EVALUATION OF ODOUR ABATEMENT CAUSES FOLLOWING ELECTRO-DEWATERING OF BIOSOLIDS

Samia Enayet

Department of Civil Engineering and Applied Mechanics

McGill University, Montréal,

Québec, Canada

December 13, 2013

Thesis submitted to McGill University in partial fulfillment of the Requirements of the degree of Masters of Engineering

Abstract

Biosolids being recycled to the land for agriculture is not only cost-effective for municipalities but it is also beneficial to the environment. To protect public and environmental health, however, land application of biosolids is regulated for concentrations of pathogens and chemical contaminants, and for production of odours. Electro-dewatering (ED) of residual biosolids from wastewater treatment is a newly commercialized technology which can produce a drier biosolids cake compared to other advanced dewatering technologies. Additionally, it has been demonstrated that ED inactivates pathogen indicators below the detection limit and reduces the regrowth potential. In the current study, using olfactometry and headspace gas chromatography - mass spectrometry (GC/MS), reduced production of odours during storage of dewatered biosolids was documented, and possible mechanisms leading to this reduction were examined.

The study compared centrifuged secondary biosolids as the untreated sample control with the same biosolids that had been either electro-dewatered for 10 min or simply heat-treated for 10 min as a secondary control. These samples were incubated at room temperature under anaerobic conditions. Qualitative analysis of the head space by a trained olfactometric panel showed that ED biosolids possessed lower perceived odour concentrations when characterized by detection threshold and recognition threshold compared to the untreated and the heat-treated biosolids (detection thresholds were 13,000 for ED biosolids, 25,000 for untreated biosolids, and 18,000 for heat-treated biosolids). Quantitative analysis by GC/MS of reduced sulphur compounds (methanethiol, dimethyl sulphide and dimethyl disulphide) showed relatively high concentrations for the untreated and heat treated samples, but these compounds remained below the detection limit (78 ppmv for methanethiol, 59 ppmv for dimethyl sulphide and 8 ppmv for dimethyl disulphide) for the ED samples during 14 days of anaerobic incubation.

To investigate the reason for the lower odour production by ED biosolids, several factors were examined: (1) the lower pH of the electro-dewatered biosolids (pH 4.5-4.8 vs. pH 6.8-7.5 for the untreated and heat-treated biosolids), (2) the removal of odour precursors by ED, (3) the production of inhibitory compounds during ED. The low pH hypothesis was tested by increasing the pH of the ED biosolids to the level found in the untreated biosolids before anaerobic incubation. Increasing the pH of ED biosolids led to an increase in methanethiol generation. This suggests that lowering the pH of biosolids is one of the main factors causing the abatement of odour production by ED. The removal of odour precursor hypothesis was tested by adding back the filtrate extracted by ED. As the filtrate had a very high pH of 12.8, which also changed the pH of the ED biosolids, the filtrate pH was manipulated such that the pH of the resulting biosolids would be either ~4.5 or ~7. As in the pH-specific experiments, methanethiol emissions were not detected for all samples with a low pH, whereas methanethiol emissions from the high pH samples were increased in the ED biosolids with added filtrate. These methanethiol emissions were above those of the untreated, ED biosolids without filtrate and the heat-treated biosolids. These final results indicate that the dominant factor responsible for reduced odours in ED biosolids is the low pH, but that the removal of precursors may also contribute to lowering odour production. Once these factors were taken into account, there was no clear evidence that ED produced inhibitory compounds. Finally, these experiments confirmed that bacterial pathogen indicators did not regrow under the conditions tested. Therefore, it can be concluded that, under the conditions tested, ED achieved irreversible inactivation of pathogen indicator organisms and reduced odour production by lowering the pH.

Résumé

La valorisation des biosolides par épandage sur des terres agricoles n'est pas seulement rentable pour les municipalités mais elle est également bénéfique pour l'environnement. Toutefois, afin de protéger la santé publique et l'environnement, l'épandage de biosolides est strictement réglementé pour ce qui est des concentrations d'agents pathogènes et de contaminants chimiques ainsi que pour la production d'odeurs. L'électro-déshydratation (ED) des biosolides résiduels découlant du traitement des eaux usées est une technologie nouvellement commercialisée qui peut produire des biosolides plus secs que d'autres technologies de déshydratation avancées. En outre, il a été démontré que l'ED inactive les pathogènes en dessous de la limite de détection et diminue le potentiel de repousse des pathogènes. Dans l'étude présentée dans ce mémoire, la réduction de la production d'odeurs durant l'entreposage des biosolides déshydratés a été documentée et les mécanismes possibles conduisant à cette réduction ont été examinés en utilisant l'olfactométrie et la spectrométrie de masse (GC/MS) en phase gazeuse de l'espace de tête. L'étude a comparé des biosolides secondaires centrifugés en tant que contrôle (échantillons non traité) avec les mêmes biosolides qui avaient été soit électro-déshydratées pendant 10 min, soit simplement traité à la chaleur pendant 10 min comme un contrôle secondaire. Ces échantillons ont été incubés à la température ambiante dans des conditions anaérobies. L'analyse qualitative de l'espace gazeux au-dessus des échantillons par un panel olfactométrique a montré que les biosolides électro-déshydratés produisaient des concentrations perçus d'odeurs inférieure selon les seuils de détection et de reconnaissance des odeurs par rapport aux échantillons non traités ou traités à la chaleur (seuils de détection étaient 13 000 pour les biosolides électro-déshydratés, 25 000 pour les biosolides non traités, et 18 000 pour les biosolides traités à la chaleur). L'analyse quantitative par détection chromatographie en phase gazeuse--spectrométrie de masse (GC/MS)des composés soufrés réduits (méthanethiol, sulfure de diméthyle et le disulfure de diméthyle) a montré des concentrations relativement élevées pour les échantillons non traités et traités à la chaleur, mais ces composés sont restés sous la limite de détection (78 ppmv pour le méthanethiol, 59 ppmv de sulfure de diméthyle et 8 ppmv pour le disulfure

de diméthyle) pour les échantillons électro-déshydratés et incubés en anaérobie pendant 14 jours.Pour determiner la cause de la réduction de la production d'odeur par les biosolides électro-déshydratés, plusieurs hypothèses ont été émises: (1) le pH inférieur des biosolides électro-déshydratée (pH 4,5-4,8 vs pH 6.8 à 7.5 pour les biosolides non-traités et traités thermiquement), (2) l'élimination des précurseurs d'odeur par le processus d'électro-déshydratation, (3) la production de composés inhibiteurs au cours de l'électro-déshydratation. L'hypothèse d'un pH faible a été testée en augmentant le pH des biosolides électro-déshydratées au niveau des biosolides non traitées avant l'incubation anaérobie. L'augmentation du pH des boues électro-déshydratées a conduit à une augmentation de la production méthanethiol. Ceci suggère que l'abaissement du pH des boues est l'un des principaux facteurs responsables de la réduction de la production d'odeur par électro- déshydratation. L'hypothèse de la suppression du précurseur d'odeur a été testée en rajoutant le filtrat extrait par l'électro-déshydratation. Comme le filtrat présente un pH très élevé (12.8), le filtrat pH a été manipulé de telle sorte que le pH des biosolides résultant serait soit de ~ 4.5 ou de ~ 7. Comme dans les expériences spécifiques au pH, les émissions de méthanethiol n'ont pas été détectées pour les échantillons dont le pH était bas, alors que les émissions méthanethiol à partir des échantillons à pH élevé ont augmentés dans les biosolides électro-déshydratées avec filtrat ajoutée. Ces émissions de méthanethiol étaient supérieures à ceux des biosolides électro-déshydratées sans filtrat, des biosolids non traités et des biosolides traités à la chaleur. Ces derniers résultats indiquent que le facteur dominant responsable de la réduction des odeurs dans les biosolides électro-déshydratées est le faible pH, mais que l'élimination des précurseurs peut également contribuer à réduire la production d'odeurs. Une fois que ces facteurs eurent été pris en compte, il n'y avait pas de preuve claire que l'électro-déshydratation produit des composés inhibiteurs. Enfin, ces expériences ont confirmé que les indicateurs de pathogènes bactériens ne se régénèrent dans les conditions testées. Par conséquent, on peut conclure que, dans les conditions testées, l'électro-déshydratation atteint une inactivation irréversible d'organisme indicateur d'agent pathogène et a réduit la production d'odeur par abaissement du pH.

Dedications

This work is dedicated to my parents

Dr. Mohammad Enayet &

Dr. Fatima Khanam

My husband Dr. Nayeem Ahmed Ninad

And my daughter Rushda Ninad

Acknowledgements

In the name of Almighty Allah, the most merciful, the most beneficent, whose blessings are always with us.

First and foremost, I would like to thank my supervisors, Professors Ronald Gehr and Dominic Frigon for their continuous support throughout the course of my study. I have benefited tremendously from Dr. Gehr's expertise in wastewater and odour treatment. With his unique blend of energy and enthusiasm, Dr. Frigon played a major role in guiding me towards the final outcome of this research. I really feel honoured to be a part of their research team.

I also specially thank my colleague, Tala Navab-Daneshmand for supporting and guiding me in every step not only as a mentor but also as a friend. I am also grateful to all my other colleagues and friends in the Benedek Integrated Laboratory of Environmental Engineering who helped me throughout my laboratory experiments.

I would like to express my utmost gratitude to Ranjan Roy for his help with his immense amount of knowledge and expertise in the Chemical Engineering Laboratory at McGill University.

I am very grateful to OVIVO, for providing partial funds and laboratory equipments along with the funding from NSERC/CRNSG.

Finally, I would like thank my family, my parents Dr. Mohammad Enayet and Dr. Fatima Khanam for their unconditional love and continuous support throughout my life. I am especially grateful to my husband, Dr. Nayeem Ahmed Ninad and my 3 years old daughter, who have always been beside me in every stage of this study with their love and support.

Table of Contents

List of Figures

List of Tables

List of Acronyms and Abbreviations

Acronyms	Meaning
BSA	Bovine albumin standard
COD	Chemical oxygen demand
CCME	Canadian Council of the Ministers of the Environment
DMDS	Dimethyl disulphide
DMS	Dimethyl sulphide
DT	Detection threshold
E. coli	*Escherichia coli*
ED	Electro-dewatered
ED+NaOH	Electro-dewatered NaOH added
EDF	Electro-dewatered filtrate added
EDF+HCl	Electro-dewatered, filtrate and HCl added
EDRAW	Electro-dewatered, raw mixed (50/50)
EDW	Electro-dewatered water added
GC/MS	Gas chromatography/mass spectrometry
HT	Heat-treated
HT+HCl	Heat-treated HCl added
MDDEP	Ministère du Développement Durable, de l'Environnement et Parcs
MT	Methanethiol
RAW+HCl	Raw HCl added
RT	Recognition threshold
SIM	Selected ion monitoring
TMA	Trimethyl amine
US-EPA	United States Environmental Protection Agency

Chapter 1. Introduction

Sewage sludge is defined as the separated solid or semi-liquid product from wastewater treatment plants. When sewage sludge is treated to meet certain jurisdictions it is termed "biosolids" (CCME 2012). Wastewater biosolids disposal has become increasingly costly as more stringent disposal regulations have been applied over the last few decades. Biosolids production rate in the United States was about 7.7 million dry metric tons per year in 2007 which is projected in increase considerably in the following years (Newbold & Schici 2011). In Canada, about 0.66 million dry metric tons of biosolids are produced annually. Biosolids handling and disposal costs are about 50% of the overall wastewater treatment plant's operational costs (CCME 2012). Biosolids can be disposed of by land-filling, incineration or land-application. Recently, land application is becoming more popular because of its lower cost and the fact that it recycles the organic matter as fertilizer. For application on land, these biosolids have to meet certain regulations in terms of environmental and public health. For instance, according to the US-EPA, Class A biosolids can be directly applied to land without restrictions, whereas Class B biosolids can only be applied if it meets a number of crop and application protocol restrictions (US-EPA 2003).

In Canada, land application of these biosolids is regulated by provincial or territorial legislation, which are largely inspired by the US-EPA regulations. Although the the United States does not have any regulations on odours for land-applied biosolids, two provinces, Quebec and Ontario, have a legislative framework for odours (CCME 2010). Though typically not properly regulated by law, biosolids odours may become the major impediment to land application. As the population increases, people tend to move closer to landfill sites or land application sites, and complaints about odours then increase. For example, in Orleans, MA, public complaints forced the treatment plant to transport their biosolids off-site for composting; in Seattle, WA, the largest composter of the state was fined $500,000 in 1997 due to neighbourhood odour complaints (Feinbaum 2000). In

Canada, a biosolids compost facility at British Columbia was forced to shut down because of similar complaints (McTavish 2008).

In order to minimize odour problems, it is important to isolate the factors responsible for them, including the identification of the associated compounds. Many factors can influence the odour of biosolids directly or indirectly, such as pH, temperature, chemical constituents, upstream processes, conditioning, exposure to aerobic or anaerobic conditions, dewatering and storage conditions. For example, in lagoons the surface layer (top 0.15 m) undergoes aerobic transformation but the rest of the pile being anaerobic, is actually responsible for most of the odours (Lukicheva et al. 2012). In another study it was shown that belt-pressed dewatered biosolids produced fewer odours than centrifuge dewatered biosolids (Murthy et al. 2006).

