layouts, positions and answer choices quickly was possible. Questions can be designed of Likert Scales as well. A certain questions can be forced or requested responses with validation. Rich text editing was possible with font, size and color easily. HTML can be used to edit things however a user interface was available too. Qualtrics library holds professionally questions from professionally designed surveys. Own libraries can be created and saved. Images can be embeded in the survey easily to make survey more visually appealing. Audio or video files can also be embeded in the survey on host media on Qualtrics' server. Any format files can be uploaded for respondant's download. This was helpful in case of educating the respondant about survey issue before taking it. Skip logic, display logic, branch logics are very helpful in optimizing the survey. List of respondants can easily be prepared using panels which was compatible with MS Excel files. Survey can be distributed by sending personalized email. A annonymous link was generated in case of distributing it to annonymous respondants. Survey can be distributed on a social media or personal websites as well. Data analysis was very easy since the data can be seen in graphic manner. Filters can be applied to the data if particular set is to be analyzed. The survey report can be customized. Either entire survey report and / or an individual response table can be exported to commonly used data analysis and publishing tools such as Excel, Powerpoint. Some of the statistical analysis can be done in the Qualtrics itself. Considering all these benefits, Qualtrics tool was used for the survey in this research.

B. METHODS – ADDITIONAL DETAILS

Sample Selection: Criteria and Properties

It is now known that siloxanes are hydrophobic and show affinity towards particulate matter when they are present in aquatic environment. The particulate matter in wastewater treatment plants is separated as sludge. In conventional activated sludge treatment plants, the sludge consists of average 87% of volatile organic matter. It was observed that, siloxanes have higher tendency to attach with the EPS (Extracellular Polymeric Substances). These extracellular polymeric substances are volatile in nature and attached to inorganic particle in the activated sludge. This is the reason why siloxanes concentrations are observed in higher concentrations in activated sludge during entire wastewater treatment. Fig 5-7 below shows the gas chromatogram of actual sludge sample full scan and microscopic picture of extracellular polymeric substance in activated sludge and the conceptual sketch of sludge particle surrounded by EPS which attracts siloxanes molecules. In wastewater treatment train, waste activated sludge has the highest amount of Total Volatile Solid content. Hence, waste activated sludge was chosen for analysis of siloxanes. It was necessary to maintain the % of TVS in the sludge in order to have correct estimate of siloxanes in the sludge.

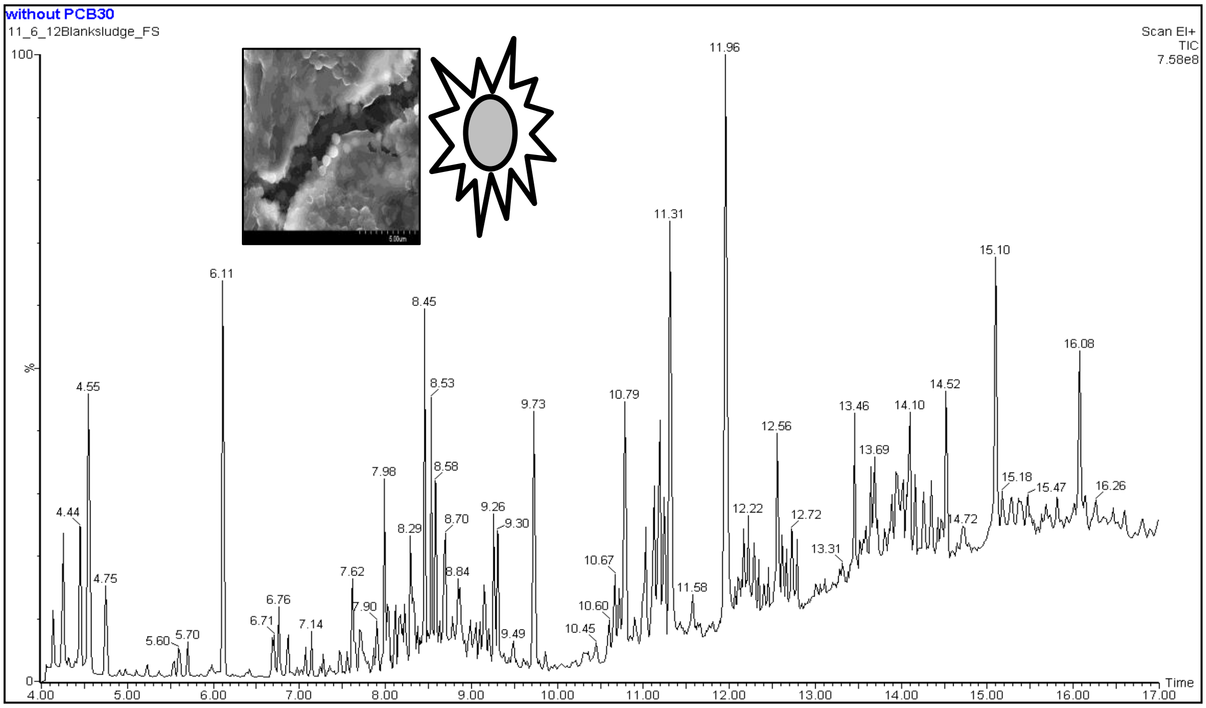

Figure B-1 Full Scan of Sludge Sample: Gas Chromatogram

External Calibration Standards

External calibration standards are used to prepare a calibration curve which helps in quantifying the concentration of siloxanes after analysis. To prepare standards, n-hexane was used as solvent and standards of Octamethylcyclotetrasiloxane (D4) and Decamethylcyclopentasiloxane (D5) are used (Section 4.1.2). Standard stock solutions are prepared fresh, every time before running the set of samples to ensure there was no volatilization and change in concentration of standards. Standard stock solutions are prepared in 50 mL clean glass amber vial. The available original concentration of Octamethylcyclotetrasiloxane (D4) was 0.956 g / mL and that of Decamethylcyclopentasiloxane (D5) was 0.958 g / mL. The external standard was prepared in combined form of D4 + D5 concentration. The expected concentrations of both D4 and D5 for calibration curve are decided as 1000 ng /mL as upper limit, 500, 250, 31.25 and 15.625 ng / mL as lower limit. Initially the original external standard was combined and diluted to 1 µg / mL stock solution by step by step method. The volume of each compound and method to prepare desired standard solutions is given in Table A-1 below.

Table B-1Three Step dilution of External Standard

Solution	Concentration	Desired Concentration	Volume Added	Volume of Solvent (n-Hexane)	New Solution
Original D4	0.956 g / mL	10 mg / mL	55 ul	4890 ul	A
Original D5	0.958 g / mL		55 ul		
A	10 mg / mL	100 µg / mL	50 ul	4950 ul	B
B	100 µg / mL	1 µg / mL	50 ul	4950 ul	C

Solution “C” with concentration of 1 µg / mL was used as stock solution for preparing further dilution and external calibration curve standards of concentration 1000, 500, 250, 31.25 and 15.625 ng / mL. These solutions are prepared directly in the glass amber 2 mL GC vial by dilution to half method. Six clean GC vials are taken. In 1st GC vial, 1 mL of solution “C” (concentration = 1 µg / mL) was inserted using glass syringe of 1 mL volume accurately. In all other (6 vials) 0.5 mL of n-hexane was inserted. Now 0.5 mL of solution “C” with 1 µg / mL concentration was added to 2nd vial which already holds 0.5 mL of n-hexane to prepare final concentration of 500 ng / mL. Internal standard was spiked to the external standard as well. To achieve 525 ng / mL concentration of internal standard in standard, 15 ul of 35 µg/mL internal standard PCB-30 was added. The vial was vigorously mixed using vortex mixer to ensure complete mixing of solution. Other concentrations are prepared in similar manner. Only vials with desired concentrations of (1000, 500, 250, 31.25, 15.625 ng / mL) are selected for analysis. GC vials containing calibration standards are prepared just before the analysis or if prepared little earlier, are stored in refrigerator until analysis starts.

Extraction

Solid liquid extraction procedure was adopted to extract siloxanes from sludge samples. Previously prepared centrifuge tubes which hold sludge + hexane mixture and spiked with a known dose of internal standard along with two blank centrifuge tubes containing only n-hexane are taken to the mechanical centrifuge. All the tubes are covered with cap tightly, turned upside down to ensure complete mixture. All tubes are centrifuged for 5 minutes at 3000 rpm. After 5 minutes, if the clear phase separation was obtained extraction was done, if not, another 5 minutes of centrifugation was done. Since n-hexane and water are highly immiscible, phase separation was usually obtained within 2 – 3 minutes of centrifugation. Water is heavier than n-hexane. The phase separation shows heaviest sludge particles collected at bottom, water resides above sludge particles and n-hexane which is the lightest amongst all will be at the top. Then 1 mL of this n-hexane extract was transferred to a clean 2 mL GC vial including blanks. One of the blank vials was spiked with similar dosage of internal standard and called as Blank_IS. Another blank was directly transferred to GC vial. This completes the extraction procedure. Summarizing, we will have GC vials for analysis as given in Table A-2 below.

Table B-2 Analysis Content

GC Vial	Content
Blank	n-hexane
Blank_IS	n-hexane + 525 ng/mL of PCB-30
External Standards series	[1000, 500, 250, 31.25, 15.625 ng /mL of (D4+D5)] + [525 ng /mL of PCB-30]
Sludge Sample	Extract containing 500 ng / mL of PCB-30

Gas Chromatography – Mass Spectrometry Analysis

As metnioned in Table 5-2, blanks, standards and samples are ready for analysis. Gas chromatography was used to separate molecules. Compounds are vaporized without degradation which leads to the separation. Typical operation of GC-MS analysis includes injection of analyte, vaporizaton of injected analyte with a temperature ramp, separation of compounds in column, electronic ionizatin of broken down molecules, quantification in mass spectrometer and data acquisition. For this research, Agilent 6890 GC connected to a Waters Quattro Micro Triple Quad Mass Spectrometer coupled with an auto Sampler and auto injection port available in Physiology department at Colorado State University was used. It is welknown that most of the instrument components have background concentrations of siloxanes, especially the columns used. To avoid this contamination special type of SLB-5ms capillary Column with 30m length, film thickness of 0.25 um and internal diameter of 0.25 mm was selected. This column is proven to have low bleed, inert, durable and consistent. Pure helium is used as carrier gas. Based on various methods, temperature profiles mentioned in the literature and with lot of brainstorming, suitable temperature profile and other instrumental conditions are set up.

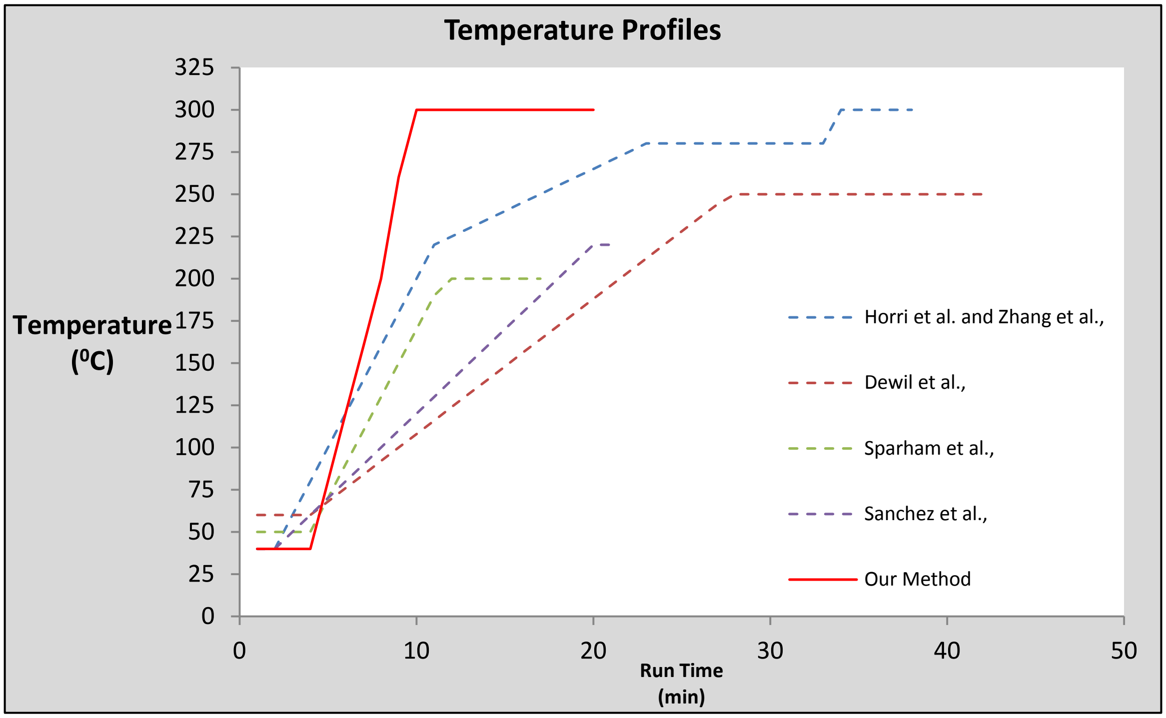

Figure B-2 Temperature Profiles Used in Past and in this method

Fig B\2 above shows the different temperature profile for GC used previously. Starting from those as baseline, we have improved temperature profile that best suited the compounds analyzed, internal standard and the instrumental properties. Modified temperature profile is based on the boiling points of D4, D5 and PCB-30. Boiling point of these compounds are 175^0C, 90^0C and 99.2^0C respectively. The temperature profile adopted satisfies all these boiling point temperatures in order to obtain a good separation. Solvent delay time of 4 minutes is allowed and MS scan data is collected using Mass Lynx v4.1.

Removal of Siloxanes

In past many researchers reported methods for removal of siloxanes from air/gas, only one has reported methods for siloxanes quantification from sediments and sludge. The methods for gaseous phase siloxanes removal are well established and commercially popularized. On the other hand, removal of siloxanes in water and solid phases is completely ignored and has much scope for developments. In effort to add on to this, in this thesis we have tested and customized methods for removal of siloxanes from waste activated sludge from a conventional wastewater treatment plant. This section describes the details of methods tested.

Sample Selection

Removal efficiency tests are performed on composite sample of 2 – 3 individual samples depending upon the volume required for tests. Composite sample is prepared from sludge samples with nearly similar properties such as %TS and TVS. This is adopted to ensure that the sample used for removal study tests is representative of sludge with average properties. Samples with lower %TS and TVS values are selected. Lower %TS samples are watery and oxidants are mixed homogenized very well on bench scale testing. Another reason is, for these tests samples are spiked with high dosage of D4 and D5, so the samples with lower %TS and TVS do possess lower background concentration of D4 and D5 and hence can be reliable for bench scale testing. From the next section onwards, the methods tested for removal studies, various parameters studied and importance of them is described.

Removal of by Hydrogen Peroxide

As described earlier, hydrogen peroxide is a well-known advanced oxidant. It is commonly used in various industrial processes and in wastewater treatment as well. The details of hydrogen peroxide are mentioned in Section 4.2.1. Here, hydrogen peroxide is used for removing D4 and D5 from waste activated sludge. Similar study has been performed before (Section 2.7.2) which studied the effect of H_2O_2 dosages on removal of D4 and D5. This bench scale study is done similar to the previous study with additional test parameters.

Effect of Dosage

The bench scales study is performed by trying out different dosages of hydrogen peroxide for fixed weight of the sludge sample and the results are reported. The efficiency of removal is tested with increasing dosage of hydrogen peroxide. For this experiment, a composite sludge sample is prepared, homogenized and stored at 3 – 4^0C overnight to ensure complete homogenization. Before the use, sample is kept in water bath at room temperature for about 1 – 2 hours. After the sample comes at room temperature, five 30 g of samples are weighed using sensitive balance and the weighing dish by standard method. Weighed samples are then transferred to five different graduated conical flasks. Samples are then mixed using vortex mixer at high speed for 3 min to achieve homogenization. Four samples are then spiked by adding 70 ul of D4 and D5 each to achieve final concentration of 100 ug / mL in the sample. Fifth sample is treated the same way without spiking siloxanes and used as Control-2 sample. Flasks are tightly closed by multiple layer of parafilm. Samples are mixed using vortex mixer at highest speed for 3 minutes to ensure complete mixing of D4, D5 and sludge and it is kept in dark overnight to ensure good adsorption of siloxanes to extracellular polymeric substances in the sludge. After the adsorption, three different doses of 30% hydrogen peroxide are added three spiked sample. Forth spiked sample is kept as it is and hydrogen peroxide is not added to it. This is used as Control-1 sample. Now three flasks have the sample spiked with exactly same amount of D4 and D5 and different doses of hydrogen peroxide. One flask will have spiked samples without hydrogen peroxide. And one flask will have un-spiked sludge sample i.e. original composite sludge sample. The three flasks are gently shaken to mix the oxidant completely. Since this is an active reaction, safety precautions are followed. All flasks are then kept in the dark with flask mouth open for predetermined period of time. At the completion of duration, 8 mL of solvent n-hexane is added to all the five flasks. Rigorous vortex mixing of 5 min is applied twice with a gap of 1 min for all the samples.

Removal of siloxanes using Hydrogen Peroxide

For 30 gram of sludge, 3.34% (1ml), 10% (3ml) and 16.67% (5ml) of 30% pure hydrogen peroxide was added. The table 5-3 below shows the details of sample preparation of removal studies using hydrogen peroxide.

Table B-3 Removal Study Sample Preparation

	3.34%	**10%**	**16.67%**	**Control 1**	**Control 2**
1 hr	Sample +D4+D5+3mL H2O2+hexane	Sample +D4+D5+3mL H2O2+hexane	Sample +D4+D5+3mL H2O2+hexane	Sample +D4+D5+hexane	Sample +hexane
2 hr	Sample +D4+D5+3mL H2O2+hexane	Sample +D4+D5+3mL H2O2+hexane	Sample +D4+D5+3mL H2O2+hexane	Sample +D4+D5+hexane	Sample +hexane
3 hr	Sample +D4+D5+3mL H2O2+hexane	Sample +D4+D5+3mL H2O2+hexane	Sample +D4+D5+3mL H2O2+hexane	Sample +D4+D5+hexane	Sample +hexane

After all the reactions are completed, samples are again vortex mixed for 3 min and then transferred to glass centrifuge tubes. The extract is then transferred to GC vial. External standards are prepared. PCB-30 as internal standard is added directly to the GC vials to achieve final concentration of 250 ng / mL. Procedural blank (only n-hexane), internal standard blank (n-hexane + PCB-30), five external standards and 12 removal study samples are then analyzed on GC using developed method. With the matrix given above, information about the effect of doses of hydrogen peroxide and the reaction time on efficiency of siloxanes is obtained. The concentrations of all 9 samples are subtracted from concentration of [(Control-1) – (Control-2)] to get the estimate of removal occurred during that particular reaction time with particular dose of hydrogen peroxide. While calculation of concentration, internal calibration is applied.

Recovery factor which is calculated previously is applied to obtain final concentrations.

Following equation is used to calculate removal efficiency.

$$\text{Removal Efficiency } \% = \frac{\{[\text{Concentration of Control1} - \text{Control2}] - \text{ Sample Concentration}\}}{[\text{Concentration of Control1} - \text{Control2}]} * 100$$

C. SURVEY

Need of Survey

As mentioned earlier, there is very less data available on siloxanes issue on geographic scale. It is necessary to understand the severity of issue and control measures being taken in the world. Since this issue is directly related with the use of siloxanes in our day to day life consumer products, variability in concentrations is expected across the country / world. Hence to fill up this knowledge gap an electronic survey is designed and distributed to water / wastewater community for responses and their opinions about this issue. The aim of this survey is to collect maximum information about occurrence of siloxanes around the world. This survey helps us to understand the level of importance for siloxane issues among Water / Waste-water infrastructure community. The survey will provide supporting information for our laboratory based research and will help us transforming this research into practical applications. The researcher has completed Institutional Review Board training offered at Colorado State University.

Design of Survey

The design of the survey is done using Qualtrics online survey tool (Section 4.3.7). This design is entirely based on the information needed with supporting information. The siloxanes issue doesn’t seem very well recognized even by the people in wastewater industry. Hence the first page of the survey gives the glimpse of this issue to the respondent. Some basic information about the siloxanes and issues associated with it are explained in simple words (without any technical information) for the respondent. It helps respondent to have slight idea of what he / she will see in the survey which helps increasing the response rate.

Potential Targets and Distribution

The prospective respondents of this survey are obviously the people working in water / wastewater industry, especially the wastewater. Engineers, researchers, plant operators, consultants, plant superintendents, bio solids experts are some of the people who were asked to take the survey. Utility managers and concerned people at water and wastewater utilities throughout the United States are contacted through email to take this survey. The contacts information is obtained by various sources such as internet, Water Environment Federation, American Water Works Association. Survey was also sent to various researchers who published their work regarding siloxanes. A water wastewater online forum was also used to distribute the survey among active group of wastewater plant operators. About 783 personnel are contacted via email who works for the wastewater utilities and design firms. Other anonymous link distribution and social media distribution would reach the survey over 1000 people.

Information to be collected

First few questions in the survey collect the preliminary information of the respondent such as geographic location of the facility regarding which respondent is filling the information. Data regarding the average flow, type of treatment, sludge production and gas production is collected during first few questions. This information is helpful to correlate the data further provided by respondent regarding siloxanes. All the questions are kept optional in case respondent doesn’t want to disclose the identity. Questions are asked whether the facility uses activated sludge process, if it uses anaerobic digestion process to treat waste activated sludge and if it uses the biogas produced for beneficial purpose. Appropriate skip and display logics were used. For the scope of this research, it is very important to identify the facilities that use the bio gas for beneficial purpose since siloxanes is expected to be huge threat to such facilities. A question was included to check the awareness about siloxanes. Another question was asked to see if facility measures the concentration of siloxanes. Various matrices were displayed as options to check and respondent was then asked to enter the concentration measured for which he checked the box. Another question is asked in general if they have seen any white / silver color scaling on the surface of gas handling equipment. Some other question related to gas treatment for siloxanes, cost per unit are also asked for group of respondents who are aware. Finally respondent’s opinion is asked to see how important this issue is for them.