Many compounds have been associated with biosolids odours. Sulphur compounds are considered to be the main odorants, as verified by many researchers. Inorganic sulphur compounds such as hydrogen sulphide and carbon di-sulphide, as well as volatile organic sulphur compounds (VOSC) such as methanethiol, dimethyl sulphide, and dimethyl disulphide are the dominant sulphur compounds (Forbes et al. 2004; Rosenfeld & Suffet 2004; Higgins et al. 2006; Novak et al. 2006). Other important odour-causing groups are nitrogenous compounds such as amines and ammonia (Rosenfeld & Suffet 2004), volatile fatty acids (Kim et al. 2002), volatile aromatic compounds such as benzene and toluene (Chen et al. 2006a), and also some aldehydes and ketones (Rosenfeld et al. 2001a).

In addition to minimizing odour production, reducing the total volume of biosolids produced has become a major concern for cities, as disposal is costly. New technologies are emerging for this purpose. One example is electro-dewatering, which has been assessed with a view to increase the solids content to produce a smaller volume of biosolids, and at the same time to produce Class A biosolids (Drogui et al. 2007; Mahmoud et al. 2010). Furthermore, this technology has been found to produce less odorous biosolids compared to other types of dewatering units (Eschborn et al. 2011; Bureau et al. 2012). A previous study has shown that electro-dewatering produces

biosolids of approximately 30 to 50% solids content, at a pH of 4.5 - 4.8, and the inactivation of pathogens in the biosolids is mainly due to high temperatures (~100 ^{o}C) caused by Joule heating (Navab-Daneshmand et al. 2012).

A quantitative study of odours emanating from electro-dewatered biosolids has not been reported; hence the main objectives of this study are to identify the different odour-causing compounds in the electro-dewatered biosolids, to quantify these compounds in different biosolids samples, and to determine the mechanisms for odour abatement due to electro-dewatering.

To accomplish these objectives three hypotheses were developed and tested, first the lower pH of the electro-dewatered biosolids (pH 4.5-4.8 vs. pH 6.8-7.5 for the untreated), second, the removal of odour precursors by the electro-dewatering process, the extractable proteins are the odour precursors and finally electro-dewatering process creates unknown inhibitory compounds that inhibits the odours. Investigations of theses hypotheses were conducted in three phases. Phase 1 was the preliminary detection of the main odorous compounds, on phase 2, olfactometry analysis by trained odour panel and measurement of the main odorous compounds by GC/MS were performed and finally phase 3 consisted of sensorial and analytical experiments to determine the key factors responsible for the odour reduction due to electro-dewatering.

The thesis is divided into six chapters. The current introductory chapter; chapter 2 provides a literature review; materials and methods are covered in chapter 3; chapter 4 documents all the results of the phases 1, 2 and 3 of the study; chapter 5 discusses the results of the phases 1, 2 and 3; the summary and conclusions are given in chapter 6.

Chapter 2. Literature Review

2.1 **Biosolids Definition and Regulations**

2.1.1 USEPA regulations on land application:

According to US-EPA Part 503 Rule: Use or Disposal of Sewage Sludge Biosolids, sewage sludge is defined as the residual product generated during domestic wastewater treatment processes which includes scum or solids removed in primary, secondary or advanced wastewater treatment processes, but excludes grit, screenings or ash generated in the incinerator (US-EPA 1993). Sewage sludge or biosolids can be disposed of in land for beneficial use if they meet the requirements under the U.S. federal regulation 40 CFR Part 503 (known as Part 503 Biosolids Rule). The regulation includes standards for pollution limits, management practices, monitoring requirements, operational standards, record keeping and reporting. The Part 503 Biosolids Rule regulates chemical contamination as a pollutant, and sets limits for pathogens and vector attraction. Land application must satisfy the pathogen standard defined by two major levels of biosolids disinfection: Class A or Class B biosolids. Class A biosolids are essentially pathogen free and can be used on land without further treatment. Class A biosolids must meet either a fecal coliforms density of 1,000 MPN per g total solids or 3 MPN *Salmonella* sp. bacteria / 4-g total solids, while using one of the other six alternatives (specifically defined temperature regimes; high pH-high temperature treatment; process monitoring for helminth ova <1 ovum/4 g DS and enteric viruses <1 PFU/4 g DS before and after pathogen treatment; determination of helminth ova and enteric viruses for each batch leaving the plant; any process to further reduce pathogens (PFRP);processes equivalent to PFRP) (Iranpour et al. 2004). For Class B, the limitation is a reduced density of fecal coliforms to below10^6MPN or CFU per g total solids. If biosolids meet the Class A pathogen requirement, the pollutant concentration limits for all the toxic metals and one of the options 1 to 8 for vector attraction reduction, the biosolids are termed as

"Exceptional Quality (EQ) Biosolids", which do not have any restriction either for applying on land or for any other use (US-EPA 2003).

2.1.2 Canadian Regulations:

According to the Canadian Council of Ministers of the Environment, sewage sludge is defined as, "Organic products produced from the treatment of wastewater sewage sludge and septage to reduce pathogens and vector attraction (odours). Municipal wastewater biosolids may be solid, semi-solid or liquid and come primarily from the treatment of domestic wastewater and municipal sludge, although municipal wastewater treatment plants may also treat some commercial and industrial sewer effluents" (CCME 2010).

In Canada, various government bodies in Federal, Provincial/Territorial and Municipal levels control biosolids management systems. Land application which is the end use of biosolids, is mainly regulated by Provincial or Territorial legislation, which follows or are based on the USEPA part 503 biosolids rule (CCME 2012).

In Saskatchewan and Manitoba, there is one set of standards for a single category of biosolids. British Columbia, Nova Scotia and the North West Territories have two classes of biosolids, Class A and Class B, whereas in Prince Edward Island, biosolids are categorized as Exceptional quality (EQ), Class A and Class B biosolids. However, similarly named categories in different provinces use different standards to qualify these classes of products. In Alberta, biosolids are classified based on their degree of treatment (wastewater lagoon, digested, undigested) and then further classified based on the receiving soil properties (Classes 1, 2 & 3) (CCME 2010). According to the General Nutrient Management Regulation under the *Nutrient Management Act, 2002,* from January 1, 2011, Ontario issued a new type of approval called a non-agricultural source materials (NASM) plan, based on material quality. The new framework categorizes NASM into three categories (1, 2 and 3), in which biosolids are in Category 3 and are further subcategorized into metal (CM1 and CM2), pathogen (CP1 and CP2) and odour (OC1, OC2 and OC3) categories. Land application sites should maintain a safe distance from wells, surface water, groundwater and bedrock determined by the metal and

pollutant category. For residential, commercial, community or institutional properties, setback distances are determined by odour category. As per the NASM guide, centrifuged biosolids (>2,000 rpm) fall under the OC3 category, where "OC3", refers to an odour detection threshold of between 1,500 and 4,500 odour units per cubic meter.

2.1.3 Quebec Legislation:

In the Province of Quebec, the production and use of biosolids is regulated by the Ministère du Développement Durable, de l'Environnement et des Parcs (MDDEP). Sewage sludge or biosolids is defined under the category fertilizing residual materials (FRMs) (Hébert 2008). FRMs are defined as industrial and municipal waste that has a beneficial effect on crops and soil.

Annually around 0.75 million tonnes (wet weight basis) of biosolids are produced in Quebec. Thirty percent of that is recycled through land application, 22% is land-filled and 48% is incinerated or burned in cement factories (mainly in larger cities such as Montreal, Quebec, and Longueuil). The Government of Quebec in its new policy Quebec Residual Material Management in 2011 has proposed the banning of land-filling and incineration of organic matter by 2020. This was based on the fact that management of land application of sewage biosolids is carbon-neutral, unlike incineration or land-filling (Hébert 2012).

In Quebec, fertilizing materials are classified by a C-P-O classification according to their chemical contaminant (C category), pathogen content (P- category) and odour (O-category). Each category rates fertilizing residuals from 1 to 2 (C and P categories) or from 1 to 3 (O category), leading to a total of twelve types of FRMs (Hébert 2008). The higher the number of the rating, the more restrictions applies to them for the use of biosolids in land. According to Quebec standards, municipal biosolids are categorized as "Strongly Malodorous" and anaerobically digested biosolids followed by centrifugation are more odorous than pig manure and are referred to as "Out of Category", therefore they cannot be applied on land (Hébert 2008).

2.2 **Biosolids generation in wastewater treatment plants (WWTP)**

Biological treatment, and specially the activated sludge process, generates a lot of sludges. Two major categories of sludge are produced by a typical biological WWTP: primary and secondary sludge. Primary sludge refers to the separated solids from the gravity settler using a physical treatment, and it usually consists of inorganic and some non-cellular organic matter which are highly biodegradable and produces odour during storage. Secondary sludge refers to sludge from biological processes. This sludge consists of adsorbed suspended solids, microorganism and colloids (Metcalf & Eddy Inc. 2003). Most treatment plants combine this primary and secondary sludge and name it "combined sludge". This combined sludge usually requires digestion for the reduction of organic matters to stabilize the sludge and to reduce the emanation of odours. The digested sludge usually has reduced dewaterability compared to primary or secondary sludges due to an increase of fine particles (Tuan et al. 2012). The third category of sludge is chemical sludge, which is the sludge produced after chemical compounds have been added to the primary or secondary sludge to improve settling or dewatering efficiency. To further reduce sludge volume mechanical dewatering or advanced dewatering is implied before final disposal. The most commonly used dewatering techniques are belt press, centrifugation, drying beds or lagoons (Metcalf & Eddy Inc. 2003).

2.3 **Water distribution in sewage sludges**

The bulk portion of sewage sludge is water. Primary sludge has around 3-7% solids content, whereas secondary sludge has 0.2-2% total solids (Chen et al. 2002). Before the dewatering step, the sludge undergoes chemical or thermal conditioning which change the structure of the sludge and improves the dewaterability. After thickening, the solids content of the sludge could be as high as 4-8% (w/w) (Oleszkiewicz & Mavinic 2002). The efficiency of removing this huge amount of water largely depends on the water distribution and dewatering process.

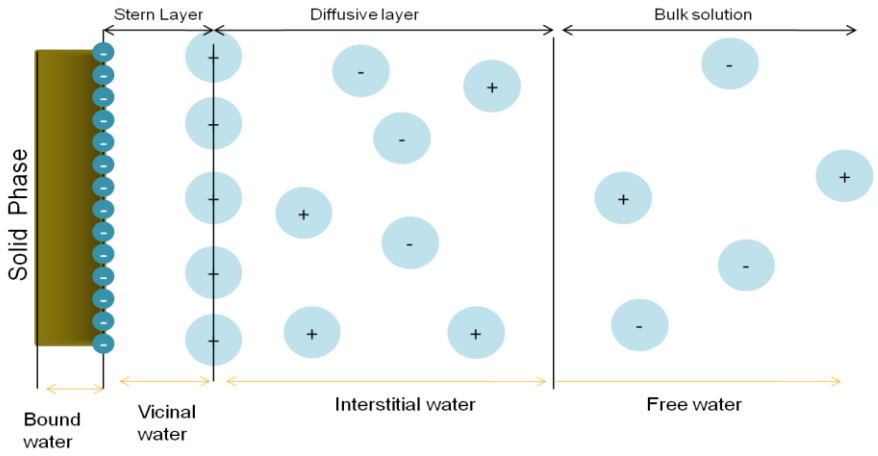


Figure 2-1 Water distribution of sewage sludge (adapted from Mahmoud et al. (2010)

The water in sludge as described by Tsang & Vesilind (1990); Vesilind (1994); Vesilind & Hsu (1997) is divided into four categories depending on their physical binding with sludge particles (*Figure 2-1*):

a) Free water: represents the largest part (70-75%) of sewage sludge; it refers mainly to the void water not affected by capillary force

b) Interstitial water: refers to the water between sludge flocs bound by capillary force

c) Surface/ vicinal water: water held onto the surface of sludge particles

d) Intracellular water: chemical bound water within solid structure.

While thickening can only remove part of the free water easily by increasing the solids content from 1 to 4-8%, mechanical dewatering is capable of removing all the free water resulting in an increase in the sludge solids content up to 20%. Surface water can be removed from sludge by treating it with chemicals, then by mechanically dewatering, thereby reaching a dryness up to 35% or, if dewatered by advanced machines, the dryness can reach 40-45% (Oleszkiewicz & Mavinic 2002).