Questionnaire

A text copy of the questionnaire is attached separately in Appendix F.

D. RESULTS

Table D-1Siloxanes Concentrations at City of Loveland

Date	D4 (ug/g dry solids	D5 ug/g dry solids	Total Siloxanes ug/g dry solids
28-Mar	1.14	6.87	8.01
30-Mar	0.03	3.42	3.44
2-Apr	0.17	2.92	3.09
4-Apr	1.21	5.12	6.33
6-Apr	0.65	8.28	8.93
9-Apr	1.35	7.48	8.82
11-Apr	0.17	4.61	4.78
13-Apr	1.61	6.11	7.73
16-Apr	0.22	3.52	3.75
18-Apr	1.52	9.91	11.43
20-Apr	1.24	5.54	6.78
23-Apr	1.45	6.41	7.86
25-Apr	3.25	17.11	20.36
26-Apr	2.14	7.44	9.58
30-Apr	1.42	5.47	6.88
9-May	0.39	6.44	6.82
14-May	0.19	4.36	4.55
16-May	1.84	7.16	9.00
18-May	0.29	5.79	6.07
21-May	1.24	6.11	7.34
23-May	0.22	3.62	3.84
25-May	0.47	5.27	5.73
28-May	1.07	5.04	6.11
30-May	0.36	5.64	6.00
1-Jun	0.35	4.50	4.85
6-Jun	0.00	5.63	5.63
8-Jun	0.42	4.93	5.35
11-Jun	0.45	4.83	5.28
13-Jun	0.09	5.47	5.55
18-Jun	0.00	8.22	8.22
19-Jun	0.30	9.51	9.81
20-Jun	0.00	7.15	7.15
22-Jun	0.00	6.15	6.15
25-Jun	0.00	4.98	4.98
27-Jun	0.00	4.74	4.74
29-Jun	0.06	3.67	3.73

2-Jul	0.28	9.69	9.97
4-Jul	0.01	2.19	2.20
6-Jul	0.00	4.48	4.48
9-Jul	0.14	3.32	3.46
11-Jul	0.05	4.50	4.55
13-Jul	0.11	3.82	3.93
16-Jul	0.00	2.81	2.81
18-Jul	0.00	6.48	6.48
20-Jul	0.00	5.69	5.69
23-Jul	0.00	4.17	4.17
25-Jul	1.17	3.66	4.83
27-Jul	1.41	5.26	6.68
30-Jul	1.08	5.15	6.24
1-Aug	0.00	3.52	3.52
3-Aug	0.00	8.25	8.25
8-Aug	0.00	5.85	5.85
10-Aug	0.00	7.34	7.34
13-Aug	0.00	6.76	6.76
15-Aug	0.00	11.20	11.20
17-Aug	0.00	5.57	5.57
20-Aug	0.00	4.40	4.40
22-Aug	0.00	7.94	7.94
24-Aug	0.00	4.98	4.98
27-Aug	0.00	4.38	4.38
29-Aug	0.12	4.24	4.36
31-Aug	0.10	3.48	3.58
3-Sep	0.32	6.86	7.18
5-Sep	0.13	4.09	4.22
7-Sep	0.21	4.43	4.64
10-Sep	0.09	3.15	3.24
12-Sep	0.00	3.05	3.05
14-Sep	0.00	1.15	1.15
17-Sep	0.00	4.65	4.65
19-Sep	0.00	2.92	2.92
21-Sep	0.00	1.32	1.32
Average	**0.43**	**5.50**	**5.92**
Maximum	**3.25**	**17.11**	**20.36**
Minimum	**0.00**	**1.15**	**1.15**

Table D-2 Monthly Average of Siloxanes at City of Loveland

Month	D4 ug/g dry solids	D5 ug/g dry solids	Total Siloxanes ug/g dry solids
March	0.58	5.14	5.73
April	1.26	6.92	8.18
May	0.67	5.49	6.16
June	0.14	5.81	5.95
July	0.33	4.71	5.04
August	0.02	5.99	6.01
September	0.08	3.51	3.60

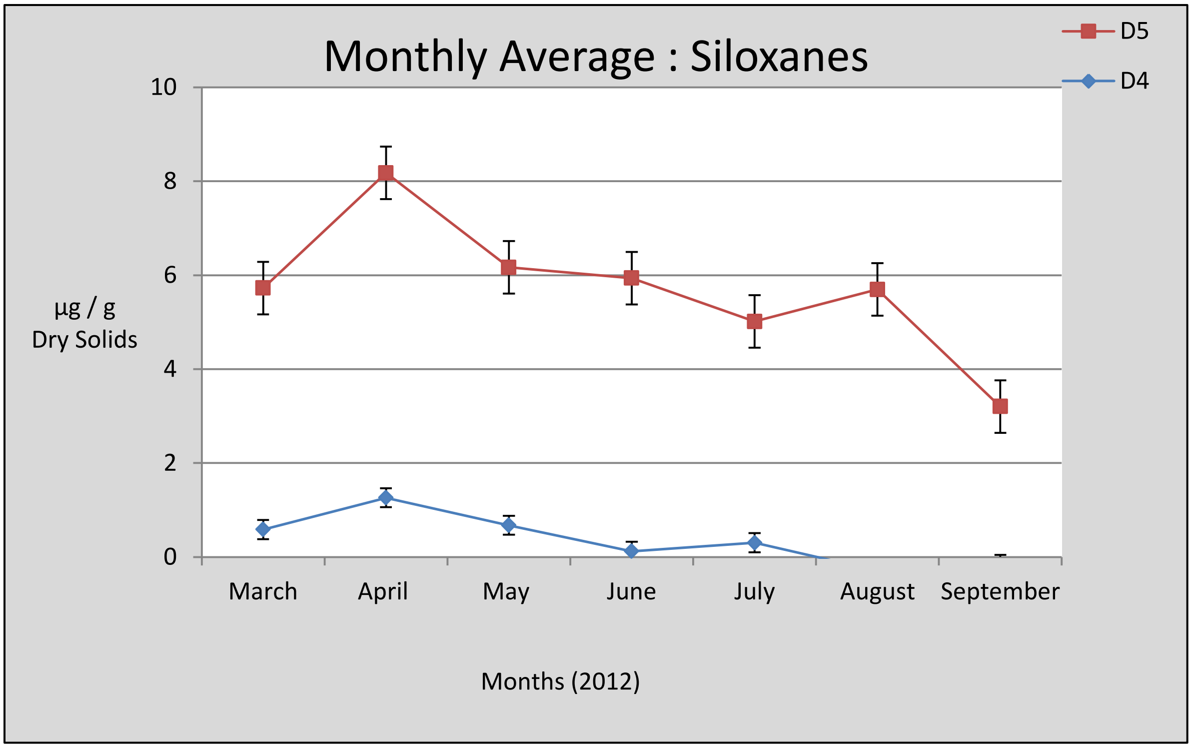

Figure D-1 Monthly Average Siloxanes Concentration

Table D-3 Data for D4 Analysis on 7/19/2012

Name	Standard	RT	Area	Blank	New Area	Response	ng/ml
Blank1		8.63	1750.07	1750.07	0.00	0.00	-24.95
Blank2		8.63	1564.07	1750.07	-185.99	-	-
Std1	1000.00	8.55	121519.98	1750.07	119769.91	0.68	1036.09
Std2	500.00	8.55	64527.77	1750.07	62777.71	0.30	441.19
Std3	250.00	8.55	38413.93	1750.07	36663.87	0.16	223.54
Std4	31.25	8.55	10719.33	1750.07	8969.26	0.04	35.60
Std5	15.62	8.55	14124.19	1750.07	12374.13	0.05	57.55
Std6	7.81	8.55	7023.29	1750.07	5273.22	0.02	11.94
Blank3		8.63	1911.69	1911.69	0.00	-	-
Blank_IS		8.59	2625.91	1911.69	714.22	0.01	-13.91
6-Jun		8.55	4308.78	1911.69	2397.09	0.01	-1.89
6-Jun		8.59	2616.15	1911.69	704.46	0.00	-17.53
6-Jun		8.59	2854.08	1911.69	942.39	0.01	-15.23
8-Jun		8.55	15826.14	1911.69	13914.45	0.09	118.21
8-Jun		8.55	16649.56	1911.69	14737.87	0.10	127.53
8-Jun		8.55	18522.20	1911.69	16610.51	0.11	145.33
Blank4		8.63	855.07	855.07	0.00	-	-
11-Jun		8.55	16238.07	855.07	15382.99	0.09	123.47
11-Jun		8.55	15924.35	855.07	15069.28	0.09	120.89
11-Jun		8.55	14448.20	855.07	13593.12	0.08	107.14
13-Jun		8.5	6598.57	855.07	5743.50	0.04	31.35

		5					
13-Jun		8.55	5535.66	855.07	4680.59	0.03	23.79
13-Jun		8.55	5197.77	855.07	4342.70	0.03	22.29
Blank5		8.63	570.73	570.73	0.00	-	-
18-Jun		8.55	3257.93	570.73	2687.20	0.02	3.15
18-Jun		8.70	421.30	570.73	-149.44	-0.09	-158.76
18-Jun		8.55	1866.27	570.73	1295.54	0.01	-10.85
19-Jun		8.55	9792.45	570.73	9221.72	0.07	82.65
19-Jun		8.55	9289.98	570.73	8719.25	0.07	79.79
19-Jun		8.55	8417.34	570.73	7846.60	0.06	75.23
Blank6		8.66	418.28	418.28	0.00	-	-
20-Jun		8.59	2310.70	418.28	1892.42	0.01	-3.73
20-Jun		8.55	2745.37	418.28	2327.09	0.02	-0.22
20-Jun		8.59	2207.91	418.28	1789.62	0.01	-7.77
22-Jun		8.59	2138.52	418.28	1720.24	0.01	-10.37
22-Jun		8.59	2069.53	418.28	1651.25	0.01	-7.77
22-Jun				418.28	-418.28	0.00	-29.60
Blank7		8.34	15499.19	418.28	15080.91	-	-
25-Jun		8.59	2050.36	418.28	1632.07	0.01	-8.17
25-Jun		8.63	1095.77	418.28	677.49	0.01	-16.82
25-Jun		8.55	4438.76	418.28	4020.48	0.03	18.33
27-Jun		8.59	1419.80	418.28	1001.52	0.01	-16.30
27-Jun		8.59	1309.99	418.28	891.71	0.00	-18.09
27-Jun		8.5	1131.90	418.28	713.62	0.00	-19.97

		5					
Blank8		8.70	374.22	374.22	0.00	-	-
29-Jun		8.55	5102.63	374.22	4728.41	0.02	8.71
29-Jun		8.55	6068.93	374.22	5694.70	0.03	22.21
29-Jun		8.55	13367.81	374.22	12993.59	0.06	70.40
2-Jul		8.55	12540.18	374.22	12165.96	0.04	39.44
2-Jul		8.55	13409.92	374.22	13035.69	0.04	37.38
2-Jul		8.55	9303.74	374.22	8929.51	0.03	25.33
Blank9		8.63	394.00	394.00	0.00	-	-
4-Jul		8.55	2673.75	394.00	2279.74	0.02	8.23
4-Jul		8.55	2249.62	394.00	1855.62	0.02	1.74
4-Jul		8.55	2121.71	394.00	1727.71	0.02	1.53
6-Jul		8.55	2934.85	394.00	2540.84	0.01	-7.33
6-Jul		8.55	2471.44	394.00	2077.44	0.01	-11.00
6-Jul		8.59	2913.96	394.00	2519.96	0.01	-9.89
Blank10		8.59	722.19	722.19	0.00	-	-
9-Jul		8.55	13725.64	722.19	13003.46	0.04	36.50
9-Jul		8.55	9326.46	722.19	8604.27	0.03	23.41
9-Jul		8.55	7487.97	722.19	6765.78	0.02	12.76
11-Jul		8.55	5927.06	722.19	5204.87	0.02	13.62
11-Jul		8.55	5688.45	722.19	4966.26	0.02	7.22
11-Jul		8.55	4090.97	722.19	3368.78	0.01	-4.13
Blank11		8.63	597.25	597.25	0.00	-	-

13-Jul		8.55	10464.52	597.25	9867.26	0.03	25.67
13-Jul		8.55	9023.08	597.25	8425.83	0.03	19.13
13-Jul		8.55	7677.49	597.25	7080.24	0.02	8.89
16-Jul		8.55	2022.74	597.25	1425.48	0.00	-18.32
16-Jul		8.55	3235.48	597.25	2638.23	0.01	-12.81
16-Jul		8.55	4768.64	597.25	4171.39	0.01	-6.10

Table D-4 Data for D5 Analysis on 7/19/2012

Name	Standard	RT	Area	Blank	New Area	Response	ng/ml
Blank1		10.09	6521.64	7157.01	-635.36	1.33	152.81
Blank2		10.09	7157.01	7157.01	0.00	-	-
Std1	1000.00	10.05	1591668.63	7157.01	1584511.62	8.96	1030.40
Std2	500.00	10.05	830646.00	7157.01	823488.99	3.90	448.54
Std3	250.00	10.05	467533.72	7157.01	460376.71	1.99	228.62
Std4	31.25	10.05	88900.98	7157.01	81743.98	0.35	40.00
Std5	15.62	10.05	71235.19	7157.01	64078.18	0.27	30.84
Std6	7.81	10.05	59283.86	7157.01	52126.85	0.23	26.25
Blank3		10.05	8864.10	8864.10	0.00	-	-
Blank_IS		10.05	10083.99	8864.10	1219.89	0.01	0.85
6-Jun		10.05	1787995.25	8864.10	1779131.15	10.92	1256.62
6-Jun		10.05	1759241.50	8864.10	1750377.40	11.76	1353.50
6-Jun		10.05	1821890.50	8864.10	1813026.40	11.93	1372.97
8-Jun		10.05	1920416.88	8864.10	1911552.78	12.55	1443.83
8-Jun		10.05	1859632.25	8864.10	1850768.15	12.22	1405.81
8-Jun		10.05	1979374.88	8864.10	1970510.78	12.89	1483.00
Blank4		10.05	8154.11	8154.11	0.00	-	-
11-Jun		10.05	1894274.13	8154.11	1886120.02	11.61	1335.92
11-Jun		10.05	1864771.00	8154.11	1856616.89	11.46	1319.14
11-Jun		10.05	1835522.88	8154.11	1827368.77	11.33	1303.57
13-Jun		10.05	1995382.63	8154.11	1987228.52	12.43	1430.08
13-Jun		10.05	2020502.25	8154.11	2012348.14	13.37	1538.52
13-Jun		10.05	1824973.63	8154.11	1816819.52	12.61	1450.88
Blank5		10.05	8593.83	8593.83	0.00	-	-
18-Jun		10.05	2499737.50	8593.83	2491143.67	16.62	1912.55
18-Jun		10.09	4089.56	8593.83	-4504.28	-2.57	-296.75

18-Jun		10.05	2275457.25	8593.83	2266863.42	15.73	1810.76
19-Jun		10.05	2654821.25	8593.83	2646227.42	19.70	2267.18
19-Jun		10.05	2730808.00	8593.83	2722214.17	20.86	2401.10
19-Jun		10.05	2742559.50	8593.83	2733965.67	22.27	2563.00
Blank6		10.05	8450.39	8450.39	0.00	-	-
20-Jun		10.05	2175769.50	8450.39	2167319.11	15.51	1784.56
20-Jun		10.05	2195465.25	8450.39	2187014.86	14.83	1706.14
20-Jun		10.05	2095350.25	8450.39	2086899.86	12.78	1470.59
22-Jun		10.05	2011209.63	8450.39	2002759.24	10.83	1245.89
22-Jun		10.05	1938663.00	8450.39	1930212.61	12.81	1473.90
22-Jun		10.05	1914550.38	8450.39	1906099.99	13.52	1556.08
Blank7		10.05	8637.05	8637.05	0.00	-	-
25-Jun		10.05	1251516.75	8637.05	1242879.70	8.15	937.72
25-Jun		10.05	1232476.13	8637.05	1223839.07	9.37	1077.81
25-Jun		10.05	1329877.50	8637.05	1321240.45	9.07	1043.94
27-Jun		10.05	2033107.88	8637.05	2024470.82	11.16	1283.81
27-Jun		10.05	1963925.50	8637.05	1955288.45	9.59	1103.97
27-Jun		10.05	1920246.50	8637.05	1911609.45	8.51	978.67
Blank8		10.05	10050.95	10050.95	0.00	-	-
29-Jun		10.05	1710305.63	10050.95	1700254.68	7.72	888.40
29-Jun		10.05	1545092.25	10050.95	1535041.31	8.11	933.15
29-Jun		10.05	1602738.75	10050.95	1592687.81	7.46	857.79
2-Jul		10.05	3306332.00	10050.95	3296281.06	11.13	1280.79
2-Jul		10.05	3777643.50	10050.95	3767592.56	11.49	1322.59
2-Jul		10.05	3278530.75	10050.95	3268479.81	11.74	1351.20
Blank9		10.05	12034.47	12034.47	0.00	-	-
4-Jul		10.05	444014.97	12034.47	431980.50	4.01	461.15
4-Jul		10.05	425358.44	12034.47	413323.97	3.79	436.14
4-Jul		10.05	419089.00	12034.47	407054.53	3.98	457.63
6-Jul		10.05	2040127.13	12034.47	2028092.66	8.97	1032.03
6-Jul		10.05	1993498.13	12034.47	1981463.66	8.49	976.78
6-Jul		10.05	2003877.88	12034.47	1991843.41	7.59	873.61
Blank10		10.05	13714.87	13714.87	0.00	-	-
9-Jul		10.05	2068111.75	13714.87	2054396.88	6.19	712.41
9-Jul		10.05	1744988.63	13714.87	1731273.76	6.21	714.15
9-Jul		10.05	1762695.38	13714.87	1748980.51	6.22	715.39
11-Jul		10.05	2045897.88	13714.87	2032183.01	9.61	1105.39
11-Jul		10.05	1982789.25	13714.87	1969074.38	8.14	936.29
11-Jul		10.05	2001198.63	13714.87	1987483.76	7.83	901.35
Blank11		10.05	12591.51	12591.51	0.00	-	-
13-Jul		10.05	2152111.25	12591.51	2139519.74	7.00	805.54

13-Jul		10.05	2045007.50	12591.51	2032415.99	6.78	780.32
13-Jul		10.05	2112570.25	12591.51	2099978.74	6.40	736.61
16-Jul		10.05	1689798.25	12591.51	1677206.74	4.97	571.87
16-Jul		10.05	1840605.25	12591.51	1828013.74	5.37	617.38
16-Jul		10.05	1751092.13	12591.51	1738500.61	5.01	576.40

Table D-5 Data for PCB30 Analysis on 7/19/2012

Name	Type	Standard	RT	Area	Blank	New Area
Blank1	Blank	1.00			476.97	-476.97
Blank2	Blank	1.00	14.76	476.97	476.97	0.00
Std1	Standard	1.00	14.94	177405.16	476.97	176928.19
Std2	Standard	1.00	14.94	211570.00	476.97	211093.03
Std3	Standard	1.00	14.94	231745.08	476.97	231268.11
Std4	Standard	1.00	14.94	232659.14	476.97	232182.17
Std5	Standard	1.00	14.94	235583.75	476.97	235106.78
Std6	Standard	1.00	14.94	224537.02	476.97	224060.05
Blank3	Analyte	1.00	14.98	443.61	443.61	0.00
Blank_IS	Analyte	1.00	14.94	101847.61	443.61	101404.00
6-Jun	Analyte	1.00	14.94	163354.70	443.61	162911.09
6-Jun	Analyte	1.00	14.94	149253.89	443.61	148810.28
6-Jun	Analyte	1.00	14.94	152394.83	443.61	151951.22
8-Jun	Analyte	1.00	14.94	152792.78	443.61	152349.17
8-Jun	Analyte	1.00	14.94	151936.66	443.61	151493.05
8-Jun	Analyte	1.00	14.94	153345.23	443.61	152901.62
Blank4	Analyte	1.00	14.90	965.75	965.75	0.00
11-Jun	Analyte	1.00	14.94	163426.02	965.75	162460.27
11-Jun	Analyte	1.00	14.94	162918.27	965.75	161952.52
11-Jun	Analyte	1.00	14.94	162269.25	965.75	161303.50
13-Jun	Analyte	1.00	14.94	160868.33	965.75	159902.58
13-Jun	Analyte	1.00	14.94	151481.03	965.75	150515.29
13-Jun	Analyte	1.00	14.94	145061.39	965.75	144095.65
Blank5	Analyte	1.00			0.00	0.00
18-Jun	Analyte	1.00	14.94	149898.09	0.00	149898.09
18-Jun	Analyte	1.00	15.12	1750.40	0.00	1750.40
18-Jun	Analyte	1.00	14.94	144067.70	0.00	144067.70
19-Jun	Analyte	1.00	14.94	134328.81	0.00	134328.81
19-Jun	Analyte	1.00	14.94	130480.74	0.00	130480.74
19-Jun	Analyte	1.00	14.94	122768.06	0.00	122768.06
Blank6	Analyte	1.00	14.54	508.20	508.20	0.00
20-Jun	Analyte	1.00	14.94	140271.22	508.20	139763.02
20-Jun	Analyte	1.00	14.94	148021.47	508.20	147513.27