2.4 **Sewage sludge electro-dewatering**

Mechanical dewatering has been the last stage of sewage sludge processing for most plants before final disposal. Due to increasing production of sewage sludge and a narrowing of the options for disposal, mechanical dewatering which produces sludge of around 20% dryness is no longer satisfactory. More advanced dewatering processes are needed which can be efficient as well as cost-effective. Electrical fields have been applied for wastewater or sludge treatment for many years in many different ways such as electro-coagulation, electro-deposition, electro-flotation, electro-oxidation and electro-kinetic processes (Drogui et al. 2007) and it has been reported to produce a drier sludge cake using less energy compared to other drying technologies (Mahmoud et al. 2010). A high electrical voltage (15,000 to 100,000 V) was implemented by Held & Chauhan (2002) to dewater and destroy bacterial cells in wastewater, but this treatment did not have any affect on malodorous compounds. Very recently, electro-kinetic remediation of sewage sludge (solids content of 3.4%) by application of low intensity current for pathogen inactivation was patented by Elektorowicz & Oleszkiewicz (2012). A new high impact wastewater treatment system was developed by Hasan (2012) by combining an electro-kinetics phenomenon and membrane bioreactor and named "Submerged Membrane Electro-Bioreactor" (SMEBR). According to the affiliated researchers, this technology offers high quality sludge as well as effluent (Elektorowicz et al. 2011), but the effect on odours has not been studied. A study on electro-chemical oxidation of liquid wastewater sludge from a sequential batch reactor showed a 6-10% increase in solids content along with the abatement of 4-5 log units of total and fecal coliforms (Bureau et al. 2012; Drogui et al. 2013). Nevertheless, these researchers also claimed that the electro-chemical treatment was efficient in removing unpleasant odours, but no data have been presented.

The key to successful operation of these electricity-assisted dewatering devices is the optimization of several parameters such as initial dryness, voltage, current intensity, time etc. (Mahmoud et al. 2010). Yet until now, advanced electrical dewatering is still at the development stage, and very few full-scale units have been installed and are in operation, either as a substitute to mechanical dewatering (Raats et al. 2002; Saveyn et al. 2006;

Tuan et al. 2008) or as a complementary process (Esmaeily et al. 2006; Citeau et al. 2011).

2.5 CINETIK™ linear electro-dewatering model

The technology used in this study was developed by Elcotech Technologies (Sherbrooke, Quebec, Canada), and given the name CINETIK™ linear electro-dewatering. This new model pressurizes the sludge (solids content 10-20%) to maintain contact with the electrodes which apply a direct current electrical field. The water is removed from the sludge by electro-osmosis (movement of bulk water molecules), electrophoresis (movement of the charged particles) and electro-migration (movement of the ions when particle sizes are close to zero) (Mahmoud et al. 2010; Eschborn et al. 2011). By electrophoresis, the negatively charged particles are drawn to the anode and the positively charged ions to the cathode. As cation concentrations exceeds the anion concentration at the solid liquid interface, the cations impar more momemtum and viscous forces to drag along the water towards the cathode. Therefore, by this electroosmosis process the water eventually escapes through the perforated cathode. No polymer addition is required when conventionally dewatered sludge cake is fed (Eschborn et al. 2011).

The first full-scale unit was installed and operated from 2005 in the City of Victoriaville, Quebec, Canada (McKay et al. 2007). When paired with mechanical dewatering devices this advanced dewatering technology has been documented to inactivate pathogen indicator organisms and enteric viruses below detection limits, potentially producing class A biosolids along with an increase of solids content from 12% (range 10-14%) to 30% (w/w) after 8-9 minutes of treatment (Paradis et al. 2008). A statement for the reduction of odours after applying this technology has been made, but again no data were presented (Eschborn et al. 2011). As these electro-dewatered biosolids do not meet US-EPA's vector attraction reduction (VAR) requirement, Eschborn et al. (2011) proposed an add-on solar drying process or liming to raise the pH above 11.5. A previous study by another researcher of the same research program as the current project using a laboratory scale

unit also showed successful pathogen inactivation to produce class A biosolids as well as an increase in solids content from 15% to 46% (Navab-Daneshmand et al. 2012).

2.6 **Sources of biosolids odours**

The main challenge of biosolids land application is the pathogen reduction requirement. Many WWTPs usually achieve the pathogen requirement under Class A or Class B biosolids. Yet, the often not well addressed odour factor can become a major issue in the land application of biosolids. Usually, odours (as they affect the outside community) become more pronounced at the final stages of wastewater treatment facilities. Typical sewage sludge treatment produces digested, thickened or dewatered sludge and for land application these sludges are preferred for their lower volume and higher nutrient content, but they are also reported to be the most odorous biosolids end products (Forbes et al. 2004). Several factors such as prior treatment processes (anaerobic/aerobic), storage and handling time, conditioning, polymer addition, and chemical constituents are responsible for these biosolids odours.

2.7 **Volatile organic compounds:**

Volatile organic compounds are emitted from biosolids as a result of chemical and biological degradation of organic materials, causing objectionable odours. Volatile organic compounds (VOCs) are defined by their high evaporation tendency at normal indoor temperature and pressure. Rosenfeld & Suffet (2004) reported that more than 50% of the nitrogen and the sulphur compounds in wastewater biosolids are in organic form. These volatile odorous compounds have been studied in different kinds of biosolids for many years. The major contributors to these biosolids odours can be classified as reduced sulphur compounds, nitrogen compounds, volatile fatty acids, volatile aromatic compounds, aldehydes and ketones. They are listed with their typical odour descriptor and air odour threshold in *Table 2-1*.

Table 2-1: Odorous compounds associated with biosolids

Compounds	Formula	Molecular Mass (g/mol)	Odour character	Air odour threshold (ppmv)
Sulphur compounds				
Hydrogen sulphide	H_2S	34.10	Rotten egg	0.0005[a]
Dimethyl sulphide	CH_3-S-CH_3	62	Rotten cabbage	0.001 [a]
Dimethyl disulphide	CH_3-S-S-CH_3	94	Rotten cabbage	0.000026 [a]
Dimethyl trisulphide	CH_3-S-S-S-CH_3	126.26	Rotten cabbage	0.0012 [a]
Carbon disulphide	CS_2	76	Disagree, sweet	0.0077 [a]
Methanethiol	CH_3-SH	48.10	Rotten cabbage	0.00002 [a]
Ethanethiol	CH_3-CH_2-SH	62.10	Rotten cabbage	0.00001 [a]
Propanethiol	CH_3-CH_2-CH_2-SH	76.16	Unpleasant	0.0001 [a]
2-propanethiol	CH_2=CH-CH_2-SH	74.15	Garlic coffee	0.0001 [a]
Benzylthiol	$C_6H_5CH_2$-SH	124.21	Unpleasant	0.0003 [a]
Nitrogen compounds				
Ammonia	NH_3	17.03	Pungent	0.038[a]
Methyl amine	CH_3NH_2	31.05	Fishy	4.7[b], 3.2[c]
Ethyl amine	CH_3-CH_2-NH_2	45.08	Ammonia like	0.27[b]
Dimethyl amine	CH_3-NH-CH_3	45.08	Fishy	0.023[d]
Triethyl amine	$(C_2H_5)_3N$	101.19	Fishy	0.48[c]
Trimethyl amine (TMA)	$(CH_3)_3N$	59.12	Fishy	0.00044[c]
Volatile fatty acids				
Formic acid	HCOOH	46	Biting	0.024 [a]
Acetic acid	CH_3COOH	60	Vinegar	1.019 [a]
Propionic acid	CH_3CH_2COOH	74	rancid, pungent	0.028 [a]
Isobutyl and butyl acid	$CH_3CH_2CH_2COOH$	88	Rancid	0.0003 [a]
Valeric acid	$CH_3(CH_2)_3COOH$	102	Unpleasant	0.0006 [a]
Aldehydes and ketones				
Formaldehyde	HCHO	30	Unpleasant	1.199 [a]
Acetaldehyde	CH3CHO	44	Green sweet	0.0001 [a]
Acetone	(CH3)2CO	58.08	Sweet, minty	20.6 [a]
Methylethyl ketone	$CH_3C(O)CH_2CH_3$	72.11	Sweet, minty	0.25 [a]
Volatile Aromatic Compounds				
Indole	C_2H_6NH	117.15	Faecal	0.00013-0.0015[e]
Skatole	C_9H_9N	131.17	Faecal	0.000065-0.00015 [e]
Toluene	C_7H_8	92.14	Sweet, pungent	2.9 [e]
Styrene	$C_6H_5CH=CH_2$	104.15	Sweet	0.32 [e]
p-cresol	$CH_3C_6H_4(OH)$	108.13	Medicine	0.000011-0.0054 [e]
Ethylbenzene	$C_6H_5CH_2CH_3$	106.17	Gasoline	2.3 [e]

[a] Ruth (1986); [b]Cooper &Alley (1994); [c]Amoore &Hautala (1983); [d] Lue-Hing et al. (1992); [e] Chen et al. (2006b)

2.7.1 Volatile organic sulphur compounds (VOSCs)

The main VOSCs include hydrogen sulphide (H_2S), methanethiol (MT; alos known as methyl mercaptan), dimethyl sulphide (DMS), dimethyl disulphide (DMDS) and carbon di-sulphide (CS_2).

Hydrogen sulphide is the compound which has been extensively studied by many researchers, as not only it is reported to be the predominant odour causing compound associated with biosolids, but also for its corrosive properties and toxicity(Metcalf & Eddy Inc. 2003). Reduction of sulphate by sulphate-reducing bacteria (SRB) and desulphurization of organic sulphides are the main reasons for the occurrence of H_2S in biosolids, mainly under anaerobic conditions. H_2S is a weak diprotic acid with its first pKa 7.04, which means that at pH 7, 50% H_2S will remain at non-ionized volatile molecular form. Consequently, at acidic conditions there will be more than 50% H_2S in molecular form causing odour problem and at basic condition more than 50% H_2S will be in the non-ionized form (Gostelow et al. 2001).

Methanethiol (MT), with an odour detection limit of 0.02 ppb, is another major odour-causing sulphur compound associated with anaerobically digested biosolids (Chen et al. 2006b) and centrifuged primary and secondary biosolids (Krach et al. 2008b). MT in biosolids is often produced from methionine, an abundant amino acid in biosolids protein, due to decomposition by microorganisms (Kadota & Ishida 1972).

Dimethyl sulphide (DMS) is also an important odour-causing compound and Zitomer et al. (2000) reported the presence of DMS as an indicator of stress or toxicity in anaerobically treated biomass. One of the pathways of formation of DMS is the methylation of MT, catalyzed by light and metals present in biosolids.

Dimethyl disulphide (DMDS) was found to account for 55-98% of the total sulphur associated with land application of aerobic biosolids (Banwart & Bremner 1976). Twenty four strains of bacteria and five species of fungi found in wastewater are known to produce DMDS (Tomita et al. 1987; Sunesson et al. 1995). DMDS has been reported to

be produced by abiotic oxidation of MT (Higgins et al. 2006) and also under strict anaerobic conditions (Turkmen et al. 2004a).

Carbon di-sulphide (CS_2) is a flammable, colourless liquid which evaporates readily when exposed to air. It is found in wastewater biosolids, when treated by digestion and heat (Murthy et al. 2003a).

Partitioning co-efficient: All of these odorous compounds are released from the biosolids according to their partitioning coefficient between the aqueous phase of the sludge and the air above it. A list of relevant Henry's law constants is given in *Table 2-2*. As listed in the table, a higher value indicates that the compounds are more concentrated in the aqueous phase than in the gas phase, and therefore the problem of their release in the air is comparatively lower. However, these values are highly dependent on factors such as temperature, pH, ion concentration, and organic suspended matter. Here H_2S and CS_2 have the lowest values of Henry's law constant, therefore they are most likely to cause odour problems, considering all other factors to be the same (Sander 1999).

Table 2-2: Henry's law constant (Sander 1999)

Compounds	Henry's law constant, dimensionless (Concentration in aqueous phase/ concentration in gas phase at 273 K)
H_2S	2.23
MT	7.97
DMS	11.30
DMDS	17.83
CS_2	0.78

Cycling of volatile organic sulphur compounds: Higgins et al. (2006a) proposed a pathway with several mechanisms leading to the production of volatile organic sulphur compounds (mainly H_2S, MT, DMS and DMDS), and closed by ultimate degradation step of these compounds. The first mechanism involves breaking down proteins by protease and peptidase enzymes sequentially to form the free amino-acids cysteine and methionine, which are metabolized to form MT and H_2S respectively. The second

mechanism is the formation of MT and DMS by methylation of H_2S and MT respectively by anaerobic bacteria in the presence of methyl group donors available in biosolids in the form of humic-like substances. The third mechanism for the formation of DMDS is the oxidation of MT in the presence of oxygen; DMDS was not found under anaerobic conditions (Higgins et al. 2006). The proposed pathway closes the loop by the removal of VOSCs and reappearance of H_2S during storage by demthylation of MT, DMS and DMDS by methanogenic bacteria.

2.7.2 Nitrogen compounds

The predominant nitrogen compound associated with biosolids odours is trimethyl amine (TMA), which remains in its dissolved phase unless the pH is higher than the pKa of protonated TMA (9.80). In the literature, it has been shown that TMA is the predominant odorous compound associated with lime-stabilized biosolids (Kim et al. 2003). In properly mixed biosolids with lime, with a pH greater than 11.50 for 30 days, fishy and ammonia smells were detected, which suggests that the compounds are most likely to be nitrogen compounds (Krach et al. 2008b). Chang et al. (2005) showed that in lime-stabilized biosolids, the precursors for these ammonia odours are mainly the polyacrylamide (PAM)-based polymers used for conditioning prior to dewatering.

2.7.3 Volatile fatty acids

Volatile fatty acids are detected in heat-dried biosolids, especially at very high temperatures above 100 ^{o}C. Murthy et al. (2003) showed that VFA production is related to the upstream primary solids which remain undigested.

2.7.4 Aldehydes and ketones

Some biosolids also emit aldehydes and ketones, but to a lesser extent than the compounds mentioned above. These compounds have sweet, pungent odours and are known to be associated with incomplete decomposition of organic matter present in the biosolids. Rosenfeld & Suffet (2004) showed that these compounds are mainly observed in composting facilities.

2.7.5 Volatile aromatic compounds

Volatile aromatic compounds are shown to be the major odour-causing compounds after 1-2 weeks of storage, when the concentrations of the other VOSCs are depleted to below detection limits (Chen et al. 2006a). These researchers identified six volatile aromatic compounds in stored biosolids sample even after 45 days of storage, due to degradation of aromatic amino acids.

2.8 **Proteins as the precursors of odours**

Researchers have shown that protein is the prevailing polymeric compound in activated sludge (Frolund et al. 1995) and also in wastewater influent (Raunkjær et al. 1994). The sources of protein in wastewater sludges are mainly exopolymeric substances (EPS) which are formed by microbial metabolism and cell lysis (proteins and polysaccharides) (Urbain et al. 1993). Around 50-70% of wastewater sludge is protein. Unless the digestion/stabilization process makes the protein more bioavailable, they remain unmetabolized. This bioavailability of proteins is primarily responsible for the release of odour compounds from wastewater sludges/biosolids (Forbes et al. 2004). Sulphur is found in L-cysteine and L-methionine which are the only 2 amino acids among 22 ribosomally incorporated protein amino acids (Bentley & Chasteen 2004). The protein extracted from activated sludge and anaerobically digested sludge has these two sulphur-containing amino acids. In particular, methionine concentrations were well correlated with the production of VOSCs, whereas cysteine was not significantly correlated to the VOSCs and odours (as determined by odour panel measurement) (Higgins et al. 2008). Furthermore, loosely bound protein extracted by phosphate buffer showed an even higher correlation to the production of VOSCs than the tightly bound protein, indicating that the bioavailable protein for odour production is mainly water soluble and biodegradable.

The quantities of protein in activated sludge and dewatered sludge extract varies widely depending on their origin and process conditions (Ras et al. 2008). Furthermore, the variety of extraction methods reported in the literature makes it even more variable. Centrifugation, ultrasonication and heating have been used for physical extraction,

whereas alkaline, ethylenediamine tetraacetic acid (EDTA) and cation exchange resin have been used for chemical extraction (Liu & Fang 2002). Amongst all the methods established, though, the colourimetric protein measurement method developed first by Lowry et al (1951), then modified by Frolund et al. (1995) to correct the interference due to humic substances, is predominantly used for protein extraction from sludge.

2.9 **Effect of shearing on biosolids odours**

It has been shown in previous studies that shearing has a great impact on the production of volatile organic sulphur compounds in biosolids. No matter what the digestion type is, centrifuge dewatering always produces more odours during storage than belt-press dewatered biosolids (Murthy et al. 2006; Chen et al. 2011). Shearing helps the generation of odorous sulphur compounds in many ways. In one way, the precursors of odours, which are proteins (containing cysteine and methionine), become more bio-available for degradation by the shear and destruction of bacterial cells. Chen et al. (2005) showed that high solids centrifuge (solids content 31-33%) generates 3.25 times greater peak methanethiol as well as 3.7 times lesser methane production rate compared to medium solids centrifuge (solids content 25-27%) postulating that shearing inhibits methanogens, which degrades the VOCS (Chen et al. 2005). On the contrary, Qi et al. (2008) showed evidence that an increase (from 10% to 19%) of solids content can potentially lessen the specific methanogenic activity regardless of the type of shearing imposed.

2.10 **Pathogen indicator regrowth and odour generation**

It has been shown that pathogen indicators such as fecal coliforms or total coliforms and odours are closely related. Chen et al. (2011) showed that in pre-pasteurization/mesophilic anaerobically digested and centrifuge dewatered biosolids, the fecal coliform regrowth pattern and the total VOSCs concentration in the headspace of the same samples during incubation followed the same trend, i.e. it peaked at 4-6 days and decreased below the detection limits after 10 days of storage. In the same study, the authors showed that *E. coli* trends were similar, but the peak of the concentration of total

VOSCs and the *E. coli* density did not appear at the same time, and they suggested that *E. coli* is one of the many odour producing bacteria in biosolids.

2.11 **Measurement of odours**

Odours are the perception experience when one or more chemical compounds come in contact with the human sensory system; odourants are the odour-causing chemical compounds.

Odour measurement is the first step to determine the factors controlling the odours as well as to develop effective control techniques. All odour measurements are classified into two groups, 1) analytical measurements, and 2) sensory measurements. Analytical measurements refer to the measurements of chemical concentration of the odourants that produces the odour, hence it does not measure the perceived effect of the odour; sensory measurement refers to the measurement of the odour itself. As there are no instruments to measure the odour directly, odour measurements are considered as subjective measurements, using the human nose. This measurement is usually performed by qualified odour panels.

2.12 **Sensory measurement of odours**

Objective parameters (i.e. those treating or dealing with facts without distortion by personal feelings) of perceived odour are:

Odour Concentration is the *dilution ratio* at which the odour is reduced to the level where it reaches either its detection threshold (probability of 0.5 of being detected, recognition not being necessary under the conditions of the test) or recognition threshold (probability of 0.5 of being recognized, which means what it smells like under the conditions of the test). The recognition threshold is 1.5 to 10 times higher than the detection threshold (Gostelow et al. 2001). Sensory methods used to measure odour concentration include the syringe static dilution method (ASTM D1391, withdrawn in

1985) and dynamic olfactometry, following standard methods ASTM E679-04 or EN 13725 (BSI 2003; ASTM 2011).

Odour Intensity is the expression of the relative strength of a perceived odour in reference to a specific odourant above the recognition threshold of the odour. Odour intensity is reported on a subjective category scale (rating the odour in a 5-point scale (0=no odour, 1=barely perceptible, 2=slight, 3=moderate, 4= strong and 5= very strong), by magnitude estimation (comparison of one odour with another odour by an arbitrary value) or by means of a referencing scale (use of butanol concentration for documentation and communication purposes in a reproducible format) (Gostelow et al. 2001). Frequently, odour intensity is expressed in parts per million (ppm) of n-butanol. Four Odour Intensity Referencing Scales (OIRS) are commonly used by odour laboratories,i.e. 12-point, 10-point, 8-point and 5-point scales (McGinley & McGinley 2000).

Odour Persistence is the dose-response function and expresses the relationship of odour concentration and odour intensity. It describes the rate at which a specific odour's perceived intensity decreases with increased dilution ratios. Odour persistency is described by two laws: One is the power Law proposed by S. S. Stevens (Gostelow et al. 2001)

$$I = kC^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq. } 1$$

The other is the Weber-Fechner law (Gostelow et al. 2001),

$$I = a \log C + b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq. } 2$$

where, I= Intensity of odour, C= Dilution ratio, k, n, a, b= Constants for each odour sample. The Weber-Fecher law is a good fit for the subjective category scale, whereas the Stevens law is appropriate for the magnitude or reference scale intensities (Gostelow et al. 2001).

Odour Character Descriptors are the reference vocabulary used to characterize odours. An odour wheel is often used for characterizing odours by assessing the intensity (levels

1-5) of eight primary odour wheel descriptors (McGinley & McGinley 2006): vegetable, fruity, floral, medicinal, chemical, fishy, offensive and earthy. Primary descriptors have been complemented by secondary descriptors. Another standard for odour descriptors is ASTM DS61: Atlas of Odour Character Profile, which gives standard odour descriptors of 146 items (ASTM 1992).

Subjective parameters (i.e. those relying on one's personal feelings or beliefs) of perceived odour are:

- Hedonic Tone –Measure of pleasantness versus unpleasantness of the odour using an arbitrary 21-point (-10 to +10) scale for ranking odours, -10 being the most unpleasant. It is independent of the odour descriptor.
- Annoyance - Interference with the comfortable enjoyment of life and property.
- Objectionable - Causes a person to avoid the odour or causes physiological effects.
- Strength - Word scales such as "faint to strong" (St. Croix Sensory Inc 2005)

2.13 **Sensory measurement of biosolids odours**

Quantitative determinations of the odour concentration, or subjective descriptions in terms of hedonic tone and strength, have become common in scientific research on wastewater biosolids. Murthy et al. (2003) distinguished four types of heat-dried biosolids in terms of hedonic tone, intensity, persistence and typical odour descriptor. Rosenfeld & Suffet (2004) defined the odourant associated with biomass, compost facility and land applied biosolids in terms of odour concentration and descriptive term. The importance of proper mixing during lime stabilization was properly described only with dilution to threshold and hedonic tone on Days 1, 3 and 7 of incubation (Krach et al. 2008a). Many researchers have focused on both sensory and analytical measurements of odours (Murthy et al. 2003b; Chen et al. 2006b; Krach et al. 2008b; Sekyiamah et al. 2008; Orzi et al. 2010; Lehtinen & Veijanen 2011b), while some used only analytical measurements of these odours (Rosenfeld et al. 2001a; Ábalos et al. 2002; Turkmen et al. 2004b; Novak et

al. 2006; van Leerdam et al. 2006; Dhar et al. 2011) as olfactometric measurements are expensive and depend highly on the human's olfactory perception.

2.14 **Analytical measurement**

Analytical measurement of odours is as important as sensory measurement, because proper mitigation of odours cannot be conducted without the knowledge of the compounds associated with the sample. Although correlation between the perceived odour and the odourants` concentration is very difficult, since a large number of compounds can create the perceived odour and analysis of every compound might not be possible, analytical measurement has been extensively used by researchers for its advantage of being reproducible, repeatable and accurate. There are two types of analytical measurements: one is on-site quantitative measurement of a single odorant and the other is off-site quantitative measurement of groups of compounds.

On-site measuring devices include electro-chemical equipment and colourimetric sorption tubes. Electro-chemical equipment can detect and provide quantitative measurement of a single compound. An example is the Jerome analyzer, which is widely used for measuring H_2S in ambient air (Adams et al. 2003). Colourimetric sorption tubes have been used by researchers to detect H_2S, DMS, mercaptans, amines and ammonia (Rosenfeld et al. 2001a; Dhar et al. 2011; Fang et al. 2012) in headspace jars. These tubes are commonly used in field measurement; although their accuracy and detection range are very limited, they give a quick indication of the presence and concentration of the particular odorous gas. Portable gas chromatographs (such as the Photovac Voyager) have also been used for *in-situ* measurement of VOSCs (Lehtinen & Veijanen 2011a).

The offsite measurement of the odorous gaseous compounds, especially volatile organic compounds and volatile sulphur compounds, is conducted mainly by gas chromatography (GC), which is the most powerful tool in terms of precision, accuracy and repeatability (Dewulf et al. 2002). A gas chromatograph carries the sample gas along with a carrier gas, typically helium or nitrogen, inside a column coated with a stationary phase. The gas

mixture is separated according to the affinity of the various constituents to the stationary phase (Sparkman et al. 2011). Several kinds of detectors and columns have been reported for detection of these compounds. VOSCs have been measured in headspace bottles using a flame ionizing detector (FID) (Chen et al. 2011), a pulse flame photometric detector (PFPD) (Du & Parker 2012) or a mass spectrometry (MS) detector (Murthy et al. 2006; Novak et al. 2006; Higgins et al. 2008; Krach et al. 2008b). The GC-MS combination is currently the most popular and the most accurate and sensitive method. Other detectors used with GC include the flame photometric detector (FPD) for DMS measurement (Dhar et al. 2011). Furthermore, a sulphur chemiluminescence detector (SCD) has been used in the petroleum and petro-chemical industries for detecting sulphur compounds (Hua et al. 2004).

Pre-concentration of the gaseous sample is necessary in many cases when the concentration in the headspace in too low. A number of techniques are available for concentration the sample, namely cryogenic sampling, sorbent tubes, thermal desorption or solid phase micro extraction (SPME) (Rosenfeld et al. 2001a). Due to some disadvantages, such as use of solvent and complicated setup of the other techniques, SPME is used extensively. It is a simple, fast and solvent-free extraction method for VOCs and VSCs (Ábalos et al. 2002).

At WWTPs, flux chambers are used to collect large volumes of biogas samples (Rosenfeld et al. 2001). For direct and simple collection canisters, tedlar bags or gas-tight vessels are used (Munoz et al. 2010).