20-Jun	Analyte	1.00	14.94	163806.92	508.20	163298.73
22-Jun	Analyte	1.00	14.94	185475.05	508.20	184966.85
22-Jun	Analyte	1.00	14.98	151207.02	508.20	150698.82
22-Jun	Analyte	1.00	14.98	141467.97	508.20	140959.77
Blank7	Analyte	1.00	15.23	106.04	106.04	0.00
25-Jun	Analyte	1.00	14.94	152595.20	106.04	152489.17
25-Jun	Analyte	1.00	14.94	130752.39	106.04	130646.35
25-Jun	Analyte	1.00	14.94	145724.78	106.04	145618.74
27-Jun	Analyte	1.00	14.98	181558.34	106.04	181452.31
27-Jun	Analyte	1.00	14.98	203892.06	106.04	203786.03
27-Jun	Analyte	1.00	15.01	224833.36	106.04	224727.32
Blank8	Analyte	1.00	14.98	1353.12	1353.12	0.00
29-Jun	Analyte	1.00	14.98	221533.08	1353.12	220179.95
29-Jun	Analyte	1.00	14.98	190610.61	1353.12	189257.49
29-Jun	Analyte	1.00	14.98	214958.16	1353.12	213605.03
2-Jul	Analyte	1.00	15.01	297493.38	1353.12	296140.25
2-Jul	Analyte	1.00	15.01	329142.13	1353.12	327789.00
2-Jul	Analyte	1.00	15.01	279700.19	1353.12	278347.06
Blank9	Analyte	1.00	15.23	609.67	609.67	0.00
4-Jul	Analyte	1.00	14.94	108319.09	609.67	107709.42
4-Jul	Analyte	1.00	14.94	109570.65	609.67	108960.98
4-Jul	Analyte	1.00	14.94	102884.20	609.67	102274.53
6-Jul	Analyte	1.00	14.98	226709.75	609.67	226100.08
6-Jul	Analyte	1.00	15.01	234001.16	609.67	233391.49
6-Jul	Analyte	1.00	15.01	262914.41	609.67	262304.74
Blank10	Analyte	1.00	14.68	277.55	277.55	0.00
9-Jul	Analyte	1.00	14.98	331991.47	277.55	331713.92
9-Jul	Analyte	1.00	15.01	279135.34	277.55	278857.79
9-Jul	Analyte	1.00	15.05	281501.78	277.55	281224.23
11-Jul	Analyte	1.00	15.05	211805.30	277.55	211527.75
11-Jul	Analyte	1.00	15.05	242233.28	277.55	241955.73
11-Jul	Analyte	1.00	15.05	253957.75	277.55	253680.20
Blank11	Analyte	1.00	14.98	1127.71	1127.71	0.00
13-Jul	Analyte	1.00	15.05	306671.94	1127.71	305544.23
13-Jul	Analyte	1.00	15.05	300749.44	1127.71	299621.73
13-Jul	Analyte	1.00	15.05	329068.91	1127.71	327941.20
16-Jul	Analyte	1.00	15.05	338427.56	1127.71	337299.86
16-Jul	Analyte	1.00	15.09	341679.16	1127.71	340551.45
16-Jul	Analyte	1.00	15.05	348008.09	1127.71	346880.39

Table D-6 Processed Data on 7/19/2012

Date	%TS	D4 ng/ml	D5 ng/ml	D4 ug/g sludge	D5 ug/g sludge
6-Jun	4.84	-16.38	1363.24	-0.07	5.63
8-Jun	5.86	122.87	1444.21	0.42	4.93
11-Jun	5.46	122.18	1319.54	0.45	4.83
13-Jun	5.27	23.04	1440.48	0.09	5.47
18-Jun	4.53	-3.85	1861.66	-0.02	8.22
19-Jun	5.22	79.23	2482.05	0.30	9.51
20-Jun	4.88	-3.91	1745.35	-0.02	7.15
22-Jun	4.93	-9.07	1514.99	-0.04	6.15
25-Jun	4.26	-2.22	1060.87	-0.01	4.98
27-Jun	5.04	-17.19	1193.89	-0.07	4.74
29-Jun	4.76	15.46	873.09	0.06	3.67
2-Jul	2.76	38.41	1336.89	0.28	9.69
4-Jul	4.13	1.64	451.64	0.01	2.19
6-Jul	4.48	-10.44	1004.40	-0.05	4.48
9-Jul	4.30	29.95	713.98	0.14	3.32
11-Jul	4.36	10.42	981.01	0.05	4.50
13-Jul	4.15	22.40	792.93	0.11	3.82
16-Jul	4.09	-12.41	574.14	-0.06	2.81

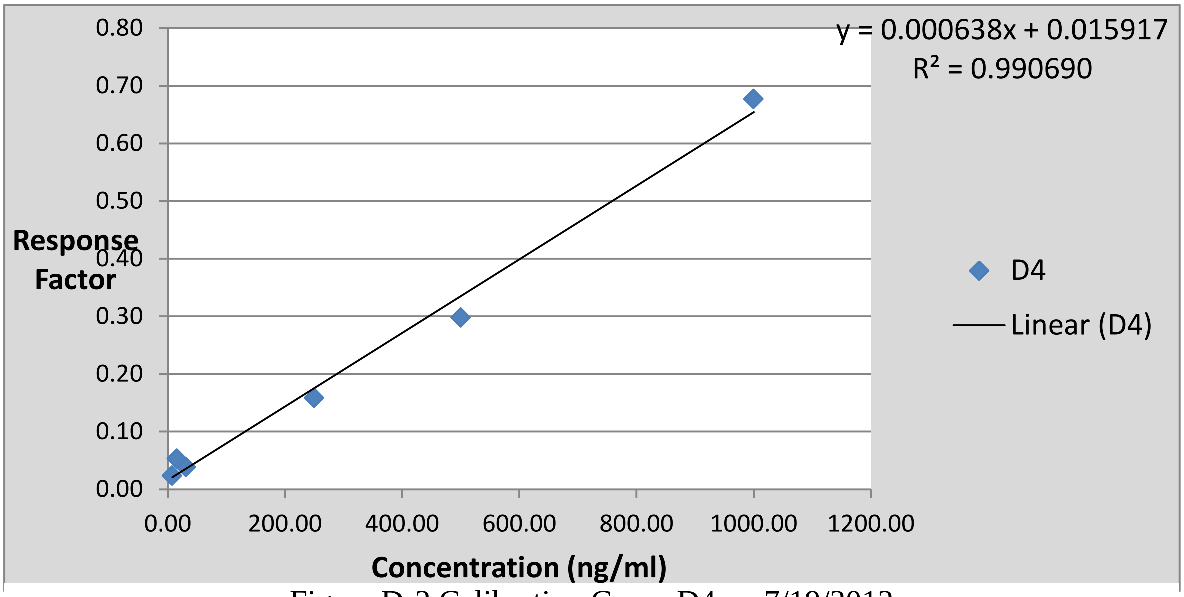

Figure D-2 Calibration Curve D4 on 7/19/2012

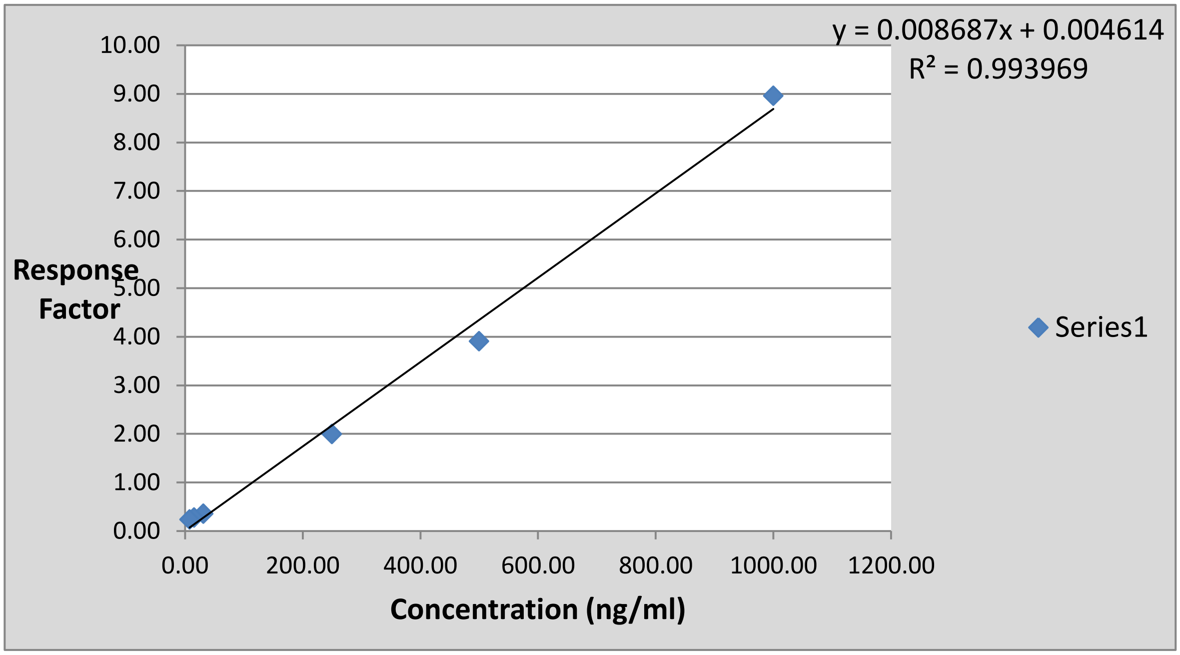

Figure D-3 Calibration Curve D5 on 7/19/2012

Table D-7 Data for D4 Analysis on 9/3/2012

Name	Std. Conc	Area	New Area	Response	Conc	DF	Actual Conc
Blank		127134.70	0.00	-	-	1.00	-
Blank_IS		332269.59	205134.90	0.47	-35.53	1.00	-35.53
1000ng_ml	1000	5232657.50	5105522.81	10.01	978.71	1.00	978.71
250ng_ml	250	2045503.63	1918368.93	3.99	338.85	1.00	338.85
125ng_ml	125	1083007.13	955872.43	2.02	129.11	1.00	129.11
62_5_ng_ml	62.5	703017.44	575882.74	1.24	46.02	1.00	46.02
15_625ng_ml	15.625	8802114.00	8674979.31	18.51	1883.21	1.00	1883.21
7_8ng_ml	7.8	300273.59	173138.90	0.36	-47.42	1.00	-47.42
Blank1		146826.77	0.00	-	-	1.00	-
BoulderSludge_1		625222.75	478395.98	0.98	18.33	2.00	36.65
BoulderSludge_2		492688.72	345861.95	0.61	-21.05	2.00	-42.11
Drake_RAS_1		350835.69	204008.92	0.48	-34.63	2.00	-69.27
Drake_RAS_2		342962.63	196135.86	0.48	-34.36	2.00	-68.72
Drake_WAS_1		311331.66	164504.89	0.41	-42.45	2.00	-84.90
Drake_WAS_2		341198.88	194372.11	0.45	-38.26	2.00	-76.52
Blank2		91223.88	0.00	-	-	1.00	-
8_27_12_1		390637.31	299413.44	0.61	-21.10	2.00	-42.20
8_27_12_2		397465.97	306242.09	0.61	-21.23	2.00	-42.46
8_24_12_1		262976.44	171752.56	0.32	-51.34	2.00	-102.68

8_24_12_2		216314.25	125090.38	0.27	-56.87	2.00	-113.75
8_22_12_1		286333.31	195109.44	0.42	-41.51	2.00	-83.03
8_22_12_2		262432.81	171208.94	0.36	-47.30	2.00	-94.59
Blank3		88927.47	0.00	-	-	1.00	-
8_20_12_1		175078.53	86151.06	0.18	-66.37	2.00	-132.74
8_20_12_2		152952.88	64025.41	0.14	-71.51	2.00	-143.02
8_17_12_1		279957.53	191030.06	0.40	-43.61	2.00	-87.22
8_17_12_2		235718.94	146791.47	0.28	-56.05	2.00	-112.09
8_15_12_1		414323.53	325396.06	0.58	-24.36	2.00	-48.71
8_15_12_2		424636.41	335708.94	0.52	-30.89	2.00	-61.77
Blank4		50112.76	0.00	-	-	1.00	-
8_13_12_1		267383.13	217270.36	0.42	-40.88	2.00	-81.76
8_13_12_2		223363.42	173250.66	0.34	-49.48	2.00	-98.96
8_10_12_1		286662.34	236549.58	0.43	-40.00	2.00	-80.00
8_10_12_2		292665.66	242552.89	0.42	-41.07	2.00	-82.13
8_8_12_1		296226.97	246114.21	0.44	-38.90	2.00	-77.80
8_8_12_2		286075.78	235963.02	0.47	-35.55	2.00	-71.11
Blank5		46286.30	0.00	-	-	1.00	-
8_3_12_1		364321.78	318035.48	0.59	-23.26	2.00	-46.51
8_3_12_2		431715.41	385429.11	0.63	-19.04	2.00	-38.08
8_1_12_1		321128.13	274841.82	0.41	-42.31	2.00	-84.62
8_1_12_2		357525.19	311238.89	0.42	-41.02	2.00	-82.05
7_23_12_1		401737.31	355451.01	0.68	-13.48	2.00	-26.95

7_23_12_2		395588.66	349302.36	0.67	-15.02	2.00	-30.03
Blank6		76042.15	0.00	-	-	1.00	-
7_20_12_1		532194.38	456152.23	0.77	-3.51	2.00	-7.02
7_20_12_2		491827.38	415785.23	0.72	-8.86	2.00	-17.73
7_18_12_1		494131.94	418089.79	0.80	-0.56	2.00	-1.11
7_18_12_2		457663.25	381621.10	0.70	-11.08	2.00	-22.16

Table D-8 Data for D5 Analysis on 9/3/2012

Name	Standard	RT	Area	Blank	New Area	Response	Conc	DF	Actual Conc
Blank		10.01	18413.45	18413.45	0.00	-	-	1.00	-
Blank_IS		10.01	32412.81	18413.45	13999.37	0.03	1.21	1.00	1.21
1000ng_ml	1000.00	10.01	2477987.00	18413.45	2459573.56	4.82	1015.54	1.00	1015.54
250ng_ml	250.00	10.01	447407.59	18413.45	428994.15	0.89	183.48	1.00	183.48
125ng_ml	125.00	10.01	282341.88	18413.45	263928.43	0.56	112.56	1.00	112.56
62_5_ng_ml	62.50	10.01	250266.44	18413.45	231852.99	0.50	100.10	1.00	100.10
15_625ng_ml	15.63	10.01	6043517.50	18413.45	6025104.06	12.86	2717.41	1.00	2717.41
7_8ng_ml	7.80	10.01	106870.02	18413.45	88456.58	0.18	33.49	1.00	33.49
Blank1		10.01	23472.88	23472.88	0.00	-	-	1.00	-
BoulderSludge_1		10.01	2257119.50	23472.88	2233646.62	4.57	963.10	2.00	1926.21
BoulderSludge_2		10.01	2296811.25	23472.88	2273338.37	4.01	842.74	2.00	1685.48
Drake_RAS_1		10.01	411074.44	23472.88	387601.56	0.92	188.22	2.00	376.43
Drake_RAS_2		10.01	398756.03	23472.88	375283.15	0.93	190.64	2.00	381.28
Drake_W		10.	980677.	23472.	957204.	2.38	497.4	2.0	994.

AS_1		01	56	88	68		8	0	97
Drake_WAS_2		10.01	1000029.94	23472.88	976557.06	2.25	470.69	2.00	941.38
Blank2		10.01	22842.62	22842.62	0.00	-	-	1.00	-
8_27_12_1		10.01	1171115.38	22842.62	1148272.76	2.34	488.99	2.00	977.98
8_27_12_2		10.01	1204580.25	22842.62	1181737.64	2.35	491.09	2.00	982.18
8_24_12_1		10.01	1269564.88	22842.62	1246722.26	2.36	493.56	2.00	987.13
8_24_12_2		10.01	1195512.00	22842.62	1172669.39	2.56	535.74	2.00	1071.47
8_22_12_1		10.01	1216171.63	22842.62	1193329.01	2.55	534.64	2.00	1069.28
8_22_12_2		10.01	1286860.63	22842.62	1264018.01	2.68	561.53	2.00	1123.06
Blank3		10.01	25491.92	25491.92	0.00	-	-	1.00	-
8_20_12_1		10.01	1226994.50	25491.92	1201502.58	2.56	536.00	2.00	1072.01
8_20_12_2		10.01	1180992.50	25491.92	1155500.58	2.44	510.63	2.00	1021.26
8_17_12_1		10.01	1761314.63	25491.92	1735822.70	3.61	759.09	2.00	1518.18
8_17_12_2		10.01	1632562.50	25491.92	1607070.58	3.07	644.66	2.00	1289.32
8_15_12_1		10.01	3268123.50	25491.92	3242631.58	5.76	1215.05	2.00	2430.10
8_15_12_2		10.01	3632865.75	25491.92	3607373.83	5.55	1170.94	2.00	2341.88
Blank4		10.01	28607.44	28607.44	0.00	-	-	1.00	-
8_13_12_1		10.01	2063053.75	28607.44	2034446.31	3.96	833.34	2.00	1666.67
8_13_12_2		10.01	2030914.25	28607.44	2002306.81	3.95	831.96	2.00	1663.91
8_10_12_1		10.01	2470500.50	28607.44	2441893.06	4.45	937.34	2.00	1874.69
8_10_12_2		10.01	2361989.50	28607.44	2333382.06	4.05	852.70	2.00	1705.41
8_8_12_1		10.01	2047512.13	28607.44	2018904.68	3.62	761.65	2.00	1523.30
8_8_12_2		10.01	1846013.13	28607.44	1817405.68	3.64	766.11	2.00	1532.22

Blank5		10.01	29433.22	29433.22	0.00	-	-	1.00	-
8_3_12_1		10.01	2589775.75	29433.22	2560342.54	4.74	998.15	2.00	1996.31
8_3_12_2		10.01	2570013.50	29433.22	2540580.29	4.14	871.57	2.00	1743.13
8_1_12_1		10.01	1463760.50	29433.22	1434327.29	2.14	447.07	2.00	894.14
8_1_12_2		10.01	1724464.63	29433.22	1695031.41	2.30	480.75	2.00	961.50
7_23_12_1		10.01	1467764.75	29433.22	1438331.54	2.75	577.71	2.00	1155.42
7_23_12_2		10.01	1432412.13	29433.22	1402978.91	2.68	561.07	2.00	1122.15
Blank6		10.01	29257.09	29257.09	0.00	-	-	1.00	-
7_20_12_1		10.01	2293436.00	29257.09	2264178.91	3.84	808.43	2.00	1616.87
7_20_12_2		10.01	2376658.25	29257.09	2347401.16	4.09	860.10	2.00	1720.20
7_18_12_1		10.01	2025853.38	29257.09	1996596.28	3.83	805.64	2.00	1611.29
7_18_12_2		10.01	2000201.50	29257.09	1970944.41	3.63	763.53	2.00	1527.06

Table D-9 Data for PCB30 Analysis on 9/3/2012

Name	Type	Std. Conc	RT	Area	Blank	New Area
Blank	Blank	1.00	15.52	109.36	109.36	0.00
Blank_IS	Analyte	1.00	15.49	433532.00	109.36	433422.65
1000ng_ml	Standard	1.00	15.49	510296.13	109.36	510186.77
250ng_ml	Standard	1.00	15.49	480610.19	109.36	480500.83
125ng_ml	Standard	1.00	15.49	473108.44	109.36	472999.08
62_5_ng_ml	Standard	1.00	15.49	464591.91	109.36	464482.55
15_625ng_ml	Standard	1.00	15.49	468788.72	109.36	468679.36
7_8ng_ml	Standard	1.00	15.49	479073.22	109.36	478963.86
Blank1	Analyte	1.00	15.52	266.89	266.89	0.00

BoulderSludge_1	Analyte	1.00	15.49	488666.47	266.89	488399.58
BoulderSludge_2	Analyte	1.00	15.49	567867.88	266.89	567600.98
Drake_RAS_1	Analyte	1.00	15.49	423802.63	266.89	423535.73
Drake_RAS_2	Analyte	1.00	15.49	405281.41	266.89	405014.51
Drake_WAS_1	Analyte	1.00	15.49	403265.09	266.89	402998.20
Drake_WAS_2	Analyte	1.00	15.49	434541.91	266.89	434275.01
Blank2	Analyte	1.00	15.49	786.39	786.39	0.00
8_27_12_1	Analyte	1.00	15.49	492526.97	786.39	491740.58
8_27_12_2	Analyte	1.00	15.49	504722.31	786.39	503935.92
8_24_12_1	Analyte	1.00	15.49	529796.88	786.39	529010.48
8_24_12_2	Analyte	1.00	15.49	459614.41	786.39	458828.01
8_22_12_1	Analyte	1.00	15.49	468645.56	786.39	467859.17
8_22_12_2	Analyte	1.00	15.49	472864.06	786.39	472077.67
Blank3	Analyte	1.00	15.52	569.03	569.03	0.00
8_20_12_1	Analyte	1.00	15.49	470446.19	569.03	469877.16
8_20_12_2	Analyte	1.00	15.49	474665.25	569.03	474096.22
8_17_12_1	Analyte	1.00	15.49	481374.16	569.03	480805.13
8_17_12_2	Analyte	1.00	15.49	524041.75	569.03	523472.72
8_15_12_1	Analyte	1.00	15.49	563247.88	569.03	562678.85
8_15_12_2	Analyte	1.00	15.49	650009.81	569.03	649440.78
Blank4	Analyte	1.00	15.52	508.88	508.88	0.00
8_13_12_1	Analyte	1.00	15.49	514158.06	508.88	513649.18
8_13_12_2	Analyte	1.00	15.49	506876.44	508.88	506367.56
8_10_12_1	Analyte	1.00	15.49	549028.31	508.88	548519.43