2.15 **Odour control strategies at WWTPs:**

Proper mitigation of odours at WWTPs is achievable through a complete understanding of the odours in terms of the chemical components of the odourant as well as the perceived odour itself. Furthermore, different operating conditions can trigger different kinds and concentrations of odours and associate odourants. Odour control or reduction at WWTPs can be achieved in three ways; operational changes, design changes and add-

on process (Adams et al. 2008). Operational process optimization is the most effective solution for odour abatement. For example, poor digester performance can enhance the odour problem related to VOSCs (Higgins et al. 2006), also larger SRTs appear to produce less odorous biosolids (Adams et al. 2008). Mechanical pre-treatment prior to digestion showed a significant reduction in H_2S and MT production from digested biosolids (Dhar et al. 2011). Proper mixing during lime stabilization, optimized polymer doses, pH control, aluminum and iron addition are all effective odour- control strategies adapted by many WWTPs (Abu-Orf et al. 2005; Krach et al. 2008a; Chun et al. 2009). As add-on processes, the adsorption of odorous gases on activated carbon or other media, biofilters, scrubbers and air stipping have been studied extensively.

Chapter 3. Materials and Methods

3.1 Study overview

The study was conducted in three phases:

Phase 1: Preliminary detection

Phase 2: Detailed analysis of Raw, ED and HT samples

Phase 3: Manipulation of sludge characteristics to explain odour behaviour

Figure 3-1 shows an outline of the study.

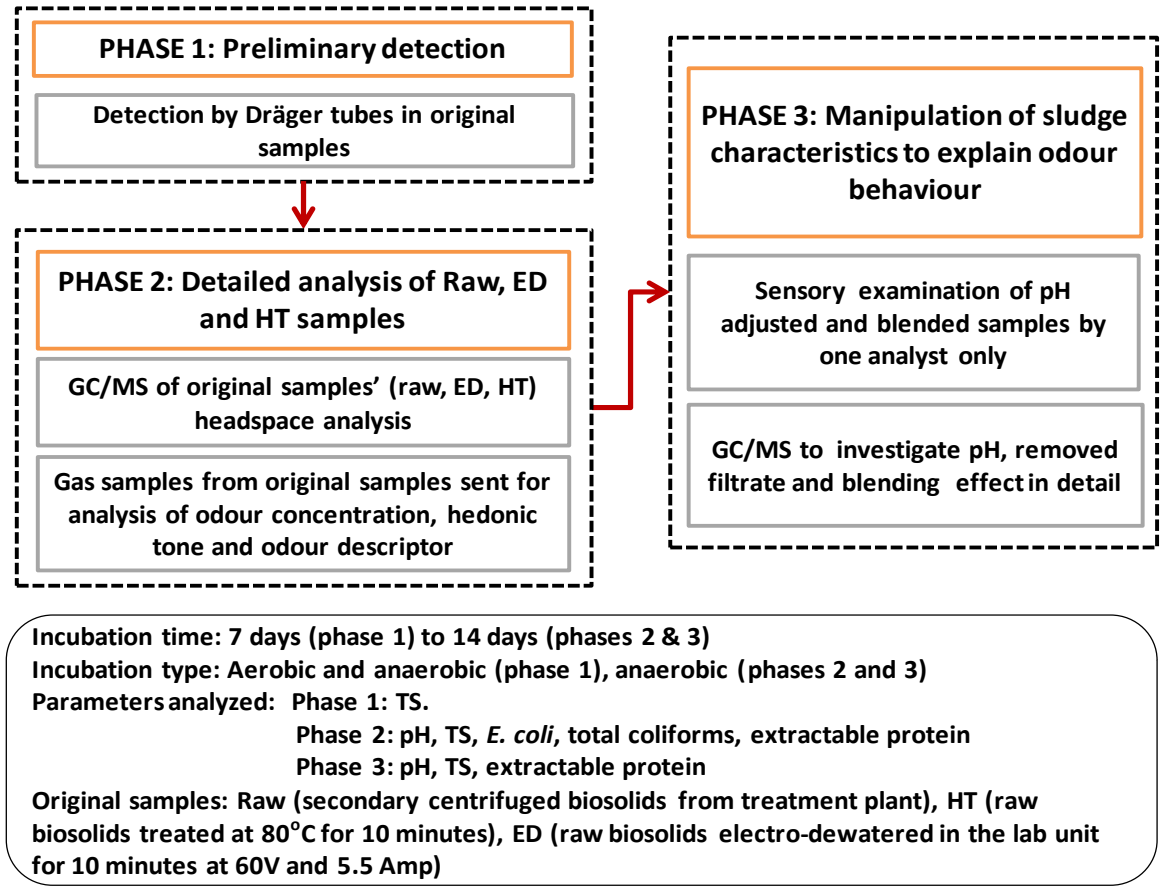


Figure 3-1: Study overview

Biosolids sample were collected from one treatment plant throughout the study. The biosolids sample was treated either by electro-dewatering or by heat treatment. Preliminary gas detection was done by Dräger short-term gas detection tubes, sensory experiments were conducted by the main experimenter in some cases and in others gas samples were sent for olfactometric evaluation by professional panellists. Analytical experiments were conducted by head space gas chromatography/mass spectrometry. Finally three hypotheses and some factors were studied to examine the different factors (regrowth potential, extractable protein, removed filtrate, inhibitory effect and pH) attributing to less odorous electro-dewatered biosolids. All sludge samples were incubated for 14 days for GC/MS analysis; analysis was done every second day. In all the experiments pH, total solids, protein, *E. coli* and total coliforms were measured.

3.2 **Biosolids samples**

Biosolids samples used in this study was collected from the Régie d'Assainissement des Eaux du Bassin de LaPrairie (RAEBL) near Montreal, Quebec. The plant layout is shown in *Figure 3-2*. The plant is a biological wastewater treatment plant. The source of the wastewater is 50% municipal from 5 municipalities and 50% industrial, mainly from the pulp and paper and food industries. The plant treats approximately 50,000-55,000 m^3/d (average) and produces around 10 dry tonnes/d of residual biosolids. The biosolids collected are secondary waste activated sludge which had been thickened by DAF, and dewatered by centrifugation. The polymer added prior to thickening was PAM-C4113 cationic polymer and added at a rate of 13-14 kg per tonne of solids to the combined sludge. The centrifuge operates at a speed of 3,000 rpm producing biosolids at 16-18% total solids. Fresh biosolids samples were collected and transported to McGill within 2 hours of collection. All sludge samples were stored at 4 ^oC and processing was done no later than 4 days after collection, but usually within 48 hours.

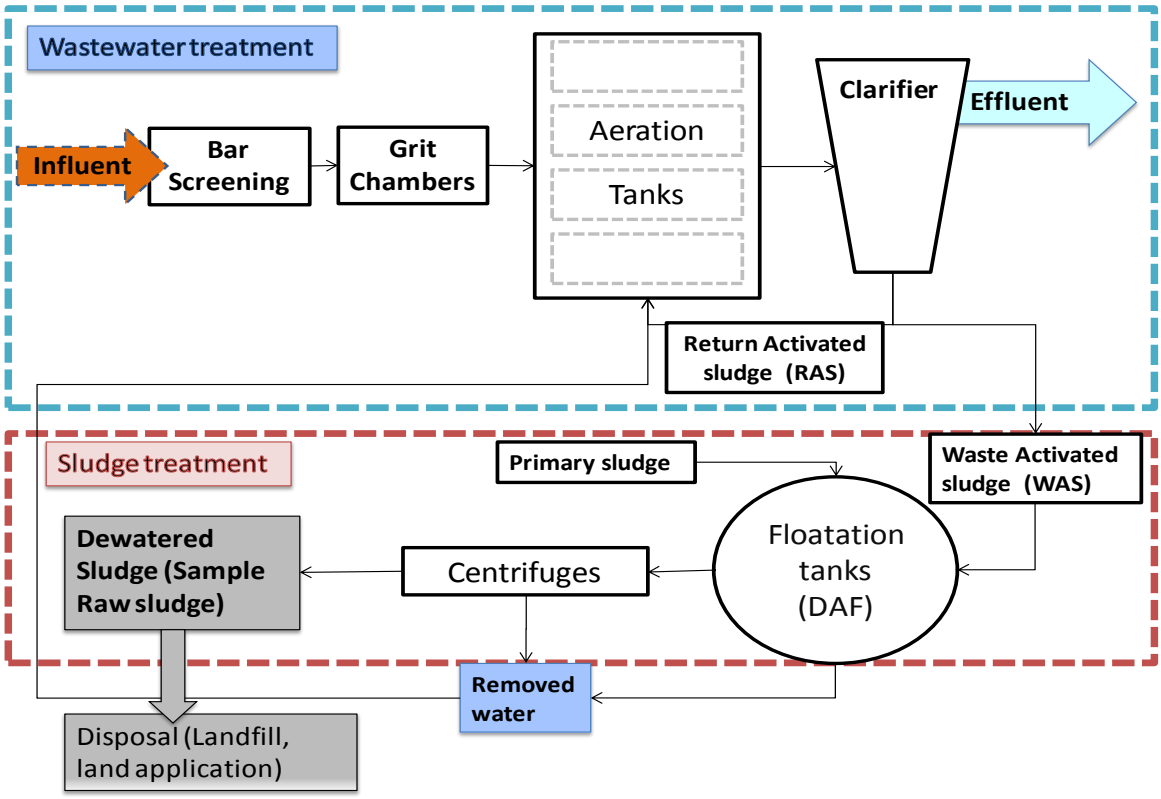


Figure 3-2: Schematic of the Régie d'Assainissement des Eaux du Bassin LaPrairie wastewater treatment plant.

3.3 Electro-dewatering

Electro-dewatering was conducted using a CINETIK® CK-laboratory model provided by OVIVO, a division of GL&V (Boucherville, Quebec, Canada). A diagram of the unit is shown in *Figure 3-3*.

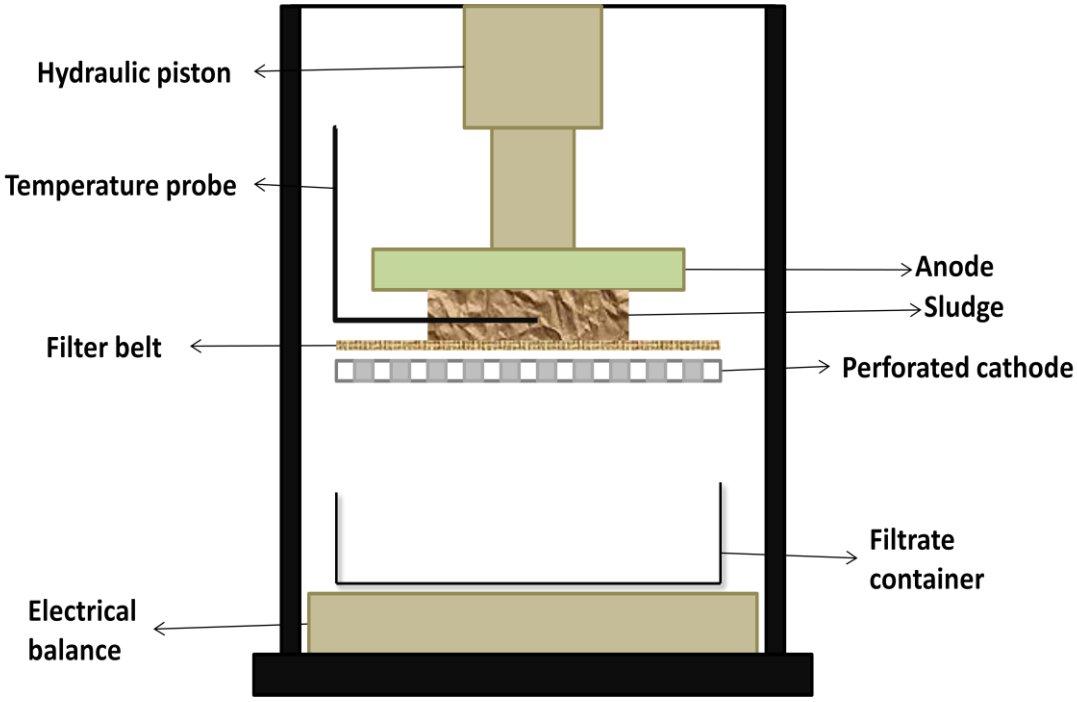


Figure 3-3: Schematic of CINETIK® CK-lab unit

On the top, a hydraulic piston was attached to the ceramic-coated titanium anode (160 mm by 160 mm), which compressed the sludge vertically between the anode and cathode. The water that was released from the sludge escaped through the perforated steel cathode (200 mm by 200 mm) and was collected in a square plastic container placed on a balance. The sludge temperature was measured by a thermocouple placed inside the sludge sample. Two additional temperature probes were attached to the anode and cathode. To prevent the sludge from falling through the perforated cathode, a filter (woven from 100% PPS Ryton) was used. To prevent spreading of the sludge sample, it was placed inside a 105 mm by 105 mm square plastic mold, a square plastic block was placed on top and the biosolids inside were pressed for 10 s at 152 kPa pressure. The mold and the block were then removed for electro-dewatering treatment.

For electro-dewatering treatment, 165 g of the wet biosolids sample were placed on the belt which was placed on the cathode. The treatment cycle was chosen to be 10 minutes (for inactivation of total coliforms and *E. coli* below detection limits), and the maximum

voltage and current were set at 60 V and 5.5 A respectively. These parameters were chosen based on previous studies with the same electro-dewatering unit (Navab-Daneshmand et al. 2012). The anode on top of the biosolids applied 152 kPa pressures to maintain contact while applying direct current electrical field. This applied pressure too low to have had an effect on dewatering and no odour experiments were conducted with only the pressure as a control test. The applied voltage remained between 40 V to 60 V, as maximum current was reached before the maximum voltage. The system continuously recorded the applied current, voltage, pressure, cake temperature, weight of removed filtrate, cake thickness and electrical energy used throughout the cycle. It should be mentioned here that only for the preliminary experiments (Phase 1), 1 mL $Ca(NO_3)_2$ at a concentration of 1 mmol/g was added to the top of the raw pre-pressed biosolids before electro-dewatering treatment to increase the conductivity of the sludge. Several other supporting electrolytes (NaCl, $CaCl_2$, $FeCl_3$, $NaNO_3$, $Fe(NO_3)_2$) were tested in previous studies, revealing no significant difference between the salts in terms of biosolids resistance, amount of removed filtrate and final biosolids temperature (Navab-Daneshmand et al. 2012). For the remaining experiments no electrolyte additive was used, as the electro-dewatering process performed well without adding any electrolyte.

3.4 **Heat-treatment**

This method was developed as a control to show the impact on inactivation of heat alone. Approximately 40 g of raw sample was placed in 50 mL glass tubes and kept inside a water bath at 80 ^{o}C for 16 minutes. During the development of the protocol, it was observed that it took around 6 minutes for the sludge to reach the final temperature and 10 minutes for inactivation below the detection limit at 80 ^{o}C, resulting in a total treatment time 16 minutes (Gul-E-Hina 2011).

3.5 **Biosolids incubation**

For the Dräger tube experiments (phase 1), biosolids were incubated both aerobically and anaerobically at room temperature (22 ^{o}C ± 0.5 ^{o}C). For anaerobic incubation,

approximately 100 g of biosolids sample were placed in 1 L mason jars, which were then capped with metal lids. The metal lids were pierced and a rubber stopper was fitted to facilitate flushing and these bottles were flushed with nitrogen gas at the sampling day after sampling. For aerobic incubation, the same procedure was used, but the bottles were left open vertically on the bench for 10 minutes every day.

For the rest of the study, for sensory analysis and gas chromatographic analysis, approximately 46 g of sludge samples were placed in 1 L media bottles capped with lids with opening to accommodate silicon septa. These analyses were done only under anaerobic conditions. These bottles were flushed with nitrogen after placing the sample inside on the first day and gas samples were collected from the headspace on a sampling day, but the bottles remained closed for the duration of the experiment (14 days). In all the experiments the bottles were placed on a roller apparatus (Wheaton Industries Inc., Millville, NJ, USA) to ensure proper mixing and uniform conditions. To observe aerobic or anaerobic conditions inside the bottles during the experiment, anaerobic indicator strips (BD GasPak ™, Franklin Lakes, NJ, USA) were placed inside the bottles. The strips remained blue if the conditions inside the bottles were aerobic, but the colour of the strips turned to white if the conditions were anaerobic.

3.6 **Physical-chemical parameters**

Biosolids were characterized initially by pH, total solids, volatile solids, total and soluble COD. The pH was measured on each sampling day. Approximately 0.8 g of wet biosolids were added to 9.2 g of distilled water and mixed for 20 minutes by magnetic stirrer at room temperature. The pH was measured with an Accumet ® gel-filled AgCl combination electrode (Fisher Scientific, Canada).

Total solids in the treated or untreated biosolids were measured initially and on each sampling day after gas sampling by Standard Method No 2540-B (APHA et al. 2012). The dryness/total solids defined by solids content within the sludge on weight by weight basis were measured for 7-14 days in each experiment. Biosolids samples were placed in

previously dried aluminium dishes and kept at 105 ^{o}C for 24 hrs. Solids with the weighing dish were weighed before and after drying, the loss of weight was used for solids calculations. The volatile solids were quantified by Standard Method No 2540-B E in previous studies (Navab-Daneshmand et al. 2012).

Total and soluble COD of the electro-dewatered filtrate were measured by Standard Method No. 5220-D (APHA et al. 2012).

3.7 **Loose protein extraction**

For the extraction of readily degradable loose protein, a method developed by Higgins et al 2008 was followed but modified. Approximately 10 g of biosolids samples were suspended in a solution of 50 mM pH 8 phosphate buffer (0.4215 g KH_2PO_4 and 8.1524 g K_2HPO_4 in 1 L distilled water) to a total volume of 100 mL (Higgins et al. 2008). Then the method was modified by placing 2 mL of these suspensions in 2 mL micro centrifuge tubes and centrifuged at 14,800 x g for 5 minutes. The supernatants were then collected for protein analysis. Analysis was performed by DC Protein Assay kit from Bio-Rad (Hercules, CA, USA) which is an improved modification of the well documented Lowry method (Lowry et al. 1951). The analyses were done in micro plates with triplicate samples. Absorbance at 750 nm in each well was measured by a Spectra Max M5 micro plate reader (Molecular devices, Sunnyvale, USA). Concentrations were calculated from a calibration curve of known bovine albumin (BSA) standards.

3.8 **Total coliform and *E. coli* enumeration**

Total coliforms and *E. coli* were measured by Standard Method No 9223 Colilert® reagent (APHA et al. 2012) from IDEXX laboratories (Westbrook, ME, USA) with some modifications for micro plates and the MPN method (Navab-Daneshmand et al. 2012). Approximately 1 g (but precisely weighed in each case) of biosolids sample was added to 40 mL of sterile PBS solution (80 g/L NaCl, 2 g/L KCl, 14.4 g/L Na_2HPO_4 and 2.4 g/L KH_2PO_4), for maintaining a constant pH during serial dilutions. For proper mixing of the biosolids, the sample and the PBS solution were homogenized with an ULTRA-

TURRAX® S10N-10G disperser (IKA® Works Inc. Wilmington, NC, USA). A selective growth medium was prepared by adding the Colilert® reagent to 100ml of PBS solution. In the microplate, 225 uL of the Colilert® medium was added to each of the well, and then 25 uL of the homogenized solution of biosolids sample was added to 4 wells of the first row of the microplate. After 7 times of serial dilution towards the end of the microplate, the plates were incubated at 35 ^{o}C for 24 ± 2 hrs. Spectra Max M5 micro plate reader (Molecular devices, Sunnyvale, USA) was used to read the absorbance at 420 nm for total coliform and fluorescence at 365 nm-excitation and 445 nm-emission for *E. coli*. The number of positive well responses (counted as positive if the reading is >2 for total coliform and >1000 for *E. coli*) was inputted in an online MPN calculator (Curiale 2004) to determine the MPN per gram of total solids. The detection limit of this method is 75-750 MPN per g total solids,.

3.9 **Gas sample analysis by Dräger short term detection tubes**

Preliminary detection experiments were conducted by Dräger short-term gas detection tubes (Dräger Safety Inc., Pittsburg, PA). Dräger tubes were small graduated glass tubes filled with appropriate chemical preparation which measured the mass reaction with the air contaminant and the length of discoloration indicated the concentration of the air contaminant of interest (Dräger Safety AG & Co KGaA 2008). Analysis was done for methanethiol (0.5-5 ppm), dimethyl disulphide (1-15 ppm), ammine (1-18mm; standard deviation ±30%; 10 mm discoloration in one strokes refer to 10 ppm ammonia, 30 ppm butylamine, 30 ppm cyclohexalamine, 20 ppm diethylamine, 20 ppm dimethylamine, 20 ppm ethylamine, 20 ppm methylamine, 20 ppm triethylamine, indicated in the instruction), H_2S (0.5-15 ppm) and ammonia (2.5 -50 ppm, discoloration less than 2.5 is measured by linear interpolation; standard deviation ±15%-20%; as indicated in the instructions). Dräger tubes detected hydrogen sulphide (H_2S) through precipitation reactions of metal salts with hydrogen sulphide by forming slightly soluble metal sulphides and detected amines by pH indicator reaction. The gas detector pump (Dräger Accuro 2000) was fitted to the tube and it pumped 100 mL of air sample in one stroke. The number of strokes required was indicated on the tube itself. The length of

discolouration indicated the amount of that particular gas present in the head space. A rubber socket was inserted (*Figure 3-4*) through the metal lids of the 1 L mason jars and silicon grease was used around to prevent any leaks (only for phase 1 experiments). Two needles were inserted through the socket, one being open to atmospheric air and the other one connected through the tube and pump system (shown in *Figure 3-4*). The dilution corrections by consecutive stroke are given in Appendix A: Preliminary experiment: Dräger tube test.

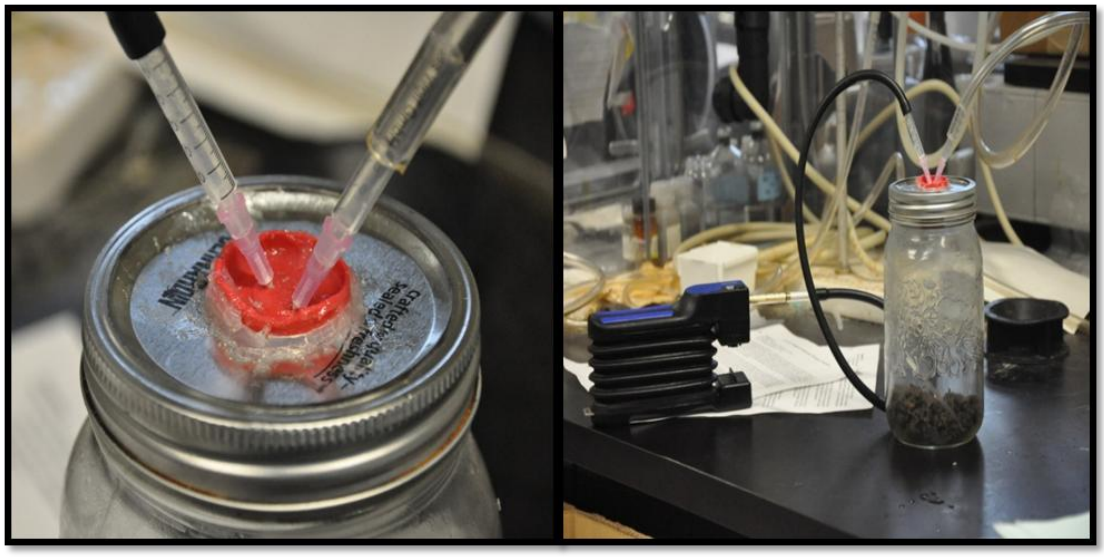


Figure 3-4: Headspace extraction for Dräger tube tests

3.10 **Olfactometric evaluation**

Olfactometric analyses of the headspaces above samples were conducted following ASTM E679-04 standard protocol and British Standard EN 13725 (BSI 2003; ASTM 2011) using an AC'SCENT® Dynamic Dilution Forced- Choice Triangular Olfactomer. Samples were sent overnight to Pinchin Environmental Ltd. (Mississauga, Ontario, Canada). There, a panel of five trained odour assessors was trained for accuracy and repeatability in accordance with BS 13725:2003. The "triangular forced choice" method

described by ASTM E679-04 was employed to present the sample to the assessors. For this analysis the headspace of the raw, electro-dewatered (ED) and heat treated (HT) samples were diluted by a factor of ~2.3 in nitrogen and sent for analysis. The pressure developed during incubation and the flow during dilution was measured by a gas flow meter (Cole Parmer, Vernon Hills, IL, USA). Samples were analyzed for detection threshold (DT), recognition threshold (RT), hedonic tone and odour descriptor.