8_10_12_2	Analyte	1.00	15.49	576338.94	508.88	575830.06
8_8_12_1	Analyte	1.00	15.49	557856.19	508.88	557347.31
8_8_12_2	Analyte	1.00	15.49	499331.31	508.88	498822.43
Blank5	Analyte	1.00	15.49	627.14	627.14	0.00
8_3_12_1	Analyte	1.00	15.49	540912.94	627.14	540285.80
8_3_12_2	Analyte	1.00	15.49	614109.38	627.14	613482.24
8_1_12_1	Analyte	1.00	15.49	671753.19	627.14	671126.05
8_1_12_2	Analyte	1.00	15.49	738817.44	627.14	738190.30
7_23_12_1	Analyte	1.00	15.49	522904.66	627.14	522277.52
7_23_12_2	Analyte	1.00	15.49	525023.75	627.14	524396.61
Blank6	Analyte	1.00	15.49	1006.15	1006.15	0.00
7_20_12_1	Analyte	1.00	15.49	590144.63	1006.15	589138.47
7_20_12_2	Analyte	1.00	15.49	575346.13	1006.15	574339.97
7_18_12_1	Analyte	1.00	15.49	522306.81	1006.15	521300.66
7_18_12_2	Analyte	1.00	15.49	543786.31	1006.15	542780.16

Table D-10 Processed Data on 9/3/2012

Sample	% TS	D4 ng/ml	D5 ng/ml	D4 ug/g sludge	D5 ug/g sludge
BoulderSludge_1	4.84	-2.73	1805.85	-0.01	7.46
Drake_RAS_1	5.86	-68.99	378.86	-0.24	1.29
Drake_WAS_1	5.46	-80.71	968.17	-0.30	3.55
8_27_12_1	5.27	-42.33	980.08	-0.16	3.72
8_24_12_1	4.53	-108.21	1029.30	-0.48	4.54
8_22_12_1	5.22	-88.81	1096.17	-0.34	4.20
8_20_12_1	4.88	-137.88	1046.63	-0.57	4.29
8_17_12_1	4.93	-99.66	1403.75	-0.40	5.69
8_15_12_1	4.26	-55.24	2385.99	-0.26	11.20
8_13_12_1	5.04	-90.36	1665.29	-0.36	6.61
8_10_12_1	4.76	-81.07	1790.05	-0.34	7.52
8_8_12_1	2.76	-74.45	1527.76	-0.54	11.07
8_3_12_1	4.13	-42.30	1869.72	-0.20	9.05

8_1_12_1	4.48	-83.33	927.82	-0.37	4.14
7_23_12_1	4.30	-28.49	1138.78	-0.13	5.30
7_20_12_1	4.36	-12.37	1668.54	-0.06	7.65
7_18_12_1	4.15	-11.64	1569.17	-0.06	7.56

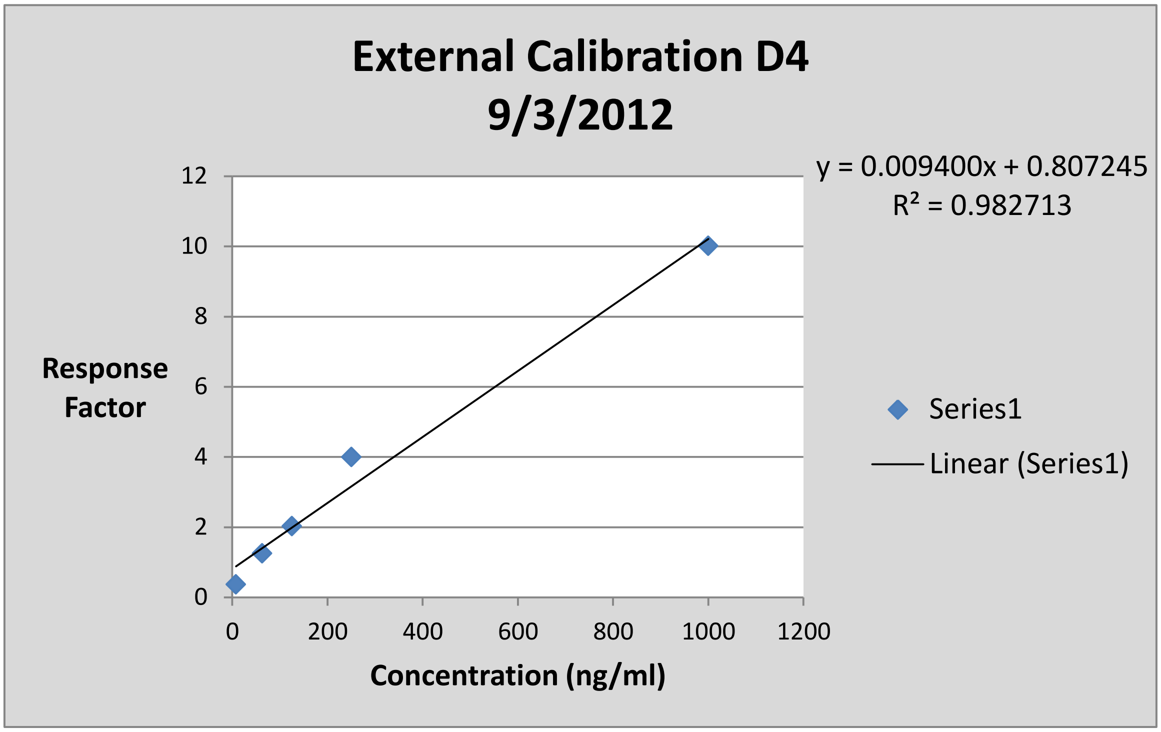

Figure D-4 Calibration Curve D4 on 9/3/2012

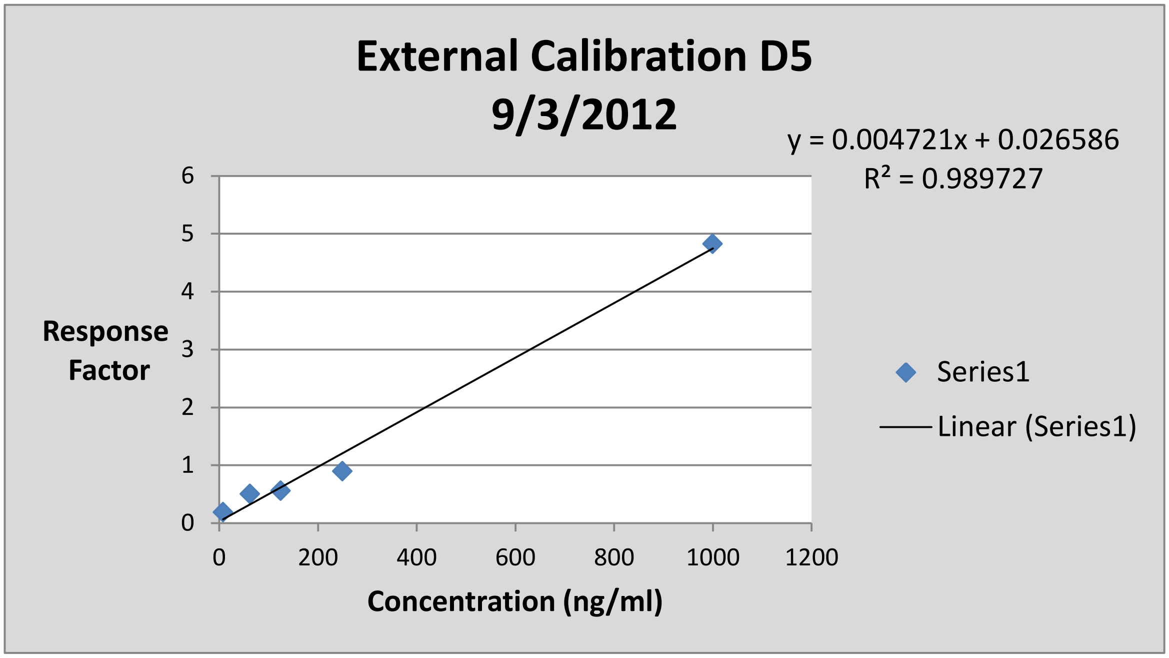

Figure D-5 Calibration Curve D5 9/3/2012

Table D-11 Data for D4 Analysis on 9/14/2012

Name	Standard	RT	Area	Response	ng/ml	DF	Actual Conc
Blank		8.52	90683.00	161.54	14120.25	1.00	14120.25
Blank_IS		8.48	1230666.25	3.40	278.70	1.00	278.70
1000ng_ml	1000.00	8.48	4994314.00	14.46	1246.39	1.00	1246.39
250ng_ml	250.00	8.48	1225159.38	3.59	294.83	1.00	294.83
125ng_ml	125.00	8.48	869820.50	2.52	201.28	1.00	201.28
62_5_ng_ml	62.50	8.48	326757.75	0.99	67.65	1.00	67.65
15_625ng_ml	15.63	8.48	116215.40	0.36	11.74	1.00	11.74
7_8ng_ml	7.80	8.48	72850.66	0.22	-0.12	1.00	-0.12
Blank1		8.52	37914.85	61.27	5343.91	1.00	5343.91
3_30_12_1		8.48	314869.31	0.34	10.72	2.00	21.43
3_30_12_2		8.44	179606.73	0.17	-4.08	2.00	-8.16
4_2_12_1		8.44	181276.50	0.36	11.89	2.00	23.78
4_2_12_2		8.44	215017.89	0.48	23.07	2.00	46.15
4_6_12_1		8.44	588436.94	1.16	82.58	2.00	165.16
4_6_12_2		8.44	417327.97	0.79	49.58	2.00	99.16
Blank2		8.44	65908.61	-	-	1.00	-

4_11_12_1		8.44	186244.61	0.40	15.93	2.00	31.86
4_11_12_2		8.44	190037.63	0.43	18.36	2.00	36.71
4_16_12_1		8.44	282643.41	0.63	35.59	2.00	71.19
4_16_12_2		8.44	255842.56	0.55	29.13	2.00	58.26
5_9_12_1		8.44	237445.39	0.53	26.63	2.00	53.27
5_9_12_2		8.44	320103.66	0.71	42.72	2.00	85.45
Blank3		8.48	56598.26	4.07	337.22	1.00	337.22
5_14_12_1		8.44	188468.48	0.46	20.53	2.00	41.06
5_14_12_2		8.44	164991.98	0.41	16.20	2.00	32.41
5_18_12_1		8.44	208743.05	0.58	31.87	2.00	63.73
5_18_12_2		8.44	170120.77	0.48	22.64	2.00	45.28
5_23_12_1		8.44	167312.94	0.50	24.83	2.00	49.67
5_23_12_2		8.44	158098.52	0.50	24.54	2.00	49.07
Blank4		8.48	62428.55	5.47	459.62	1.00	459.62
5_25_12_1		8.44	362650.66	0.95	64.03	2.00	128.05
5_25_12_2		8.44	282909.13	0.72	44.03	2.00	88.06
5_30_12_1		8.44	236558.20	0.64	36.30	2.00	72.59
5_30_12_2		8.44	263701.84	0.72	43.83	2.00	87.66
6_1_12_1		8.44	216196.45	0.66	38.24	2.00	76.48
6_1_12_2		8.44	233629.17	0.73	44.22	2.00	88.45
Blank5		8.44	62794.40	-	-	1.00	-
8_29_12_1		8.44	108207.54	0.38	14.22	2.00	28.44
8_29_12_2		8.44	85625.06	0.32	8.32	2.00	16.63
8_31_12_1		8.44	98270.25	0.37	13.09	2.00	26.18
8_31_12_2		8.44	97430.75	0.37	13.44	2.00	26.87
9_3_12_1		8.44	179739.86	0.66	38.30	2.00	76.60
9_3_12_2		8.44	189816.59	0.67	39.70	2.00	79.40
Blank6		8.44	62940.49	24.13	2092.42	1.00	2092.42
9_7_12_1		8.44	126652.06	0.49	23.16	2.00	46.33
9_7_12_2		8.44	116906.51	0.45	20.40	2.00	40.81
9_10_12_1		8.44	78808.98	0.33	9.41	2.00	18.82
9_10_12_2		8.44	83036.09	0.36	12.11	2.00	24.23
9_5_12_1		8.44	96224.38	0.39	14.66	2.00	29.31
9_5_12_2		8.44	102152.88	0.43	18.02	2.00	36.05
Blank7		8.44	55547.92	84.07	7338.94	1.00	7338.94
3_28_12_1		8.44	754220.69	1.92	148.36	2.00	296.73
3_28_12_2		8.44	753216.44	1.75	134.16	2.00	268.33
4_4_12_1		8.44	583463.00	1.96	152.61	2.00	305.22
4_4_12_2		8.44	535858.38	1.82	140.14	2.00	280.29
4_9_12_1		8.44	678620.31	1.96	151.85	2.00	303.70
4_9_12_2		8.44	710394.38	2.11	165.53	2.00	331.06

Blank8		8.44	46778.46	1.30	94.73	1.00	94.73
4_13_12_1		8.44	644973.00	2.10	164.88	2.00	329.75
4_13_12_2		8.44	687285.06	2.25	177.79	2.00	355.58
4_18_12_1		8.44	621416.50	1.71	130.08	2.00	260.16
4_18_12_2		8.44	505536.47	1.35	98.84	2.00	197.69
4_20_12_1		8.44	629309.38	1.72	131.33	2.00	262.65
4_20_12_2		8.44	641026.81	1.87	144.07	2.00	288.13
Blank9		8.44	37510.62	14.92	1286.96	1.00	1286.96
4_23_12_1		8.44	710259.56	2.55	204.22	2.00	408.43
4_23_12_2		8.44	466395.31	1.79	137.09	2.00	274.19
4_25_12_1		8.44	636505.81	1.64	123.82	2.00	247.65
4_25_12_2		8.44	568201.38	1.71	129.96	2.00	259.92
4_26_12_1		8.44	669603.94	2.50	199.43	2.00	398.86
4_26_12_2		8.44	524782.31	1.88	145.49	2.00	290.97
Blank10		8.44	35698.31	32.57	2831.15	1.00	2831.15
4_30_12_1		8.44	484511.13	1.52	113.74	2.00	227.48
4_30_12_2		8.44	677570.50	2.22	174.56	2.00	349.11
5_16_12_1		8.44	719659.81	2.08	163.15	2.00	326.30
5_16_12_2		8.44	754166.00	2.29	181.37	2.00	362.75
5_21_12_1		8.44	862862.69	2.06	161.01	2.00	322.02
5_21_12_2		8.44	807164.94	1.34	98.34	2.00	196.68
Blank11		8.44	73340.19	14.27	1229.99	1.00	1229.99
5_28_12_1		8.44	942658.31	1.61	121.80	2.00	243.59
5_28_12_2		8.44	1002424.44	1.55	116.77	2.00	233.54
7_25_12_1		8.44	702909.13	1.84	141.63	2.00	283.27
7_25_12_2		8.44	485733.09	1.41	103.66	2.00	207.33
7_27_12_1		8.44	614358.56	1.97	152.94	2.00	305.89
7_27_12_2		8.44	575839.50	1.91	147.54	2.00	295.07
Blank12		8.44	70385.13	14.85	1280.26	1.00	1280.26
7_30_12_1		8.44	570458.06	1.74	132.71	2.00	265.42
7_30_12_2		8.44	408427.19	1.31	95.12	2.00	190.25

Name	Standard	RT	Area	Response	ng/ml	DF	Actual Conc
Blank		9.98	460851.75	820.94	152677.70	1.00	152677.70
Blank_IS		9.98	1050792.25	2.91	541.68	1.00	541.68
1000ng_ml	1000.00	9.98	1854790.25	5.37	999.76	1.00	999.76
250ng_ml	250.00	9.98	384301.03	1.13	210.38	1.00	210.38
125ng_ml	125.00	9.98	203778.25	0.59	110.81	1.00	110.81
62_5_ng_ml	62.50	9.98	100915.48	0.31	58.08	1.00	58.08
15_625ng_ml	15.63	9.98	36876.50	0.11	21.95	1.00	21.95
7_8ng_ml	7.80	9.98	17051.01	0.05	10.55	1.00	10.55
Blank1		9.98	340010.75	549.48	102191.71	1.00	102191.71
3_30_12_1		9.98	2681252.25	2.92	544.66	2.00	1089.33
3_30_12_2		9.90	1586124.00	1.54	287.24	2.00	574.47
4_2_12_1		9.90	744071.38	1.46	273.29	2.00	546.58
4_2_12_2		9.90	817350.06	1.84	343.50	2.00	687.00
4_6_12_1		9.90	2603050.00	5.15	958.89	2.00	1917.79
4_6_12_2		9.90	2078450.38	3.92	730.24	2.00	1460.49
Blank2		9.90	267320.38	-	-	1.00	-
4_11_12_1		9.90	1109733.00	2.40	447.44	2.00	894.89
4_11_12_2		9.90	1151416.25	2.61	486.19	2.00	972.38
4_16_12_1		9.94	1269194.63	2.82	525.06	2.00	1050.12
4_16_12_2		9.90	1244791.38	2.69	501.98	2.00	1003.95
5_9_12_1		9.90	1302745.25	2.88	536.84	2.00	1073.68
5_9_12_2		9.94	1483333.63	3.29	611.99	2.00	1223.98
Blank3		9.94	271294.91	19.53	3632.35	1.00	3632.35
5_14_12_1		9.94	964402.94	2.33	434.42	2.00	868.83
5_14_12_2		9.90	872896.81	2.15	400.45	2.00	800.91
5_18_12_1		9.94	1051712.75	2.95	549.08	2.00	1098.16
5_18_12_2		9.90	1053555.00	2.97	553.32	2.00	1106.63
5_23_12_1		9.94	719434.06	2.17	404.52	2.00	809.03
5_23_12_2		9.90	696464.06	2.21	411.60	2.00	823.20
Blank4		9.94	264543.06	23.19	4313.27	1.00	4313.27
5_25_12_1		9.94	1270730.50	3.34	621.62	2.00	1243.24
5_25_12_2		9.90	1247506.75	3.19	594.64	2.00	1189.29
5_30_12_1		9.90	1231994.00	3.31	616.57	2.00	1233.13
5_30_12_2		9.90	1224292.25	3.35	624.05	2.00	1248.10
6_1_12_1		9.94	942253.75	2.87	534.12	2.00	1068.25
6_1_12_2		9.94	923006.94	2.87	534.50	2.00	1069.00
Blank5		9.94	303359.06	-	-	1.00	-
8_29_12_1		9.94	607024.88	2.15	400.95	2.00	801.91
8_29_12_2		9.94	569784.50	2.10	391.94	2.00	783.87

8_31_12_1		9.94	638918.50	2.41	448.86	2.00	897.72
8_31_12_2		9.94	692868.44	2.66	496.11	2.00	992.23
9_3_12_1		9.94	1275044.00	4.67	869.63	2.00	1739.26
9_3_12_2		9.90	1242702.88	4.42	822.18	2.00	1644.36
Blank6		9.90	257364.08	98.65	18347.85	1.00	18347.85
9_7_12_1		9.90	624034.94	2.39	445.90	2.00	891.80
9_7_12_2		9.94	659870.31	2.56	477.55	2.00	955.11
9_10_12_1		9.94	514938.94	2.15	400.02	2.00	800.05
9_10_12_2		9.90	451056.34	1.95	363.94	2.00	727.87
9_5_12_1		9.90	677232.81	2.73	509.29	2.00	1018.57
9_5_12_2		9.90	672528.00	2.81	523.56	2.00	1047.12
Blank7		9.94	271497.53	410.88	76415.34	1.00	76415.34
3_28_12_1		9.94	1853149.75	4.71	876.46	2.00	1752.92
3_28_12_2		9.94	1897935.13	4.42	822.79	2.00	1645.57
4_4_12_1		9.94	1030762.25	3.47	646.40	2.00	1292.81
4_4_12_2		9.94	930990.00	3.17	589.70	2.00	1179.39
4_9_12_1		9.90	1627477.63	4.69	873.27	2.00	1746.54
4_9_12_2		9.94	1603368.88	4.77	887.51	2.00	1775.03
Blank8		9.94	305116.47	8.50	1581.74	1.00	1581.74
4_13_12_1		9.90	1102214.25	3.60	669.86	2.00	1339.72
4_13_12_2		9.90	1030706.94	3.38	629.12	2.00	1258.24
4_18_12_1		9.90	1514302.38	4.16	774.60	2.00	1549.20
4_18_12_2		9.90	1440151.75	3.85	716.29	2.00	1432.59
4_20_12_1		9.90	1144740.75	3.13	583.29	2.00	1166.58
4_20_12_2		9.90	1190537.25	3.47	645.79	2.00	1291.58
Blank9		9.90	271560.78	108.04	20094.40	1.00	20094.40
4_23_12_1		9.90	1180895.38	4.25	790.71	2.00	1581.43
4_23_12_2		9.90	1007860.81	3.86	719.22	2.00	1438.44
4_25_12_1		9.90	1393378.38	3.58	666.86	2.00	1333.71
4_25_12_2		9.90	1194191.00	3.58	667.68	2.00	1335.35
4_26_12_1		9.90	897679.75	3.35	624.14	2.00	1248.27
4_26_12_2		9.90	864880.00	3.10	578.14	2.00	1156.29
Blank10		9.94	289172.25	263.80	49061.05	1.00	49061.05
4_30_12_1		9.94	897540.44	2.82	524.77	2.00	1049.53
4_30_12_2		9.94	965211.81	3.16	587.85	2.00	1175.69
5_16_12_1		9.94	1258193.25	3.64	678.86	2.00	1357.73
5_16_12_2		9.94	1172040.25	3.56	663.73	2.00	1327.46
5_21_12_1		9.94	1775153.38	4.24	789.31	2.00	1578.62
5_21_12_2		9.94	1590737.00	2.65	493.73	2.00	987.47
Blank11		9.94	461177.63	89.75	16692.70	1.00	16692.70
5_28_12_1		9.94	1873105.75	3.20	596.83	2.00	1193.66

5_28_12_2		9.94	1816075.38	2.82	524.91	2.00	1049.82
7_25_12_1		9.94	822948.06	2.15	401.41	2.00	802.82
7_25_12_2		9.90	676813.19	1.96	365.13	2.00	730.27
7_27_12_1		9.90	1008061.13	3.23	601.61	2.00	1203.21
7_27_12_2		9.90	837094.69	2.77	516.40	2.00	1032.81
Blank12		9.90	341482.91	72.03	13397.69	1.00	13397.69
7_30_12_1		9.90	983765.56	3.00	558.10	2.00	1116.19
7_30_12_2		9.90	882643.56	2.83	526.55	2.00	1053.10

Table D-12 Data for D5 Analysis on 9/14/2012

Name	Std. Conc	RT	Area
Blank	1.00	15.45	561.37
Blank_IS	1.00	15.41	361436.97
1000ng_ml	1.00	15.41	345378.22
250ng_ml	1.00	15.41	341352.91
125ng_ml	1.00	15.41	345113.94
62_5_ng_ml	1.00	15.41	328814.72
15_625ng_ml	1.00	15.41	327322.66
7_8ng_ml	1.00	15.41	331923.34
Blank1	1.00	15.45	618.79
3_30_12_1	1.00	15.45	917207.69
3_30_12_2	1.00	15.45	1030557.94
4_2_12_1	1.00	15.41	508207.41
4_2_12_2	1.00	15.41	443823.56
4_6_12_1	1.00	15.45	505387.94
4_6_12_2	1.00	15.45	530062.25
Blank2	1.00		
4_11_12_1	1.00	15.45	462287.53
4_11_12_2	1.00	15.45	441345.94
4_16_12_1	1.00	15.45	450409.41
4_16_12_2	1.00	15.45	462103.56
5_9_12_1	1.00	15.45	452151.09
5_9_12_2	1.00	15.45	451508.19
Blank3	1.00	15.60	13894.21
5_14_12_1	1.00	15.41	413820.84
5_14_12_2	1.00	15.41	406402.09
5_18_12_1	1.00	15.45	356871.88
5_18_12_2	1.00	15.45	354755.03
5_23_12_1	1.00	15.41	331582.09
5_23_12_2	1.00	15.41	315455.66
Blank4	1.00	15.45	11409.06

5_25_12_1	1.00	15.45	380792.97
5_25_12_2	1.00	15.45	390819.91
5_30_12_1	1.00	15.45	372215.41
5_30_12_2	1.00	15.45	365443.78
6_1_12_1	1.00	15.45	328700.47
6_1_12_2	1.00	15.45	321757.53
Blank5	1.00		
8_29_12_1	1.00	15.45	282264.59
8_29_12_2	1.00	15.45	271060.25
8_31_12_1	1.00	15.45	265315.53
8_31_12_2	1.00	15.45	260258.64
9_3_12_1	1.00	15.45	272992.88
9_3_12_2	1.00	15.45	281441.19
Blank6	1.00	15.41	2608.83
9_7_12_1	1.00	15.45	260860.28
9_7_12_2	1.00	15.45	257517.66
9_10_12_1	1.00	15.41	240002.53
9_10_12_2	1.00	15.41	231131.89
9_5_12_1	1.00	15.41	247792.94
9_5_12_2	1.00	15.41	239349.77
Blank7	1.00	15.45	660.77
3_28_12_1	1.00	15.45	393672.59
3_28_12_2	1.00	15.45	429519.16
4_4_12_1	1.00	15.45	297020.63
4_4_12_2	1.00	15.45	294112.69
4_9_12_1	1.00	15.45	346995.28
4_9_12_2	1.00	15.45	336362.66
Blank8	1.00	15.41	35897.57
4_13_12_1	1.00	15.45	306471.16
4_13_12_2	1.00	15.45	305178.66
4_18_12_1	1.00	15.45	364044.75
4_18_12_2	1.00	15.45	374441.47
4_20_12_1	1.00	15.45	365617.81
4_20_12_2	1.00	15.45	343387.59
Blank9	1.00	15.74	2513.47
4_23_12_1	1.00	15.45	278100.72
4_23_12_2	1.00	15.45	260977.61
4_25_12_1	1.00	15.45	389177.97
4_25_12_2	1.00	15.45	333133.59
4_26_12_1	1.00	15.45	267916.28
4_26_12_2	1.00	15.45	278697.28

Blank10	1.00	15.74	1096.20
4_30_12_1	1.00	15.45	318695.91
4_30_12_2	1.00	15.45	305885.34
5_16_12_1	1.00	15.45	345195.63
5_16_12_2	1.00	15.45	328900.91
5_21_12_1	1.00	15.45	418791.59
5_21_12_2	1.00	15.45	600407.13
Blank11	1.00	15.27	5138.40
5_28_12_1	1.00	15.45	584654.63
5_28_12_2	1.00	15.45	644668.44
7_25_12_1	1.00	15.45	382230.38
7_25_12_2	1.00	15.45	345674.56
7_27_12_1	1.00	15.45	312145.38
7_27_12_2	1.00	15.45	302055.88
Blank12	1.00	15.45	4740.58
7_30_12_1	1.00	15.45	328413.56
7_30_12_2	1.00	15.45	312342.75

Table D-13 Processed Results on 9/14/2012

Date	% TS	D4 ng/ml	D5 ng/ml	D4 ug/g sludge	D5 ug/g sludge
28-Mar	4.95	282.53	1699.24	1.14	6.87
30-Mar	4.87	6.64	831.90	0.03	3.42
2-Apr	4.22	34.96	616.79	0.17	2.92
4-Apr	4.83	292.75	1236.10	1.21	5.12
6-Apr	4.08	132.16	1689.14	0.65	8.28
9-Apr	4.71	317.38	1760.79	1.35	7.48
11-Apr	4.05	34.29	933.63	0.17	4.61
13-Apr	4.25	342.67	1298.98	1.61	6.11
16-Apr	5.83	64.72	1027.04	0.22	3.52
18-Apr	3.01	228.92	1490.90	1.52	9.91
20-Apr	4.44	275.39	1229.08	1.24	5.54
23-Apr	4.71	341.31	1509.93	1.45	6.41
25-Apr	1.56	253.79	1334.53	3.25	17.11
26-Apr	3.23	344.92	1202.28	2.14	7.44
30-Apr	4.07	288.30	1112.61	1.42	5.47
9-May	3.57	69.36	1148.83	0.39	6.44
14-May	3.83	36.73	834.87	0.19	4.36
16-May	3.75	344.52	1342.59	1.84	7.16

18-May	3.81	54.51	1102.40	0.29	5.79
21-May	4.20	259.35	1283.05	1.24	6.11
23-May	4.51	49.37	816.12	0.22	3.62
25-May	4.62	108.06	1216.26	0.47	5.27
28-May	4.45	238.57	1121.74	1.07	5.04
30-May	4.40	80.12	1240.62	0.36	5.64
1-Jun	4.75	82.46	1068.63	0.35	4.50
25-Jul	4.19	245.30	766.55	1.17	3.66
27-Jul	4.25	300.48	1118.01	1.41	5.26
30-Jul	4.21	227.83	1084.65	1.08	5.15
29-Aug	3.74	22.54	792.89	0.12	4.24
31-Aug	5.43	26.52	944.97	0.10	3.48
3-Sep	4.93	78.00	1691.81	0.32	6.86
5-Sep	5.05	32.68	1032.85	0.13	4.09
7-Sep	4.17	43.57	923.45	0.21	4.43
10-Sep	4.85	21.52	763.96	0.09	3.15

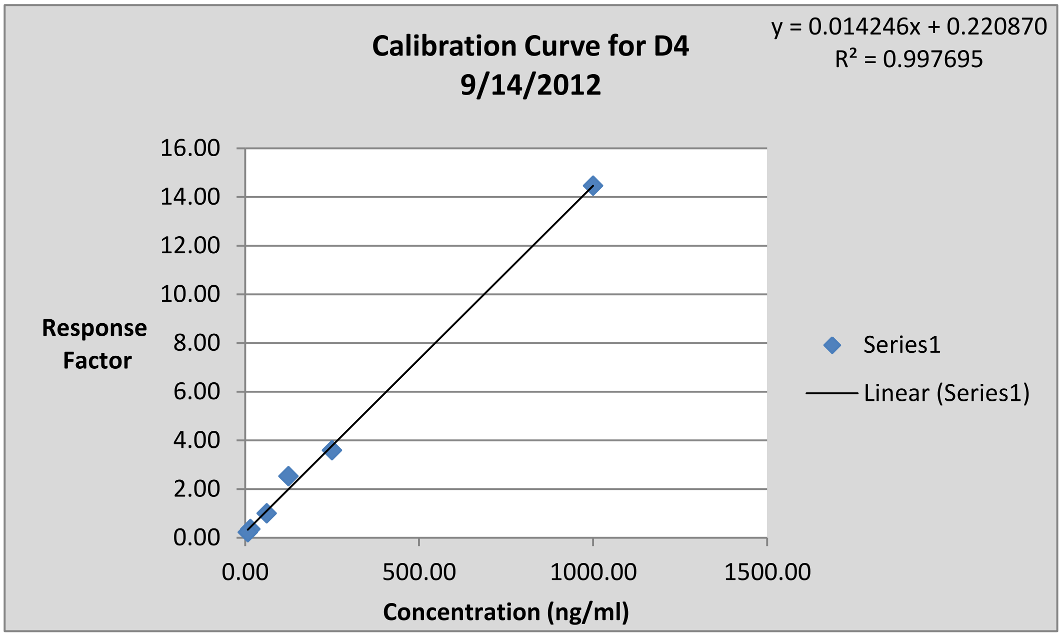

Figure D-6 Calibration Curve D4 9/14/2012

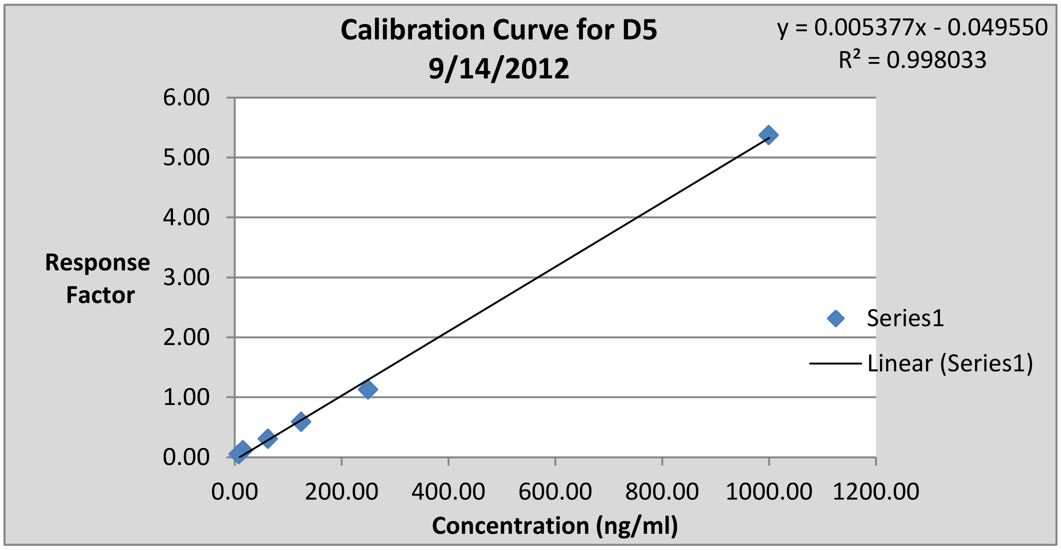

Figure D-7 Calibration Curve D5 9/14/2012

Table D-14 Data for D4 Analysis on 10/17/2012

Name	Standard	RT	Area	New Area	Response	Conc	DF	ng/ml
Blank1		8.37	154195.30	0.00	-	-	1.00	-
1000ng_ml	1000.00	8.41	7238489.30	7084294.00	13.60	994.99	1.00	994.99
250ng_ml	250.00	8.41	2358052.30	2203857.00	4.10	280.71	1.00	280.71
125ng_ml	125.00	8.34	1072698.50	918503.20	1.84	111.00	1.00	111.00
62_5_ng_ml	62.50	8.34	705099.60	550904.30	1.11	55.67	1.00	55.67
15_62ng_ml	15.63	8.34	550751.00	396555.70	0.79	32.05	1.00	32.05
7_8_ng_ml	7.80	8.34	242448.62	88253.32	0.20	-12.70	1.00	-12.70
Blank2		8.37	257733.08	0.00	-	-	1.00	-
2ndOctGreeleyWAS		8.34	687415.25	429682.17	0.49	9.46	2.00	18.92
2ndOctGreeleyWAS		8.34	587515.56	329782.49	0.39	1.96	2.00	3.93
5thOctGreeleyWAS		8.34	445735.56	188002.49	0.22	-10.87	2.00	-21.74
5thOctGreeleyWAS		8.34	470251.50	212518.42	0.25	-8.87	2.00	-17.74
8thOctGreeleyWAS		8.34	414757.72	157024.64	0.18	-13.84	2.00	-27.69
8thOctGreele		8.34	426276.2	168543.20	0.20	-	2.0	-

yWAS			8			12.58	0	25.16
Blank3		8.37	219056.00	0.00	-	-	1.00	-

Analyte		8.34	486114.69	0.32	-3.17	2.00	-6.35
Analyte		8.34	388329.78	0.22	-11.33	2.00	-22.67
Analyte		8.34	777063.63	0.68	23.91	2.00	47.82
Analyte		8.34	414481.91	0.24	-9.26	2.00	-18.52
Analyte		8.41	2654491.25	3.51	236.26	2.00	472.51
Analyte		8.34	6925573.00	7.72	552.98	2.00	1105.96
Analyte		8.37	228900.22	-	-	1.00	-
Analyte		8.34	6411240.50	6.32	447.80	2.00	895.60
Analyte		8.34	5473226.50	6.21	439.44	2.00	878.88
Analyte		8.34	3595855.50	3.87	263.70	2.00	527.39
Analyte		8.37	2937415.50	3.26	217.45	2.00	434.90

Table D-15 Data for D5 Analysis on 10/17/2012

Name	Standard	RT	Area	Blank	New Area	Response	Conc	DF	ng/ml
Blank1		9.87	5875.62	5875.62	0.00	-	-	1.00	-
1000ng_ml	1000.00	9.83	3284322.50	5875.62	3278446.88	6.29	1005.94	1.00	1005.94
250ng_ml	250.00	9.83	860005.50	5875.62	854129.88	1.59	221.82	1.00	221.82
125ng_ml	125.00	9.83	489298.34	5875.62	483422.72	0.97	118.64	1.00	118.64
62_5_ng_ml	62.50	9.83	311933.59	5875.62	306057.97	0.62	59.48	1.00	59.48
15_62ng_ml	15.63	9.83	233647.91	5875.62	227772.28	0.46	32.88	1.00	32.88
7_8_ng_ml	7.80	9.83	174235.38	5875.62	168359.75	0.38	19.83	1.00	19.83
Blank2		9.83	13312.17	13312.17	0.00	-	-	1.00	-
2ndOctGreeleyWAS		9.83	460530.53	13312.17	447218.36	0.51	42.40	2.00	84.79
2ndOctGreeleyWAS		9.83	497072.72	13312.17	483760.55	0.58	52.99	2.00	105.99
5thOctGreeleyWAS		9.83	266967.41	13312.17	253655.24	0.30	6.91	2.00	13.81
5thOctGreeleyWAS		9.83	267966.16	13312.17	254653.99	0.30	6.64	2.00	13.27
8thOctGreeleyWAS		9.83	272234.88	13312.17	258922.71	0.30	7.13	2.00	14.26
8thOctGreeleyWAS		9.83	278799.53	13312.17	265487.36	0.31	9.30	2.00	18.59
Blank3		9.83	18347.79	18347.79	0.00	-	-	1.00	-
3rdOctFoCoWAS		9.83	500355.03	18347.79	482007.24	0.59	54.56	2.00	109.12
3rdOctFoCoWAS		9.83	493984.34	18347.79	475636.56	0.61	58.08	2.00	116.15
5thOctFoCoWAS		9.83	443838.53	18347.79	425490.74	0.52	43.99	2.00	87.97

5thOctFoCoWAS		9.83	488810.97	18347.79	470463.18	0.59	54.65	2.00	109.30
5thOctGreeleyPrim		9.83	5325491.50	18347.79	5307143.71	7.65	1231.34	2.00	2462.68
5thOctGreeleyPrim		9.83	5347066.00	18347.79	5328718.21	6.13	979.48	2.00	1958.95
Blank4		9.83	27696.10	27696.10	0.00	-	-	1.00	-
8thOctGreeleyPrim		9.83	4913832.00	27696.10	4886135.90	5.00	789.78	2.00	1579.56
8thOctGreeleyPrim		9.83	5032451.50	27696.10	5004755.40	5.93	944.88	2.00	1889.77
8thOctFoCoPrim		9.83	5192312.00	27696.10	5164615.90	5.94	947.32	2.00	1894.63
8thOctFoCoPrim		9.83	5421685.00	27696.10	5393988.90	6.49	1038.60	2.00	2077.20

Table D-16 Data for PCB30 Analysis on 10/17/2012

Name	Standard	RT	Area	Blank	New Area	Response
Blank1	1.00			0.00	0.00	0.00
1000ng_ml	1.00	15.27	520903.97	0.00	520903.97	520903.97
250ng_ml	1.00	15.27	537526.06	0.00	537526.06	537526.06
125ng_ml	1.00	15.27	498402.53	0.00	498402.53	498402.53
62_5_ng_ml	1.00	15.27	497651.56	0.00	497651.56	497651.56
15_62ng_ml	1.00	15.27	500164.16	0.00	500164.16	500164.16
7_8_ng_ml	1.00	15.27	446513.34	0.00	446513.34	446513.34
Blank2	1.00	15.38	247.96	247.96	0.00	0.00
2ndOctGreeleyWAS	1.00	15.23	872895.31	247.96	872647.35	872647.35
2ndOctGreeleyWAS	1.00	15.23	840022.19	247.96	839774.23	839774.23
5thOctGreeleyWAS	1.00	15.23	847084.63	247.96	846836.67	846836.67
5thOctGreeleyWAS	1.00	15.23	855023.56	247.96	854775.60	854775.60
8thOctGreeleyWAS	1.00	15.23	860775.50	247.96	860527.54	860527.54
8thOctGreeleyWAS	1.00	15.23	846093.19	247.96	845845.23	845845.23
Blank3	1.00	15.38	454.11	454.11	0.00	0.00
3rdOctFoCoWAS	1.00	15.23	823755.19	454.11	823301.08	823301.08
3rdOctFoCoWAS	1.00	15.23	784606.75	454.11	784152.64	784152.64
5thOctFoCoWAS	1.00	15.23	815542.56	454.11	815088.45	815088.45
5thOctFoCoWAS	1.00	15.23	803286.56	454.11	802832.45	802832.45
5thOctGreeleyPrim	1.00	15.67	694548.13	454.11	694094.01	694094.01
5thOctGreeleyPrim	1.00	15.30	869037.38	454.11	868583.26	868583.26
Blank4	1.00			0.00	0.00	0.00
8thOctGreeleyPrim	1.00	15.27	977855.94	0.00	977855.94	977855.94
8thOctGreeleyPrim	1.00	15.27	844342.56	0.00	844342.56	844342.56
8thOctFoCoPrim	1.00	15.23	869171.81	0.00	869171.81	869171.81
8thOctFoCoPrim	1.00	15.23	831163.31	0.00	831163.31	831163.31

Table D-17 Processed Data on 10/17/2012

Date	%TS	D4 ng/ml	D5 ng/ml	D4 ug/g sludge	D5 ug/g sludge
2ndOctGreeleyWAS	2.00	11.42	95.39	0.11	0.95
5thOctGreeleyWAS	2.00	-19.74	13.54	-0.20	0.14
8thOctGreeleyWAS	2.00	-26.43	16.43	-0.26	0.16
3rdOctFoCoWAS	2.00	-14.51	112.64	-0.15	1.13
5thOctFoCoWAS	2.00	-18.52	98.64	-0.19	0.99
5thOctGreeleyPrim	5.00	789.23	2210.82	3.16	8.84
8thOctGreeleyPrim	5.00	887.24	1734.66	3.55	6.94
8thOctFoCoPrim	5.00	481.15	1985.91	1.92	7.94