3.11 **Gas sample analysis by gas chromatography/mass spectrometry (GC-MS)**

Samples from the headspace of the incubation bottles were analysed by GC-MS for the quantification of volatile sulphur compounds and trimethylamine. For each sampling day, 1 mL of headspace gas sample collected through the silicon septa was manually injected into the GC-MS using a gas tight syringe (Pressure Lok® Precision Sampling Corp. Baton Rouge, LA, USA). Headspace gas chromatography was performed with a Trace GC Ultra equipped with an ITQ 1100 external ion trap mass spectrometer (Thermo Scientific, Milan, Italy) using a 30 m 0.25 mm I.D. Rtx-5MSi column (Restek, Bellefonte, PA, USA). The carrier gas was helium with a flow rate of 0.5 mL/min. All gases were purchased from Praxair Canada Inc. (Mississauga, Ontario, Canada). The inlet temperature was 120^{o}C in split mode. The split flow was 75 mL/min and the split ratio was 150. Initially the oven temperature was 45 °C for 0.5 min, and then ramped to 100 °C at a rate of 45 °C per min, which was then held for 0.5 min. This was followed by another ramp to 300 °C at a rate of 30 °C per min that was then held for 1 min for a total run time of 20 minutes for each sample. Here, the selected compound detection was performed in full scan (mass range 10-350) and selected ion monitoring mode (SIM mode). DMS (≥99%) and DMDS (≥99%) (Sigma-Aldrich, St. Louis, MO, USA), and MT (2000ppm in nitrogen) (Linde Canada Limited, Mississauga, Ontario) standards were used to construct quantitative calibration curves. The ions for SIM mode for every compound were selected based on the relative abundance of the ion associated with each compound. The average retention times of the compounds MT, DMS and DMDS are respectively 2.09 s, 2.34 s and 4.34 s. The quantification ions and the confirmation ions used in this study for the

compounds selected are documented in *Table 3-1*. The calibrations curves of the compounds analysed are given in Appendix B: Calibration of MT, DMS and DMDS.

Table 3-1: Quantification and confirmation ion

Compounds	Quantification ions m/z	Other ions m/z (relative abundance)a
Methanethiol	47 (99.9%)	48 (89.9%), 46 (11.5%), 44(7.4%), 33 (5.1%)
Dimethyl sulphide	62 (99.9%)	47 (95.4%), 35(32.2%), 27 (20.7%),
Dimethyl disulphide	94 (99.9%)	79 (57%), 45 (47.8%)
Trimethyl amine	58 (99.9%)	59(68.3%), 30 (32.3%), 42 (24.8%)

[a] *(NIST 2005)*

3.12 **Adjustments of pH for phase 3**

In the last phase of the study, biosolids pH was adjusted for testing the pH hypothesis. For high pH ED samples (ED+NaOH, pH 6.8-7.1), NaOH was added to ED biosolids immediately after treatment. For low pH raw and HT samples, HCl was added to raw or HT biosolids before incubating in jars. The amount of NaOH and HCl added in each experiment varied slightly and this amount used was obtained from previous trial and error pH adjustment tests.

Chapter 4. Results

4.1 **Phase 1: Preliminary experiments: Dräger tube tests**

4.1.1 Physical characteristics of biosolids sample

Biosolids samples under the scope of the study, i.e. electro-dewatered (ED), heat-treated (HT) and raw (untreated) were characterized based on their physical parameters. The total solids of the HT samples were 18% (w/w), the same as the untreated biosolids (18%). The dryness (w/w) of the ED biosolids was 42%, achieved under the following conditions: 60 V, 5.5 A, treatment time 10 minutes and 1 mL of Ca $(NO_3)_2$ electrolyte added.

4.1.2 Dräger tube tests

Indication of the concentration of ammines and ammonia by Dräger tubes was based on a proprietary indicator reaction. The colour changed from yellow to blue for both of these tubes. For ammines the basic reacting gases (ammonia, butylamine, cyclohexalamine, diethylamine, dimethylamine, ethylamine, methylamine, triethylamine) indicated the discolouration, and differentiation was not possible by this test. Results of ammine and ammonia detection are shown in *Table 4-1*.

Table 4-1: Maximum concentrations of ammines and ammonia in aerobic and anaerobic samples

Maximum detected concentrations in AEROBIC samples (6^{th} day)		
	Ammines (ppm as per ammonia)	Ammonia (ppm)
Raw	13	5.3
ED	4.2	4.2
Maximum detected concentrations in ANAEROBIC samples (6^{th} day)		
Raw	3.7	3.3
ED	2.7	1.5

Table 4-1 shows that the highest concentrations of ammines (13 ppm as ammonia) or ammonia (5.3 ppm) were observed in the raw aerobic samples at day 6. Hydrogen sulphide (H_2S) in the preliminary experiment was only detected twice in raw aerobic

samples, but not in any other anaerobic samples. Reduced sulphur compounds methanethiol (MT) and dimethyl sulphide (DMS) detection results are documented in the following *Table 4-2*. The table shows that for anaerobically incubated samples, MT and DMS concentrations were above the detection range for the raw (untreated) and the heat-treated (HT) biosolids and the electro-dewatered (ED) samples showed lower concentrations on all sampling days.

Table 4-2: Methanethiol (MT) and dimethyl sulphide (DMS) concentrations in untreated (Raw), electro-dewatered (ED) and heat-treated (HT) biosolids samples following anaerobic incubation

Biosolids samples	MT (ppm)				DMS (ppm)			
	Day 4	Day 5	Day 6	Day 7	Day 4	Day5	day 6	Day 7
Raw	>100	>100	>100	>100	~	>300	>300	~
ED	~	100	1.4	6.7	~	300	86.5	25.9
HT	~	>100	>100	>100	~	~	~	~

4.2 **Phase 2: Detailed analysis of Raw, ED and HT samples**

4.2.1 Physical-chemical characteristics of biosolids samples

In phase 2, biosolids pH and total solids (w/w) were measured only immediately after the treatment and after 14 days of anaerobic incubation. The pH and the total solids are shown in *Figure 4-1*. The average dryness of the electro-dewatered biosolids was 41% immediately after treatment which decreased to 35% after 14 days of incubation. The total solids of the HT and raw sample remained virtually constant over the incubation period; on Day 0 they were 17% and 18% respectively. The average pH of the ED, HT and raw biosolids also remained almost constant between Days 0 and 14; on Day 0, they were 5.0, 6.8 and 6.8, respectively. It is noteworthy that the temperature of the biosolids during ED treatment gradually increased due to the increase in apparent resistivity of the sludge, and it reached a plateau of around 100 ^{o}C after 10 minutes of treatment. Details of the temperature and the sludge resistance results can be found in Navab-Daneshmand et al.(2012).

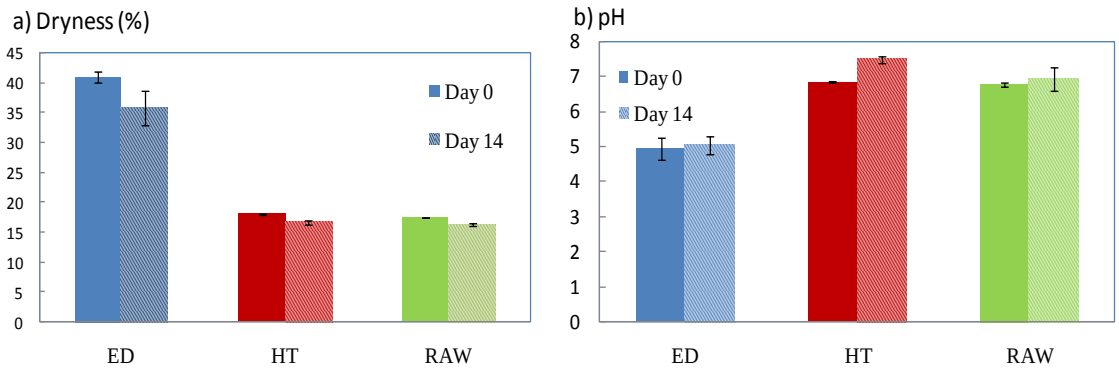


Figure 4-1: a) Dryness and b) pH of electro-dewatered (ED), heat-treated (HT) and raw (RAW) samples on Days 0 and 14 under anaerobic conditions. Bars represent the range of two replicates.

Protein concentrations were measured at the beginning and at the end of anaerobic incubation. HT samples had the highest amount of readily extractable protein (74 mg/g-TS) and the raw sample had the lowest (26 mg/g-TS) on day 0. These protein concentrations increased after 14 days in the ED and raw samples, but decreased in the HT samples, as shown in *Figure 4-2*.

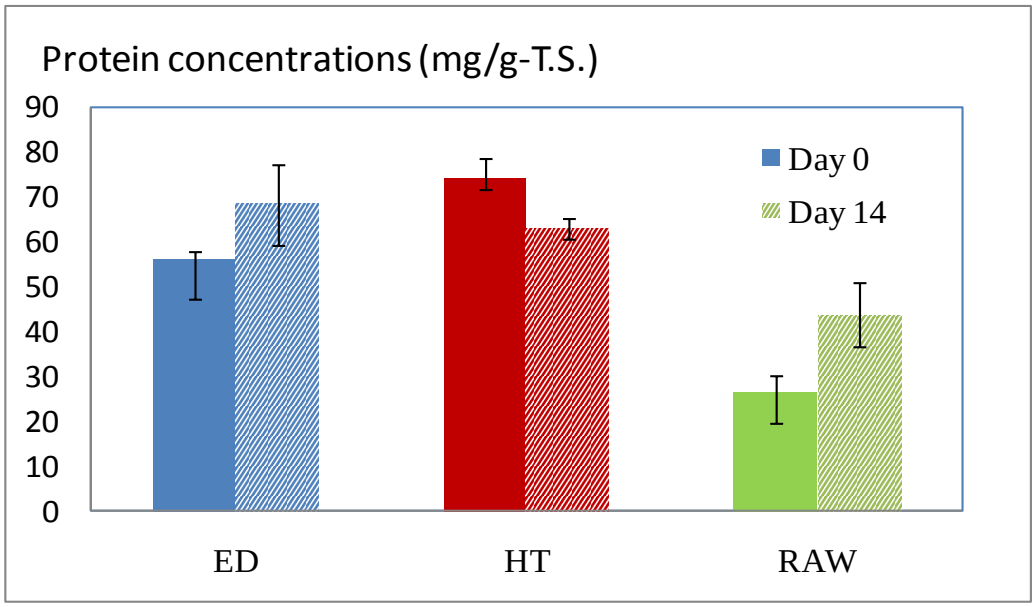


Figure 4-2: Protein concentrations in mg/g of total solids for electro-dewatered (ED), heat-treated (HT) and raw (RAW) samples on Days 0 and 14 under anaerobic conditions. Bars represent the range of two replicates.

4.2.2 Microbial characteristics of biosolids samples

E. coli and total coliforms for the samples tested showed the same trend (*Figure 4-3*). Both the *E. coli* and the total coliforms for the ED samples immediately after the treatment were below the detection limit (210 MPN/g-TS) and remained low after 14 days of incubation. Similarly, the MPN counts for HT biosolids were also below the detection limit (380 MPN/g-TS) before and after incubation. The raw sample had *E. coli* concentrations of 4.8 logs MPN/g-TS and total coliform concentrations of 7.5 logs MPN/g-TS, and showed a decrease of 1 log and 2.5 logs in *E. coli* and total coliform counts respectively after storage.

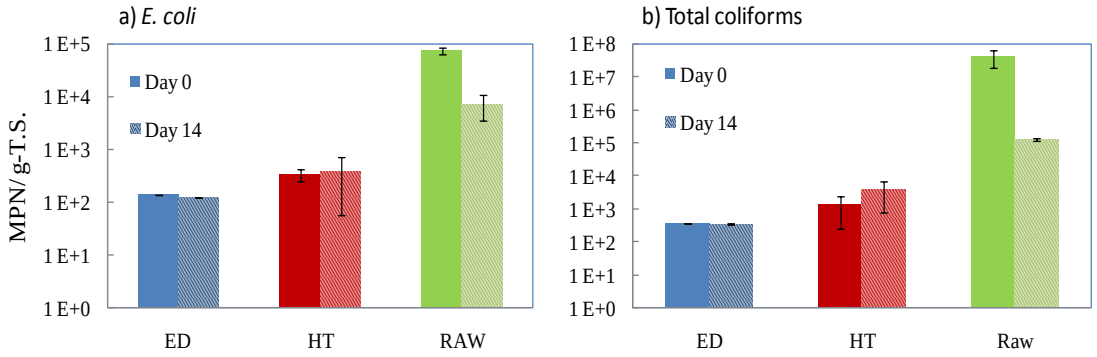


Figure 4-3: a) E. coli and b) Total coliforms in MPN/ g of total solids for electro-dewatered (ED), heat-treated (HT) and raw (RAW) samples on days 0 and 14 under anaerobic conditions. Bars represent the range of two replicates.

4.2.3 Sensory evaluation

An olfactometry analysis of the original samples (untreated (raw), heat treated (HT) and electro-dewatered (ED)) as well as a blank (nitrogen gas) for control was conducted by Pinchin Environmental Inc. (Mississauga, Ontario, Canada), who provided a detailed odour evaluation report (Appendix C: Odour evaluation report). The detection threshold (DT) and the recognition thresholds (RT) were adjusted to the actual field dilutions. Values obtained after the analysis are presented in the *Table 4-3*.