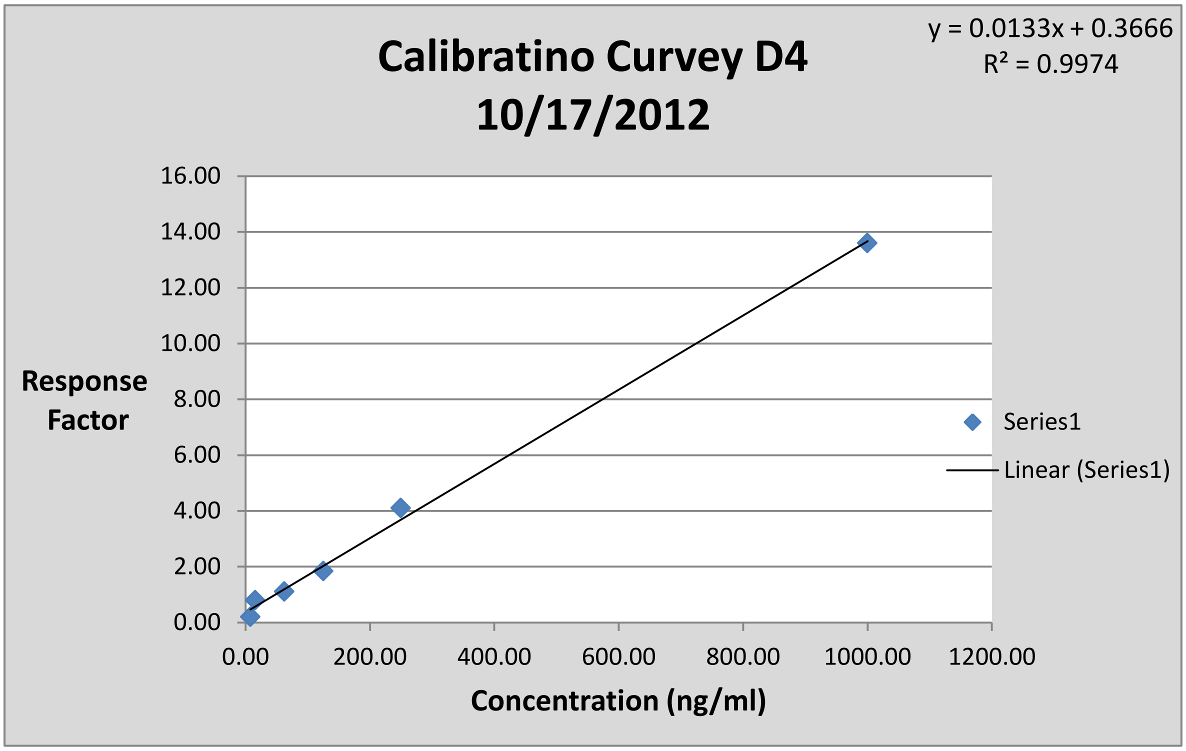

Figure D-8 Calibration Curve D4 10/17/2012

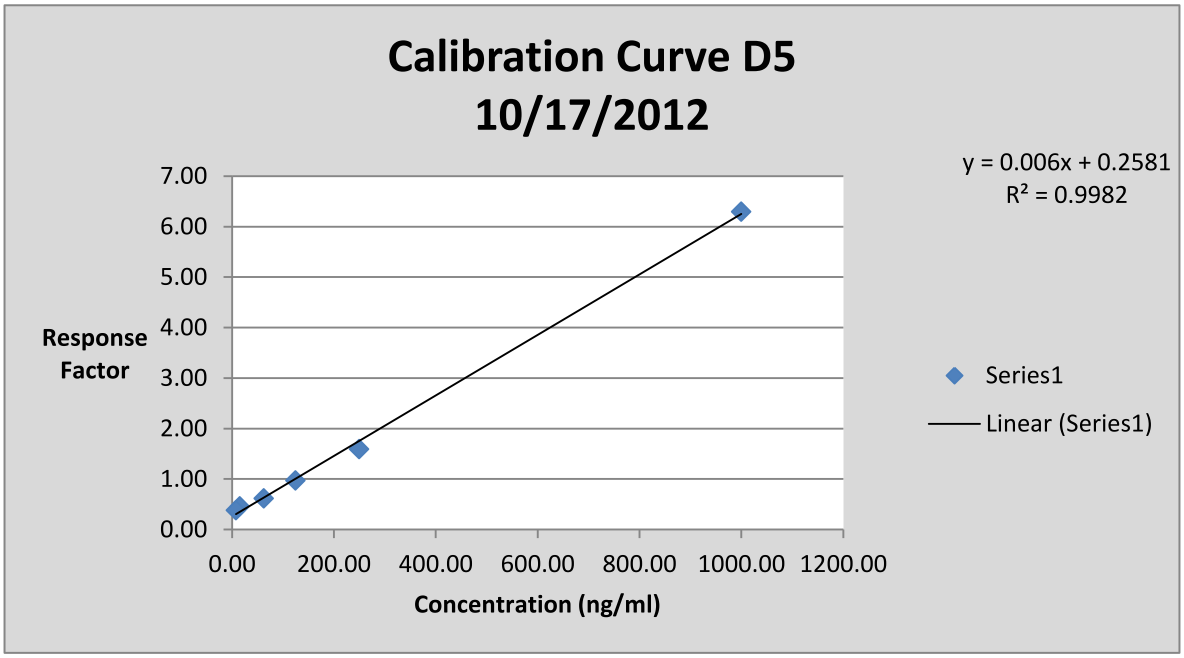

Figure D-9 Calibration Curve D5 10/17/2012

Table D-18 Recovery Study and Validation D4

Name	RT	Area	Blank	New Area	Response
7_10_12Blank1	8.59	106774.58	106774.58	0.00	-
7_10_12std1	8.59	5110739.00	106774.58	5003964.42	6.25
7_10_12std2	8.59	5195201.00	106774.58	5088426.42	6.15
7_10_12std3	8.59	5114658.50	106774.58	5007883.92	6.31
7_10_12std4	8.59	5119751.50	106774.58	5012976.92	6.17
7_10_12std5	8.59	5137598.00	106774.58	5030823.42	6.15
7_10_12checkblank1	8.59	114880.03	114880.03	0.00	-
7_10_12spikedsludge1	8.59	3491410.25	114880.03	3376530.22	6.33
7_10_12spikedsludge2	8.59	3231607.50	114880.03	3116727.47	5.94
7_10_12spikedsludge3	8.59	3577676.75	114880.03	3462796.72	6.40
7_10_12spikedsludge4	8.59	3471530.00	114880.03	3356649.97	6.44
7_10_12spikedsludge5	8.59	3869887.50	114880.03	3755007.47	7.13
7_10_12checkblank3	8.59	77590.79	77590.79	0.00	-
7_10_12unspikedsludge1	8.59	753619.56	77590.79	676028.77	0.95
7_10_12unspikedsludge2	8.59	741045.44	77590.79	663454.65	0.99
7_10_12unspikedsludge3	8.59	757872.31	77590.79	680281.52	0.97
7_10_12unspikedsludge4	8.59	771047.94	77590.79	693457.15	0.90
7_10_12unspikedsludge5	8.59	816878.06	77590.79	739287.27	0.96

Table D-19 Recovery Study and Validation D5

Name	RT	Area	Blank	New Area	Response
7_10_12Blank1	10.09	44001.71	44001.71	0.00	-
7_10_12std1	10.09	1751238.50	44001.71	1707236.79	2.13
7_10_12std2	10.09	1836783.25	44001.71	1792781.54	2.17
7_10_12std3	10.09	1681898.25	44001.71	1637896.54	2.06
7_10_12std4	10.09	1747580.25	44001.71	1703578.54	2.10
7_10_12std5	10.09	1723869.75	44001.71	1679868.04	2.05
7_10_12checkblank1	10.09	43901.74	43901.74	0.00	-
7_10_12spikedsludge1	10.09	2446494.75	43901.74	2402593.01	4.50
7_10_12spikedsludge2	10.09	2390058.25	43901.74	2346156.51	4.47
7_10_12spikedsludge3	10.09	2473342.25	43901.74	2429440.51	4.49
7_10_12spikedsludge4	10.09	2379280.00	43901.74	2335378.26	4.48
7_10_12spikedsludge5	10.09	2447976.50	43901.74	2404074.76	4.56
7_10_12checkblank3	10.09	42418.47	42418.47	0.00	-
7_10_12unspikedsludge1	10.09	1214169.75	42418.47	1171751.28	1.64
7_10_12unspikedsludge2	10.09	1171310.75	42418.47	1128892.28	1.69
7_10_12unspikedsludge3	10.09	1183164.00	42418.47	1140745.53	1.62
7_10_12unspikedsludge4	10.09	1139071.00	42418.47	1096652.53	1.43
7_10_12unspikedsludge5	10.09	1158393.88	42418.47	1115975.40	1.45

Table D-20 Recovery Study and Validation PCB30

Name	RT	Area	Blank	New Area	Response
7_10_12Blank1	15.05	1861.52	1861.52	0.00	0.00
7_10_12std1	14.98	802912.13	1861.52	801050.61	801050.61
7_10_12std2	14.98	828644.06	1861.52	826782.54	826782.54
7_10_12std3	14.98	795638.69	1861.52	793777.17	793777.17
7_10_12std4	14.98	814809.56	1861.52	812948.04	812948.04
7_10_12std5	14.98	820224.50	1861.52	818362.98	818362.98
7_10_12checkblank1	15.09	1858.32	1858.32	0.00	0.00
7_10_12spikedsludge1	14.98	535608.25	1858.32	533749.93	533749.93
7_10_12spikedsludge2	14.98	526872.31	1858.32	525013.99	525013.99
7_10_12spikedsludge3	14.98	543318.31	1858.32	541459.99	541459.99
7_10_12spikedsludge4	14.98	523260.16	1858.32	521401.83	521401.83
7_10_12spikedsludge5	14.98	528539.75	1858.32	526681.43	526681.43
7_10_12checkblank3	14.98	1470.54	1470.54	0.00	0.00
7_10_12unspikedsludge1	14.98	716645.38	1470.54	715174.84	715174.84
7_10_12unspikedsludge2	14.98	670769.81	1470.54	669299.28	669299.28
7_10_12unspikedsludge3	14.98	705363.25	1470.54	703892.71	703892.71
7_10_12unspikedsludge4	14.98	769175.63	1470.54	767705.09	767705.09
7_10_12unspikedsludge5	14.98	768722.94	1470.54	767252.40	767252.40

Table D-21 Percent Deviation and Recovery

Sample Type	D4	D5	PCB-30
Standard	1.14	2.28	1.63
Spiked Samples	6.69	0.84	1.51
Unspiked Samples	3.43	7.43	5.88

Table D-22 Recovery Study

Replicates	Internal Standard Peak Areas in Blanks	Internal Standard Peak Areas in Sludge Sample	Recovery %
1	801050.6	715174.837	89.28
2	826782.5	669299.275	80.95
3	793777.2	703892.712	88.68
4	812948	767705.087	94.43
5	818363	767252.4	93.75

Table D-23 Processed Validation Data

D4	1	2	3	4	5	Average	Stdev	% Dev
Standards	6.25	6.15	6.31	6.17	6.15	6.20	0.07	1.14
Spiked Sludge Samples	6.33	5.94	6.40	6.44	7.13	6.45	0.43	6.69
Unspiked Sludge Samples	0.95	0.99	0.97	0.90	0.96	0.95	0.03	3.43

D5	1	2	3	4	5	Average	Stdev	% Dev
Standards	2.13	2.17	2.06	2.10	2.05	2.10	0.05	2.28
Spiked Sludge Samples	4.50	4.47	4.49	4.48	4.56	4.50	0.04	0.84
Unspiked Sludge Samples	1.64	1.69	1.62	1.43	1.45	1.57	0.12	7.43

PCB-30	1	2	3	4	5	Average	Stdev	% Dev
Standards	801051	826783	793777	812948	818363	810584	13246	1.63
SS Samples	533750	525014	541460	521402	526681	529661	7978	1.51
US Samples	715175	669299	703893	767705	767252	724665	42582	5.88

Table D-24 Processed Recovery Study Data

Replicates	Standard	Sludge Sample	Recovery %
1	801050.605	715174.837	89.27
2	826782.543	669299.275	80.95
3	793777.168	703892.712	88.67
4	812948.043	767705.087	94.43
5	818362.98	767252.4	93.75

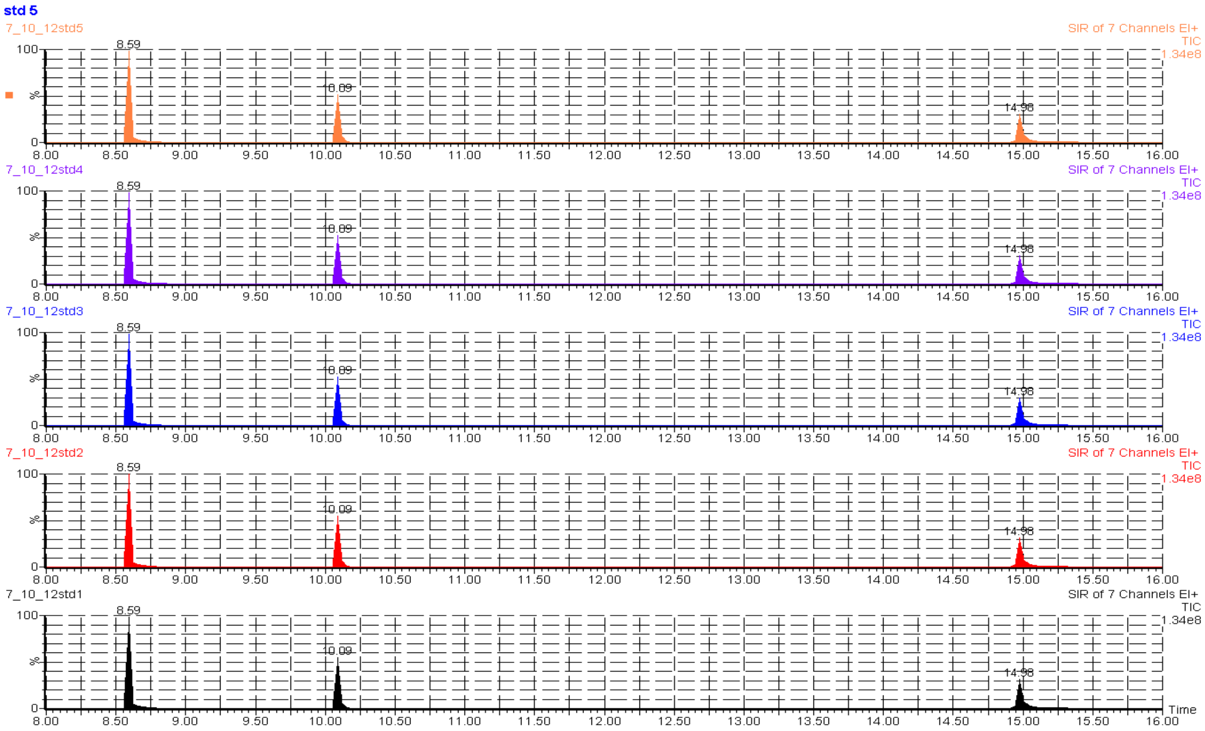

Figure D-10 Recovery Study Chromatogram - Standards

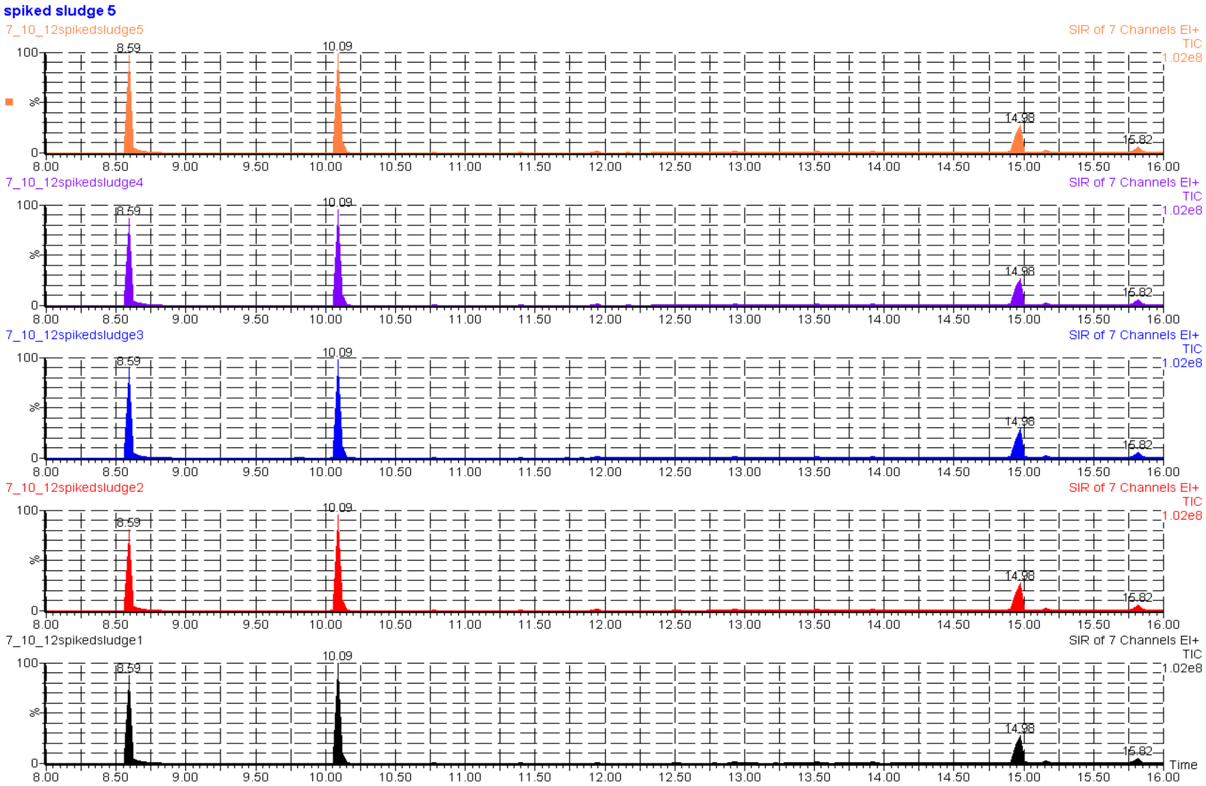

Figure D-11 Recovery Study Chromatograms - Spiked Sludge

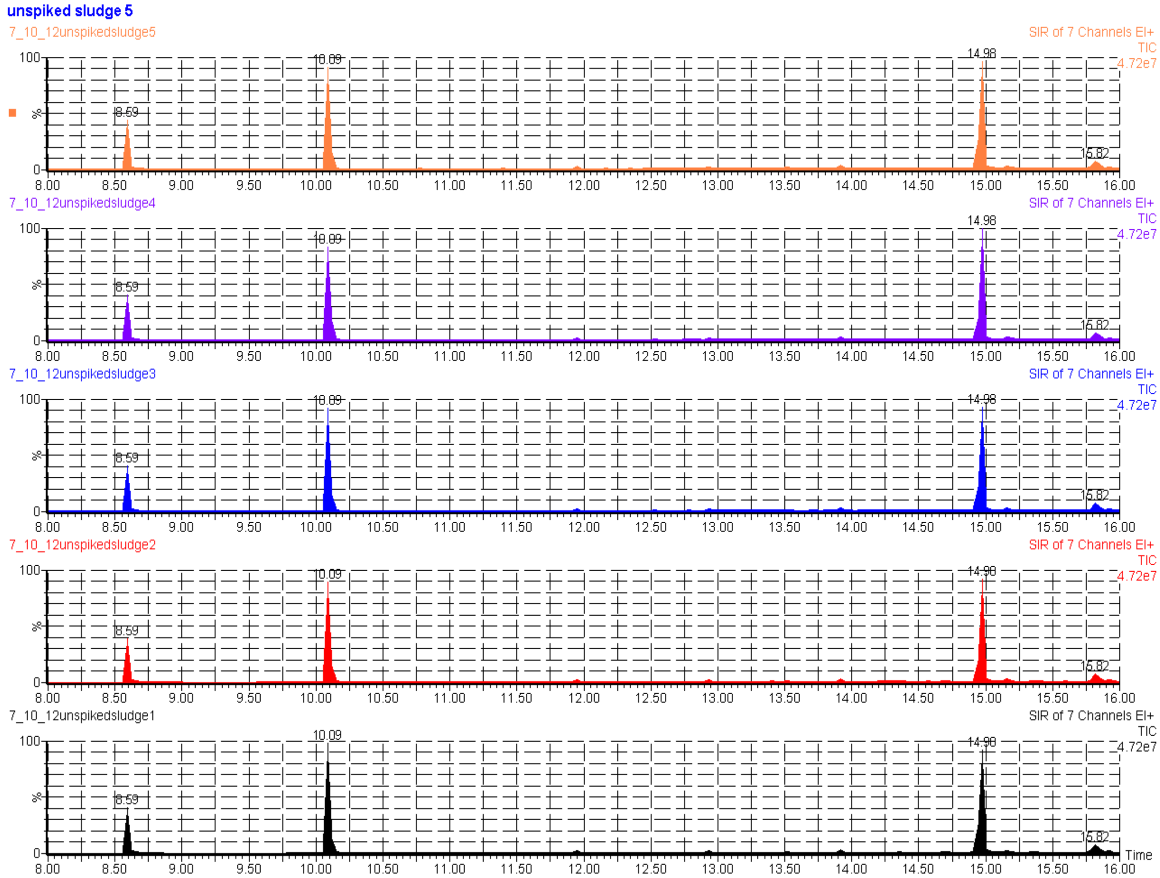

Figure D-12 Recovery Study Chromatograms - Unspiked Samples

Removal Study

Results obtained from the removal study using 30% Hydrogen Peroxide were comparable with previous study done by Appels et al., (2008). Up to 90% removal of D4 and up to 85% removal of D5 with 16.67% dose of hydrogen peroxide was obtained. Figures below show the results obtained in this test. A removal study done by Appels et al., 2008 using hydrogen peroxide showed the removal up to 42% for D5 with 2ml of Hydrogen Peroxide. In this study, experiments were set up to study effect of dosage and reaction time as well for hydrogen peroxide. Removal up to 76% for D5 was obtained using maximum 5m l of hydrogen peroxide reacted for 3 hours. However, not much effect of reaction time was observed.

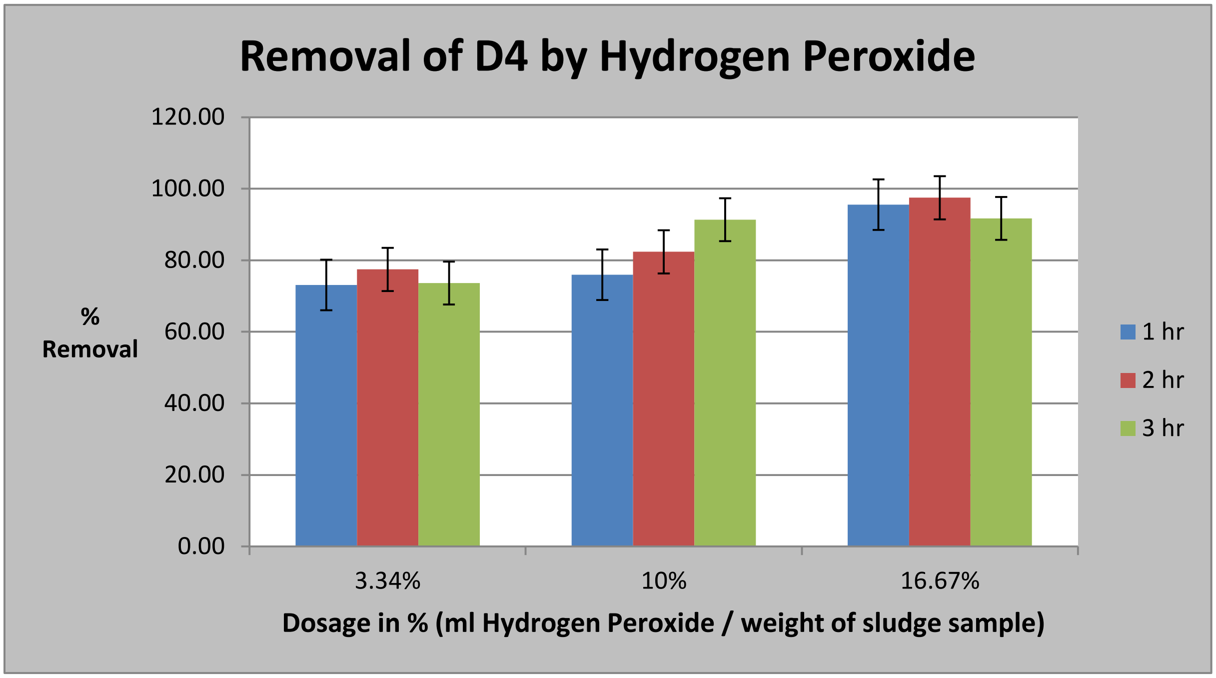

Figure D-13 Removal of D4

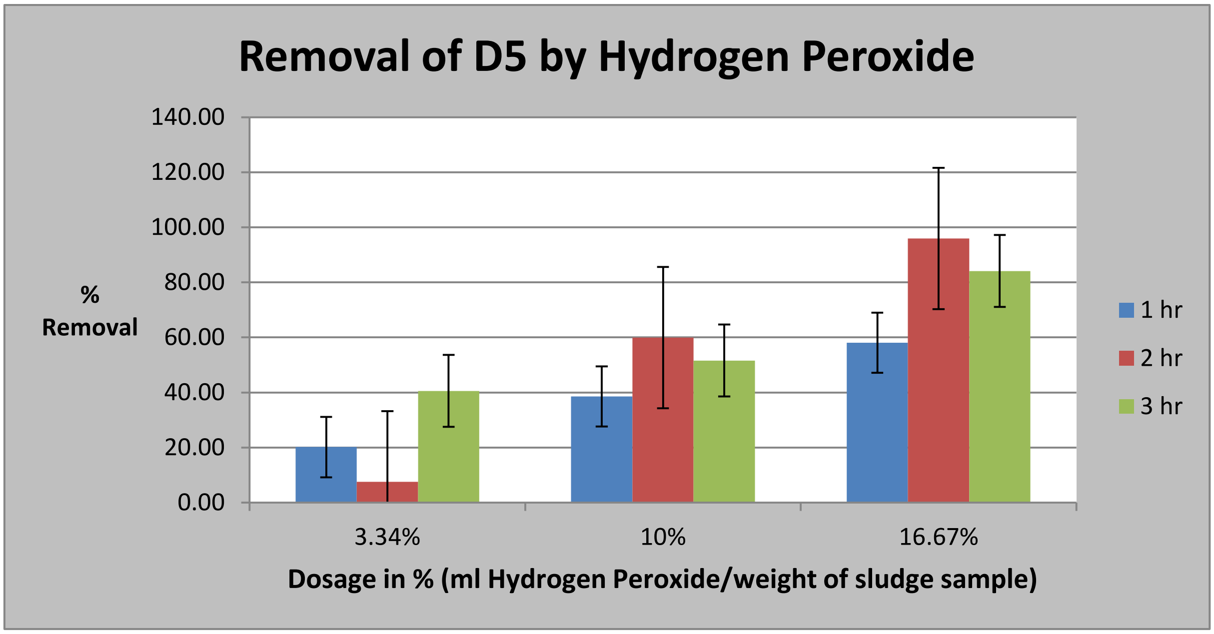

Figure D-14 Removal of D5

Table D-25 Removal Study Data D4

Name	Standard	RT	New Area	Response	ng/ml	DF	new ng/ml
Blank		8.41	0.00	-	-	1.00	-
Blank_IS		8.41	-376.43	0.00	-44.52	1.00	-44.52
1000ng_ml	1000.00	8.41	2197891.91	14.37	989.45	1.00	989.45
250ng_ml	250.00	8.41	422207.07	4.70	293.65	1.00	293.65
125ng_ml	125.00	8.41	189395.36	2.02	100.73	1.00	100.73
62_5ng_ml	62.50	8.41	200015.85	2.22	115.28	1.00	115.28
15_625ng_ml	15.63	8.41	15334.50	0.17	-31.83	1.00	-31.83
7_8ng_ml	7.80	8.41	46927.25	0.52	-6.65	1.00	-6.65
Blank2		8.44	-19491.95	-2.85	-249.27	1.00	-249.27
Control_1		8.41	575034.66	3.49	206.68	2.00	413.36
1ml_1hr		8.41	161608.47	0.94	23.18	2.00	46.36
3ml_1hr		8.41	158932.60	0.84	16.08	2.00	32.17
5ml_1hr		8.41	35383.08	0.16	-33.21	2.00	-66.41
Blank3		8.44	-5357.90	-0.11	-52.23	1.00	-52.23
Control_2		8.41	1009180.79	4.76	298.33	2.00	596.65
1ml_2hr		8.41	262144.50	1.07	32.93	2.00	65.86
3ml_2hr		8.41	213407.88	0.84	16.10	2.00	32.19
5ml_2hr		8.41	37908.28	0.12	-35.71	2.00	-71.42
Blank4		8.41	12892.89	0.13	-35.22	1.00	-35.22
Control_3		8.41	1606651.29	5.66	362.86	2.00	725.73
1ml_3hr		8.41	406942.13	1.49	62.97	2.00	125.94
3ml_3hr		8.41	152118.97	0.49	-9.09	2.00	-18.17
5ml_3hr		8.41	154219.85	0.47	-10.63	2.00	-21.26
Blank5		8.41	6335.85	0.06	-40.07	1.00	-40.07
9_12_12_1		8.41	90213.35	0.30	-22.65	2.00	-45.29
9_12_12_2		8.44	-6193.13	-0.02	-46.03	2.00	-92.07
9_14_12_1		8.41	53549.39	0.21	-29.21	2.00	-58.41
9_14_12_2		8.41	31722.39	0.12	-35.79	2.00	-71.57
Blank6		8.44	-13259.67	-0.14	-54.19	1.00	-54.19
9_17_12_1		8.41	38449.50	0.12	-35.67	2.00	-71.33
9_17_12_2		8.41	76702.50	0.21	-29.28	2.00	-58.57
9_19_12_1		8.41	10005.50	0.03	-42.09	2.00	-84.17
9_19_12_2		8.41	4882.57	0.02	-43.25	2.00	-86.49
9_21_12_1		8.41	58592.25	0.20	-29.71	2.00	-59.42
9_21_12_2		8.41	61322.90	0.20	-29.78	2.00	-59.56
Boulder_Primary_1		8.41	2407606.41	2.04	102.47	2.00	204.94
Boulder_Primary_2		8.44	2807710.16	2.49	134.68	2.00	269.36
Boulder_WAS_1		8.41	958713.29	3.07	176.59	2.00	353.19
Boulder_WAS_2		8.41	896733.66	3.13	181.09	2.00	362.17

Table D-26 Removal Study Data D5

Name	Standard	RT	New Area	Response	ng/ml	DF	new ng/ml
Blank		9.90	0.00	-	-	1.00	-
Blank_IS		9.90	2350.18	0.01	-49.06	1.00	-49.06
1000ng_ml	1000.00	9.90	771966.72	5.05	999.62	1.00	999.62
250ng_ml	250.00	9.90	152882.34	1.70	302.55	1.00	302.55
125ng_ml	125.00	9.90	50057.76	0.53	59.17	1.00	59.17
62_5ng_ml	62.50	9.90	73788.51	0.82	118.67	1.00	118.67
15_625ng_ml	15.63	9.90	30923.80	0.35	21.27	1.00	21.27
7_8ng_ml	7.80	9.90	9491.44	0.11	-29.79	1.00	-29.79
Blank2		9.90	1219.19	0.18	-14.76	1.00	-14.76
Control_1		9.90	418261.62	2.54	476.89	2.00	953.79
1ml_1hr		9.90	357440.56	2.08	380.71	2.00	761.42
3ml_1hr		9.90	313219.40	1.66	293.08	2.00	586.16
5ml_1hr		9.90	275934.31	1.21	200.03	2.00	400.06
Blank3		9.90	8729.68	0.18	-14.74	1.00	-14.74
Control_2		9.90	512162.06	2.42	451.75	2.00	903.50
1ml_2hr		9.90	550190.84	2.25	417.87	2.00	835.74
3ml_2hr		9.90	283712.22	1.12	180.87	2.00	361.74
5ml_2hr		9.90	106320.34	0.34	18.37	2.00	36.74
Blank4		9.90	16447.05	0.16	-18.12	1.00	-18.12
Control_3		9.90	681429.03	2.40	448.28	2.00	896.56
1ml_3hr		9.90	416825.62	1.53	266.49	2.00	532.98
3ml_3hr		9.90	400396.22	1.29	216.99	2.00	433.98
5ml_3hr		9.90	194227.65	0.59	71.14	2.00	142.28
Blank5		9.90	18066.93	0.17	-16.48	1.00	-16.48
9_12_12_1		9.90	526626.03	1.76	315.17	2.00	630.34
9_12_12_2		9.90	525552.09	1.97	359.51	2.00	719.03
9_14_12_1		9.90	223148.67	0.88	131.00	2.00	261.99
9_14_12_2		9.90	219625.79	0.83	120.03	2.00	240.06
Blank6		9.90	23187.04	0.24	-2.09	1.00	-2.09
9_17_12_1		9.90	764691.34	2.40	448.75	2.00	897.49
9_17_12_2		9.90	842691.22	2.30	427.80	2.00	855.59
9_19_12_1		9.90	558238.84	1.76	315.46	2.00	630.91
9_19_12_2		9.90	554939.78	1.76	314.32	2.00	628.64
9_21_12_1		9.90	246868.86	0.86	126.87	2.00	253.74
9_21_12_2		9.90	241999.34	0.80	114.74	2.00	229.47
Blank7		9.90	22918.98	0.21	-8.00	1.00	-8.00

Boulder_Primary_1		9.90	1532900.09	1.30	218.85	2.00	437.69
Boulder_Primary_2		9.90	1678457.09	1.49	258.06	2.00	516.13
Boulder_WAS_1		9.90	1323236.84	4.24	831.26	2.00	1662.51
Boulder_WAS_2		9.90	1377822.59	4.81	951.23	2.00	1902.46

Table D-27 Removal Study Data PCB30

Name	Standard	RT	Area	Blank	New Area
Blank	1.00	15.30	100563.14	100563.14	0.00
Blank_IS	1.00	15.30	274252.63	100563.14	173689.48
1000ng_ml	1.00	15.30	253513.52	100563.14	152950.38
250ng_ml	1.00	15.30	190427.16	100563.14	89864.02
125ng_ml	1.00	15.30	194477.61	100563.14	93914.47
62_5ng_ml	1.00	15.30	190699.67	100563.14	90136.53
15_625ng_ml	1.00	15.30	188640.61	100563.14	88077.47
7_8ng_ml	1.00	15.30	190085.67	100563.14	89522.53
Blank2	1.00	15.30	107406.63	100563.14	6843.49
Control_1	1.00	15.30	265356.72	100563.14	164793.58
1ml_1hr	1.00	15.30	272706.97	100563.14	172143.83
3ml_1hr	1.00	15.30	289730.81	100563.14	189167.67
5ml_1hr	1.00	15.30	328767.34	100563.14	228204.20
Blank3	1.00	15.30	149540.22	100563.14	48977.08
Control_2	1.00	15.30	312428.03	100563.14	211864.89
1ml_2hr	1.00	15.30	344574.50	100563.14	244011.36
3ml_2hr	1.00	15.30	354518.38	100563.14	253955.23
5ml_2hr	1.00	15.30	415889.75	100563.14	315326.61
Blank4	1.00	15.30	202082.05	100563.14	101518.91
Control_3	1.00	15.30	384403.97	100563.14	283840.83
1ml_3hr	1.00	15.30	373329.50	100563.14	272766.36
3ml_3hr	1.00	15.30	410812.47	100563.14	310249.33
5ml_3hr	1.00	15.30	429496.06	100563.14	328932.92
Blank5	1.00	15.30	206902.27	100563.14	106339.13
9_12_12_1	1.00	15.30	399473.34	100563.14	298910.20
9_12_12_2	1.00	15.30	366710.25	100563.14	266147.11
9_14_12_1	1.00	15.30	354781.38	100563.14	254218.23
9_14_12_2	1.00	15.30	366727.22	100563.14	266164.08
Blank6	1.00	15.30	197583.72	100563.14	97020.58
9_17_12_1	1.00	15.30	418788.75	100563.14	318225.61
9_17_12_2	1.00	15.30	466565.59	100563.14	366002.45
9_19_12_1	1.00	15.30	417170.38	100563.14	316607.23
9_19_12_2	1.00	15.30	416276.13	100563.14	315712.98
9_21_12_1	1.00	15.30	388298.69	100563.14	287735.55

9_21_12_2	1.00	15.30	403162.94	100563.14	302599.80
Blank7	1.00	15.30	209400.25	100563.14	108837.11
Boulder_Primary_1	1.00	15.30	1280206.00	100563.14	1179642.86
Boulder_Primary_2	1.00	15.34	1228779.13	100563.14	1128215.98
Boulder_WAS_1	1.00	15.34	412718.88	100563.14	312155.73
Boulder_WAS_2	1.00	15.34	386721.25	100563.14	286158.11

Table D-28 Sample Analysis

Date	%TS	D4 ng/ml	D5 ng/ml	D4 ug/g sludge	D5 ug/g sludge
12-Sep	4.95	-45.29	674.68	-0.28	3.05
14-Sep	4.87	-64.99	251.03	-0.41	1.15
17-Sep	4.22	-64.95	876.54	-0.47	4.65
19-Sep	4.83	-85.33	629.78	-0.54	2.92
21-Sep	4.08	-59.49	241.61	-0.45	1.32
Boulder Primary	4.08	237.15	476.91	1.78	2.61
Boulder WAS	4.08	357.68	1782.48	2.68	9.77

Table D-29 Removal Study D4 (ng/ml)

Reaction Time (Hr)	% Dosage of Hydrogen Peroxide (ml / g of sludge)			Control
	3.34%	10%	16.67%	
1 hr	195.60	175.05	32.31	727.03
2 hr	223.84	175.09	25.05	992.45
3 hr	310.84	102.16	97.69	1179.36

Table D-30 Removal Study D5 (ng/ml)

Reaction Time (Hr)	% Dosage of Hydrogen Peroxide (ml/g of sludge)			Control (ng/ml)
	3.34%	10%	16.67%	
1 hr	761.42	586.16	400.06	953.79
2 hr	835.74	361.74	36.74	903.50
3 hr	532.98	433.98	142.28	896.56

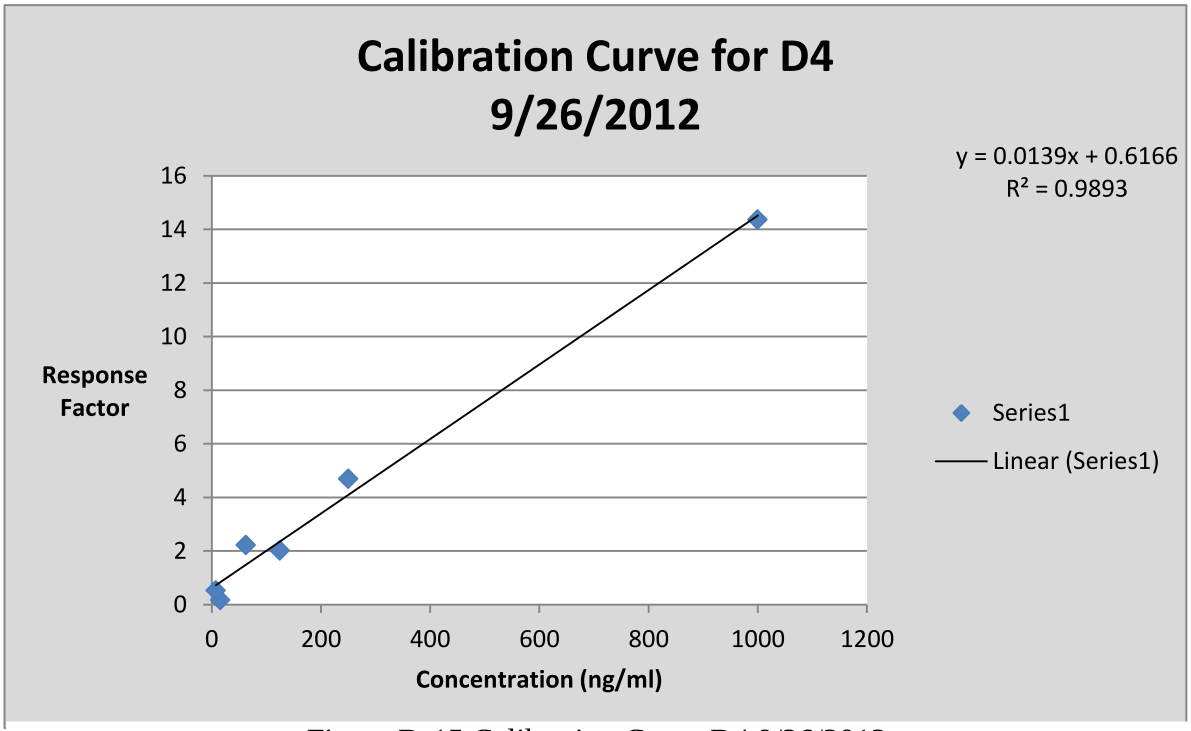

Figure D-15 Calibration Curve D4 9/26/2012

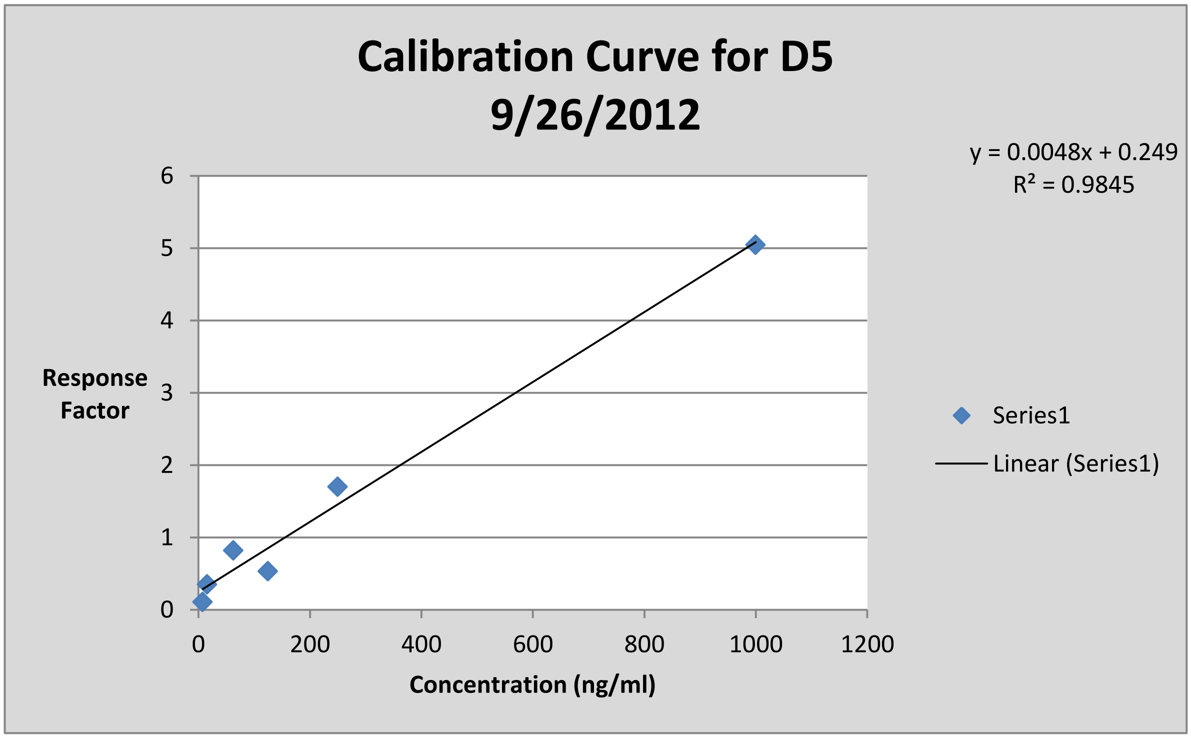

Figure D-16 Calibration Curve D5 9/26/2012

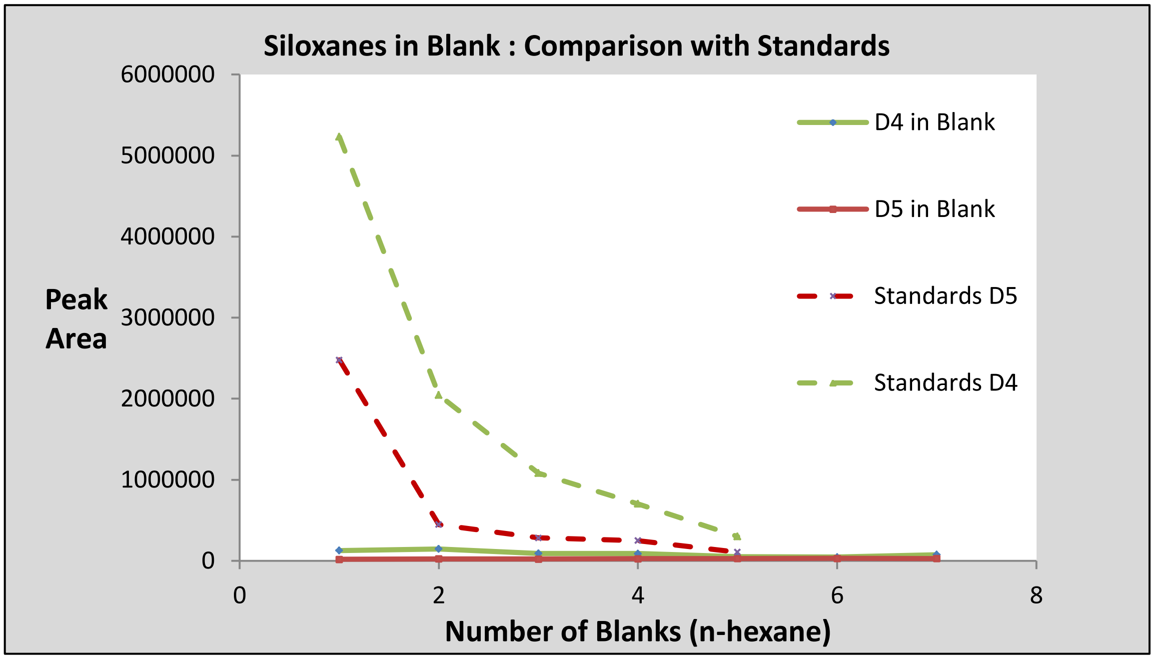

Figure D-17 Concentration of Siloxanes: In blank and standards

Survey Result

This survey was taken by Utility managers, plant operators, engineers, researchers, lab supervisors, wastewater treatment plant superintendents and many other personal related to wastewater treatment and sludge handling from utilities, consulting firms and wastewater industries from United States, India, South Africa, Spain and South America. About 78% facilities in the survey uses anaerobic digestion to treat waste activated sludge. Out of those 78%, 83% utilities use the biogas produced for beneficial purpose. This higher percentage of utilities using biogas for beneficial purpose was notable. Further, it was observed that 72% of the utilities, who use biogas for beneficial purpose, were aware about the siloxane issue and 28% were not aware. Surprisingly, although 72% utilities were aware of siloxanes, only 27% utilities actually measure the siloxanes concentrations at their utilities (mostly in gaseous phase). About 73% utilities were aware of siloxanes but they don't measure siloxanes. It was observed that all of the utilities measure the siloxanes (D4, D5, D6, Linear siloxanes) in gas phase. The utilities that were not aware of siloxanes were asked if they observe any white/silver color scaling on gas handling equipment, and about 49% utilities said YES. This means that even if few utilities said they were not aware of siloxanes, almost half of those utilities have siloxanes issue in operation. Further, it was found that only 45% utilities treat / purify the gas before use, however, only 57% of utilities specifically treats the gas for removing the siloxanes. Finally, 41% utilities thought that siloxanes issue was at High Importance to them, 31% utilities thought it's a Medium Importance Issue to them and it was of Low Importance to 28% of Utilities.

Table D-31 Role of Person Taking Survey

Role of Person Taking Survey	Response	%
Utility Manager	17	21%
Plant Operator (Water / Wastewater Treatment)	11	14%
Engineer	26	33%
Researcher Lab/IW Supervisor WWTP Supt Process & Research Engineer Water Quality Coordinator Biosolids Operation Manager Consultant Operations Director WWTP Superintendent Process Analyst GAs Tech/Co-gen COO Environmental Advisor Wastewater Treatment Analyst Treatment Division Manager Assets consultant waste water Regulator Lab Consultant Principal Environment, Health & Safety Executive Lecturer Research Scholar Research environmental executive	26	33%
Total	80	100%

Table D-32 Survey Questions and Responses

	Answer	Response	%
Does your facility use Activated Sludge Process as part of treatment?	YES	56	72%
	NO	22	28%
	Total	78	100%

	Answer	Response	%
Does your facility use anaerobic digestion to treat waste activated sludge?	YES	35	78%
	NO	10	22%
	Total	45	100%

	Answer	Response	%
Does your facility use bio-gas produced for beneficial purpose?	YES	29	83%
	NO	6	17%
	Total	35	100%

	Answer	Response	%
Are you aware of Siloxanes?	YES	48	72%
	NO	19	28%
	Total	67	100%

	Answer	Response	%
Does your facility monitor / measure concentration of “Siloxanes”?	YES	13	27%
	NO	35	73%
	Total	48	100%

	Answer	Response	%
Have you observed any white / silver color scaling on any gas handling equipment?	YES	31	49%
	NO	32	51%
	Total	63	100%

	Answer	Response	%
Does your facility treat / purify the gas before use?	YES	14	45%
	NO	17	55%
	Total	31	100%

	Answer	Response	%
How important to you feel the need to obtain monitoring data or information on siloxanes?	High Importance	25	41%
	Medium Importance	19	31%
	Low Importance	17	28%
	Total	61	100%

	Answer	Response	%
Does your facility treat the gas for removal of Siloxanes?	YES	8	57%
	NO	6	43%
	Total	14	100%

Sources: Esri, DeLorme, NAVTEQ, TomTom, Intermap, iPC, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), and the GIS User Community

Figure D-18 Siloxanes Distribution in USA (Survey Data)

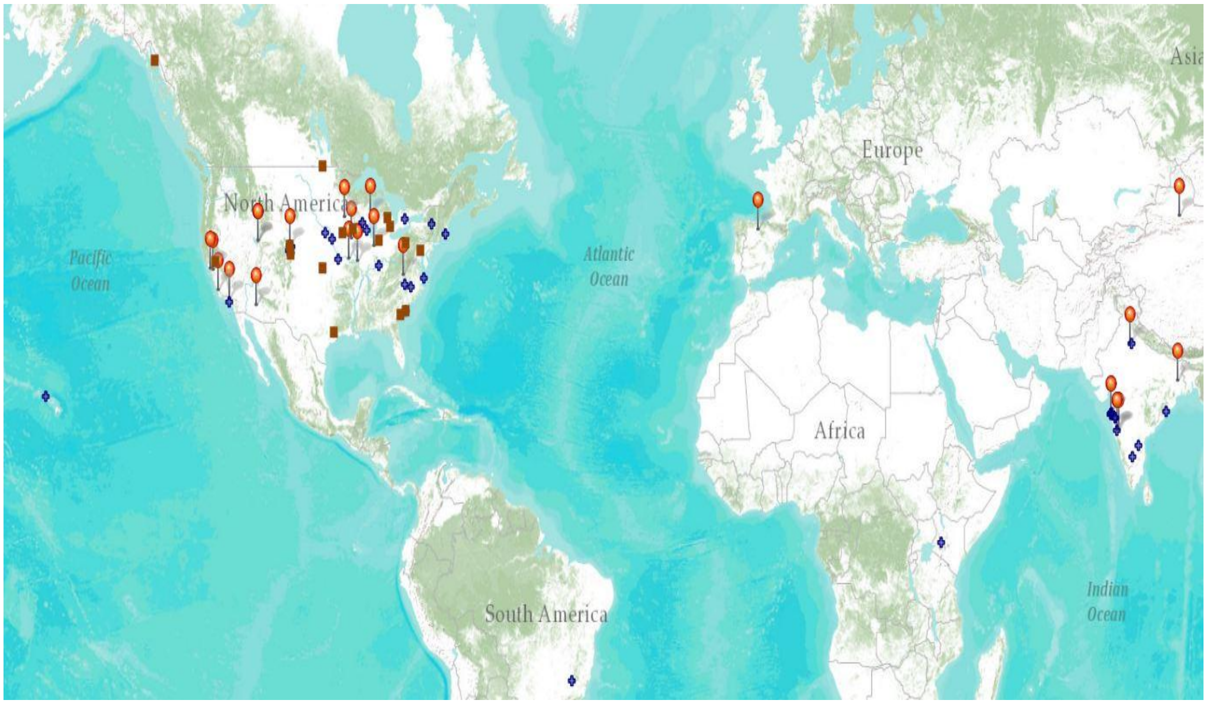

Figure D-19 Distribution of Siloxanes World (Survey Data)

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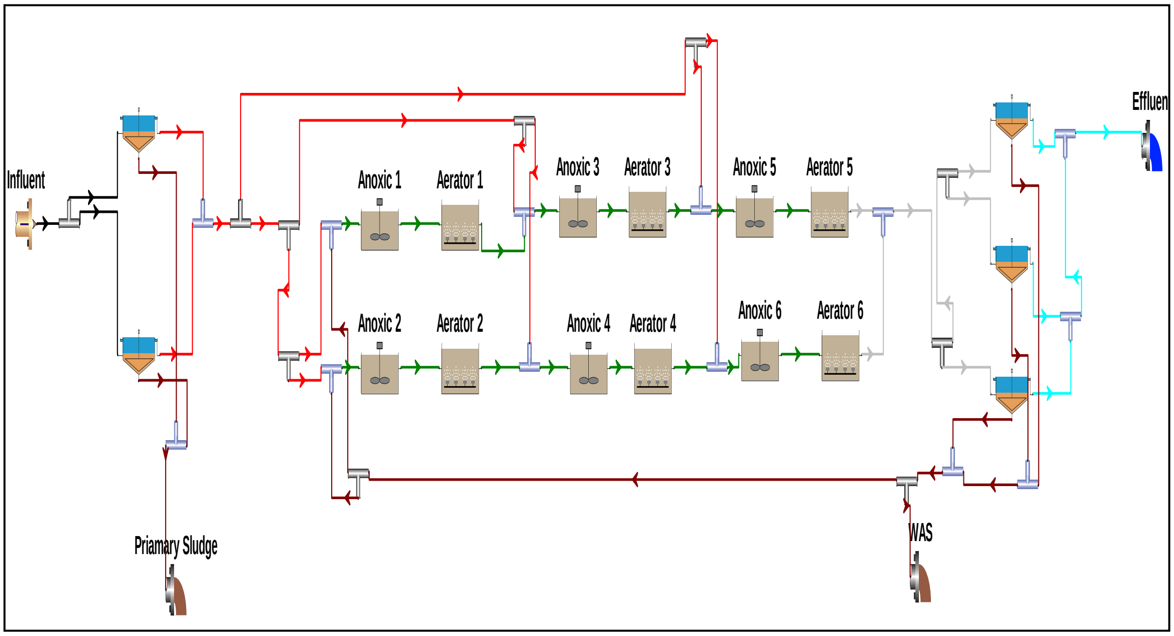

Figure E-1 Process Flow Diagram - City of Loveland

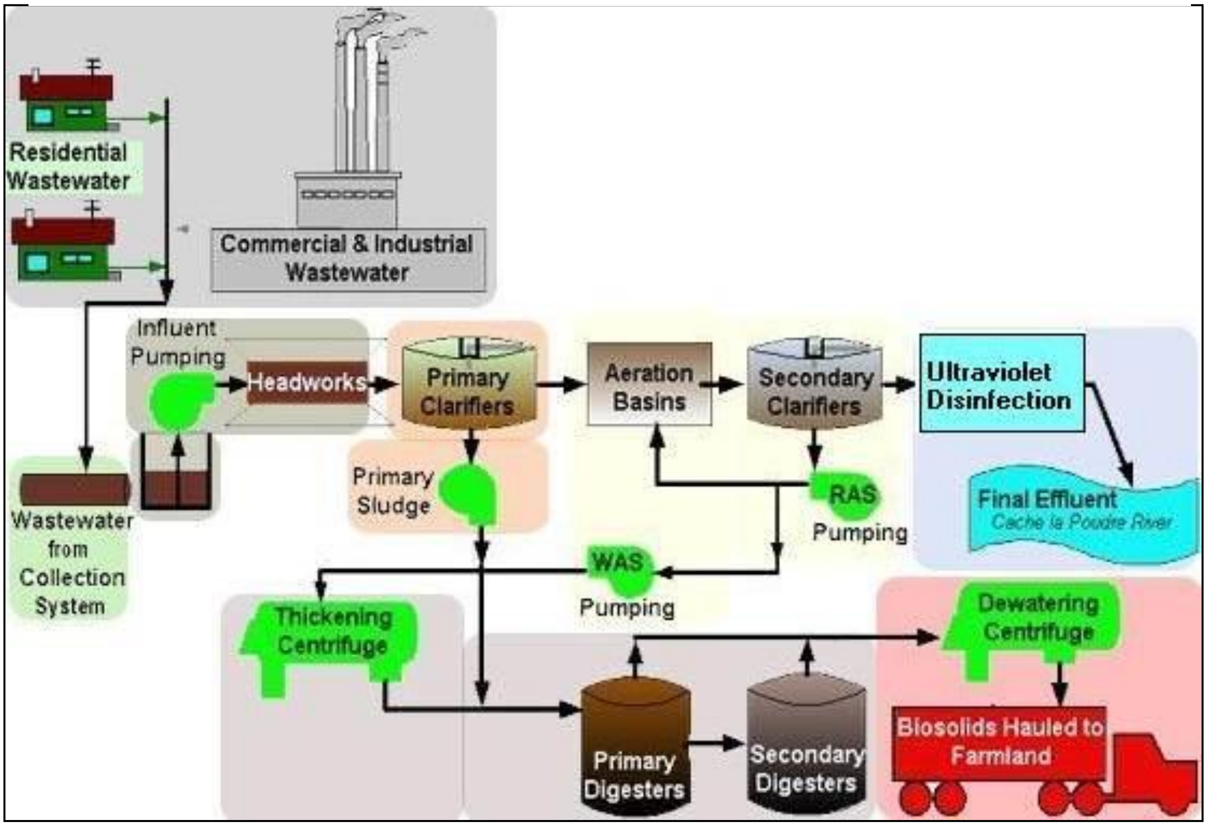

Figure E-2 Process Flow Diagram (City of Greeley)

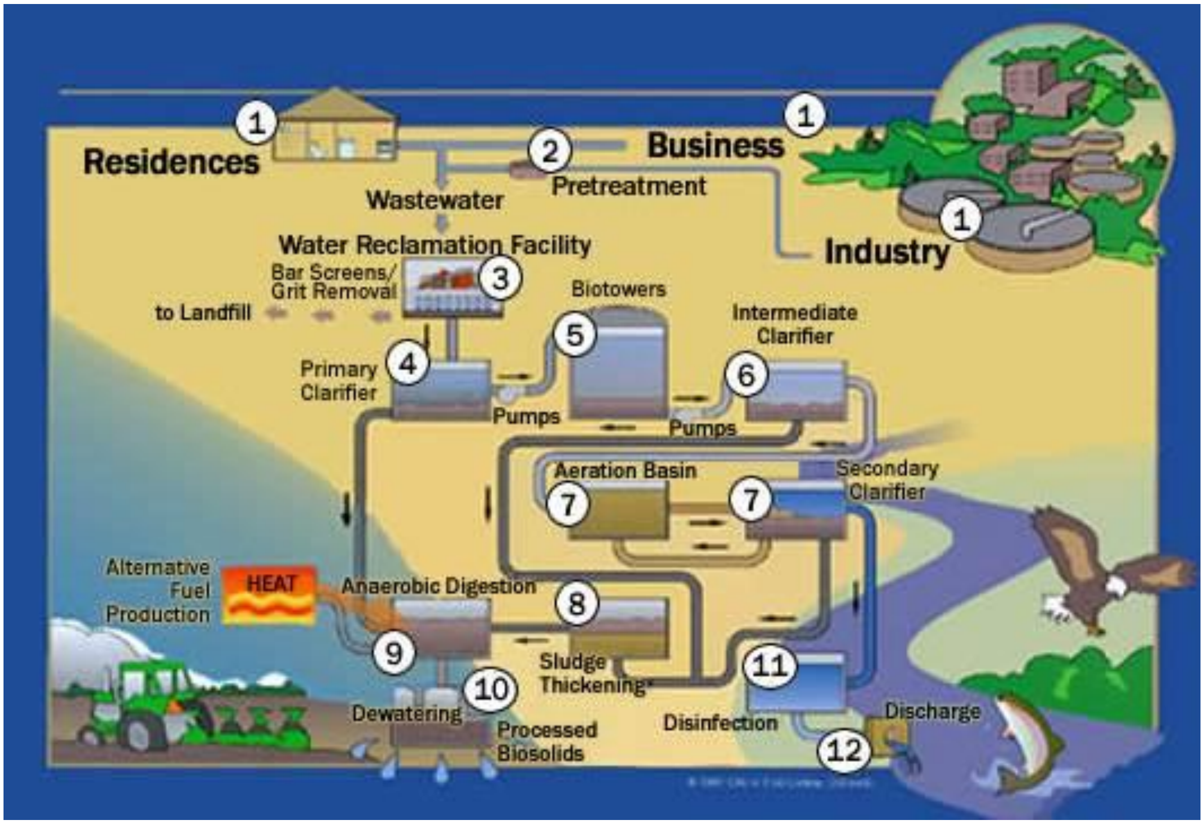

Figure E-3 Process Flow Diagram (City of Boulder)

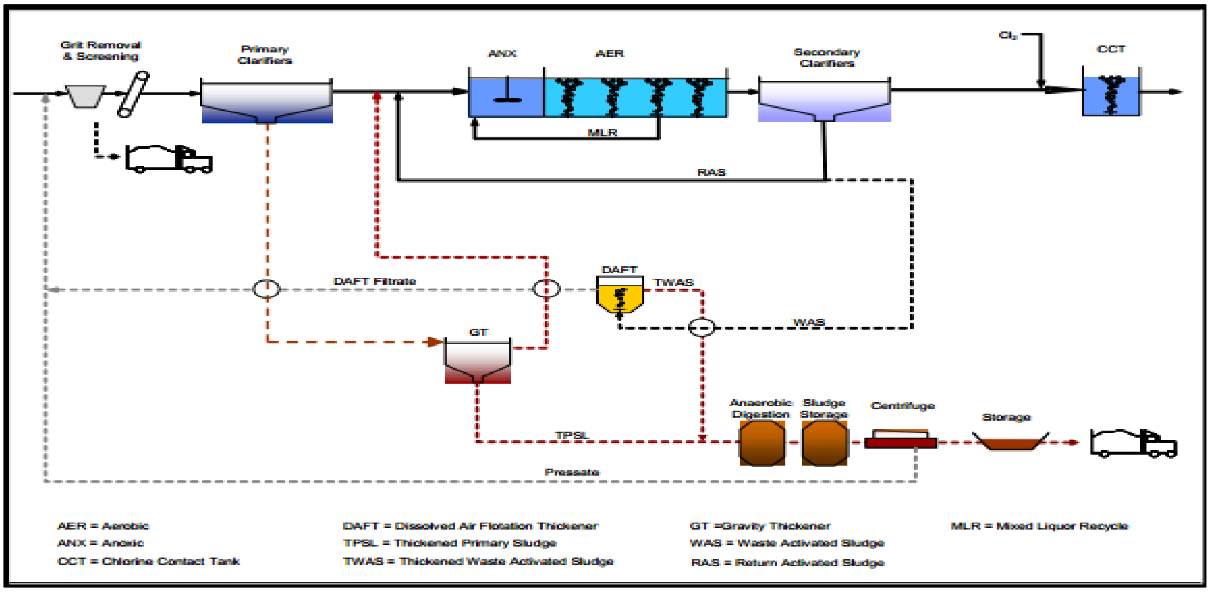

Figure E-4 Process Flow Diagram (City of Fort Collins)