Table 4-3: Sensory odour characterization results

Parameter	Biosolids samples			
	Blank	Raw	HT	ED
Detection threshold	361	25,012	17,871	12,918
Recognition threshold	214	11,455	8,328	5,618
Hedonic tone (range)[1]	-5 (-2 to –9)	−3 (−5 to −2)	−3 (−7 to −2)	−3 (−4 to −2)
Main primary odour descriptor	Fishy	Offensive	Offensive	Offensive

[1]Hedonic tone scale: unpleasant −10, neutral 0, pleasant +10

Table 4-4: The odour descriptors' relative intensity

Parameter	Biosolids samples		
	Untreated	Heat-treated	Electro-dewatered
Odour characters in reference vocabulary wheel[1]			
Offensive	1.50	2.15	1.35
Earthy	0.50	0.90	1.15
Fishy	0.50	0	0
Vegetable	0	0	0
Fruity	0.4	0	0.2
Floral	0	0	0
Medicinal	0.4	0	0.25
Chemical	0.2	0	0
Most commonly selected specific descriptor	garbage, musty, sewer, rancid	offensive	musty, sewer
Other descriptor	chemical, chlorinus, fruity, lemon, manure, maple, medicinal, offensive, orange, raw meat, sour vinegar	earthy, eucalyptus, garbage, manure, mashroom, musty, pine, raw meat, rose like, rotten eggs, sewer, sour, swampy, urine, yeast	anesthetic, blood, cloves, disinfectant, earthy, fruity, garbage, manure, medicinal, melon, offensive, raw meat, sour, swampy

[1]Primary descriptor relative intensity scale: not utilized by panelists 0, mild odour 1, strong odour 5

The detection and the recognition thresholds for the untreated raw samples were the highest whereas the electro-dewatered sample had the lowest. Though the average hedonic tone of the raw, HT and ED biosolids were the same, describing the odour as

equally offensive, the relative odour intensity scale of the different odour descriptors provided by the report in a histogram showed that the heat-treated sample was the most offensive *(Table 4-4*). When characterized by the odour reference vocabulary scale (McGinley & McGinley 2006) the odours from the untreated biosolids were described as garbage, musty, sewer and rancid whereas the odours from the ED biosolids were described mainly as musty, earthy and sewer.

4.2.4 Analytical experiments

Results of methanethiol (MT), dimethyl sulphide (DMS) and dimethyl disulphide (DMDS) measurements from phase 2 are shown in *Figure 4-4.* The concentrations of these three gases for the ED sample were at the detection limit (78 ppmv for MT, 59 ppmv for DMS and 8 ppmv for DMDS) throughout the incubation period. In contrast, the average concentrations of MT for the HT and raw samples increased and peaked on Day 11 at 267 ppmv and 164 ppmv respectively, then decreased. The DMS concentrations peaked at Day 7, then decreased rapidly and returned to the detection limit. DMDS was only identified in the HT sample and showed an average peak concentration of 966 ppmv on Day 7, then decreased to 146 ppmv on Day 14. *Figure 4-5* shows the total elemental sulphur which is the sulphide-weighted concentrations of MT. DMS and DMDS (1 MT + 1 DMS + 2 DMDS). The total average sulphur concentrations peaked at 2,292 ppmv and 830 ppmv on day 7 for the HT and raw biosolids respectively then decreased to 588 ppmv and 178 ppmv on day 14 respectively.

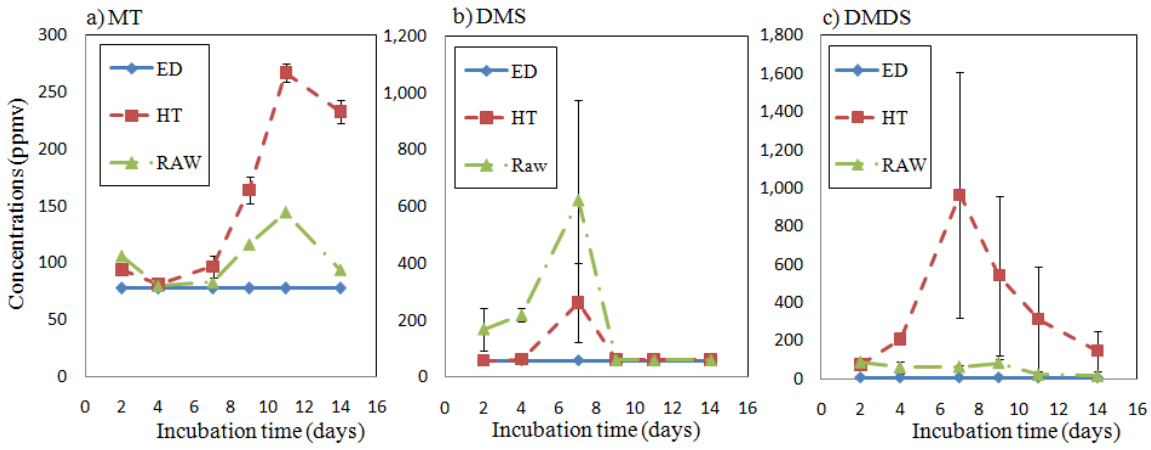


Figure 4-4: Concentrations of a)methanethiol (MT) b)dimethyl sulphide (DMS) and c)dimethyl disulphide (DMDS)in the headspace of anaerobically incubated electro-dewatered (ED), heat-treated (HT) and untreated (RAW) samples. Bars represent the ranges of two replicates. Note that the vertical scale of a, b and c are different.

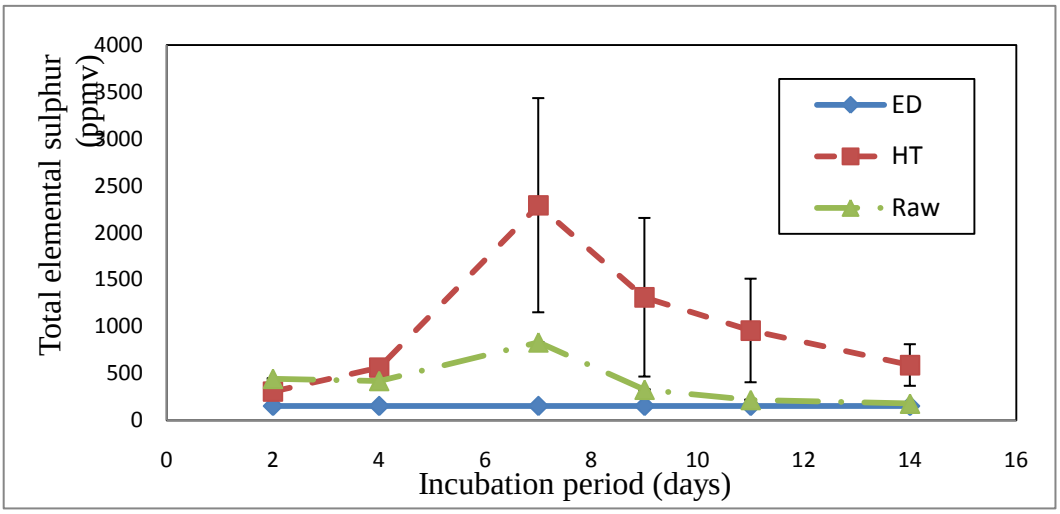


Figure 4-5: Concentrations of total elemental sulphur (S) in the headspace of anaerobically incubated electro-dewatered (ED), heat-treated (HT) and untreated (RAW) samples. Bars represent the ranges of two replicates..

4.3 Phase 3: Manipulation of biosolids characteristics to explain ED effects on odour production

So far, in phases 1 & 2, it has been clearly demonstrated that ED process reduces the odours and to investigate the odour behaviour of these ED biosolids, three hypotheses

were tested as mentioned in introduction. In this phase, biosolids characteristics (pH, dryness) were adjusted and manipulated to investigate those hypotheses (low pH, odour precursors and inhibitory effects).

4.3.1 Electro-dewatering treatment parameters and filtrate characteristics

During each cycle of electro-dewatering treatment, approximately 60-70 mL of filtrate were collected; this filtrate had a high pH of 12.86 ± 0.04 (*Table 4-5*) and a distinct ammonia smell. It also contained a high concentration of total COD (16,400 mg/L) and protein (3,280 mg/L as BSA). Unlike phase 1 ED treatments, no salt ($Ca(NO_3)_2$) was added before the treatment.

Table 4-5: ED treatment parameters and filtrate characteristics

Parameters	
Raw biosolids treated in one cycle	165 g
Treatment time	10 minutes
Maximum applied voltage	60 V
Maximum applied current	5.5 A
Filtrate volume collected	60-70 mL
Filtrate pH	12.86
Filtrate total solids	1.9 % (w/w)
Filtrate total COD	16,400 mg O_2/L
Filtrate soluble COD	16,000 mg O_2/L
Filtrate protein	3,280 mg/L as BSA 8 mg/g-TS of raw

4.3.2 Physical chemical characteristic of biosolids samples

In phase 2, two types of experiments were conducted. In the first experiment (E1) only the pH of the biosolids was adjusted; the total solids for these pH-adjusted samples remained the same as the original samples. In the second experiment (E2), biosolids pH as well as biosolids dryness were also adjusted. The total solids in E1 and E2 hardly changed after the incubation period for all the samples. The total solids (w/w) in percentage for these two experiments are listed in *Table 4-6.* The total solids of the ED

samples (30-36%) were slightly lower than those of phase 2. In E2 the total solids were adjusted at the beginning before incubation; except for the ED sample, the total solids for all the other pH-amended samples were adjusted to 16-20%, which was that original raw sample.

Table 4-6: Total solids (%) of biosolids samples in E1 and E2

E1		E2	
	Day 0 (%)		Day 0 (%)
ED	35.6	ED	30.4
HT	19.6	RAW	16.7
RAW	17.0		
EDF[1]	17.8	EDF	19.4
ED+ NaOH[2]	34.1	ED+ NaOH	19.4
RAW+HCl[3]	18.0	EDF+HCl[5]	20.1
HT+HCl[4]	18.4	EDW[6]	17.8
		EDRAW[7]	19.8

[1]EDF: Electro-dewatered, filtrate added (pH 6.8-7.1)
[2]ED+NaOH: Electro-dewatered, base added (pH 6.8-7.1)
[3]RAW+HCl: Raw, acid added (pH 4.5-4.8)
[4]HT +HCl: Heat treated, acid added (pH 4.5-4.8)
[5]EDF+HCl: Electro-dewatered, filtrate and acid added (pH 4.5-4.8)
[6]EDW: Electro-dewatered, distilled water added (pH 4.5-4.8)
[7]EDRAW: Electro-dewatered and raw blended (50/50%), HCl added (pH 4.5-4.8)

Similar to previous experiments (section 4.2), biosolids pH measured on each sampling day remained relatively constant through the incubation period at 6.6 for the untreated biosolids, 7.15 for the HT biosolids, and 4.4 for the ED biosolids (*Figure 4-6*). The pHs of the untreated raw, ED and HT biosolids were adjusted immediately before incubation such as to generate a sample of near neutral pH and low pH for each treatment. Thus, HCl was added to the untreated and heat-treated biosolids to lower the pH to the level of the ED biosolids, and NaOH was added to the ED biosolids to neutralize them. Finally, the filtrate was also added to the ED biosolids (EDF) as an alternative pH neutralization, which also added back some of the removed COD and loose proteins. This last sample (EDF) showed a slightly lower pH (6.0) than the raw sample after mixing with the high

pH filtrate and the ED biosolids (*Figure 4-7*). The unadjusted pH and high pH adjusted samples kept relatively constant pHs during the incubation.

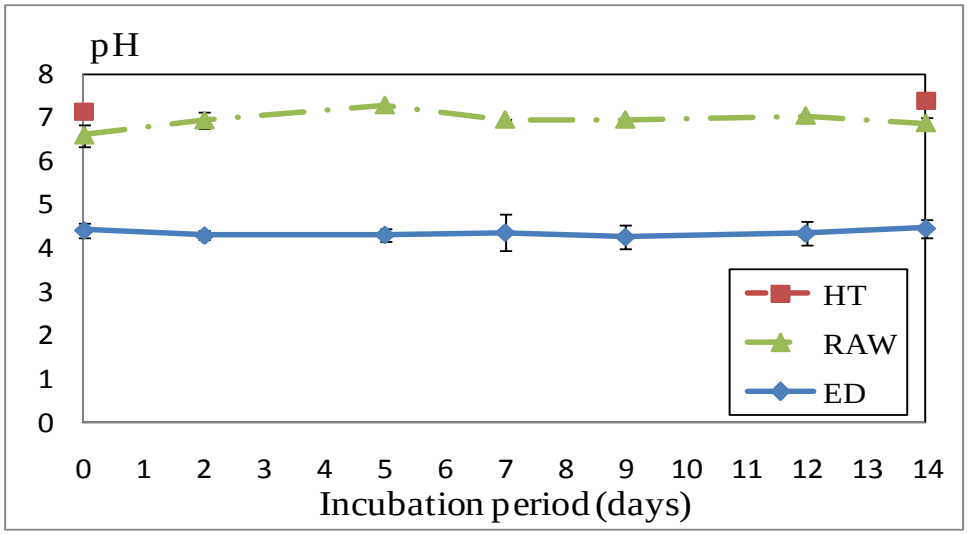


Figure 4-6: Biosolids pH for electro-dewatered (ED), heat-treated (HT) and raw samples over 14 days under anaerobic conditions. Bars represent the range of two replicates. The pH of HT was measured only once on Days 0 and 14.

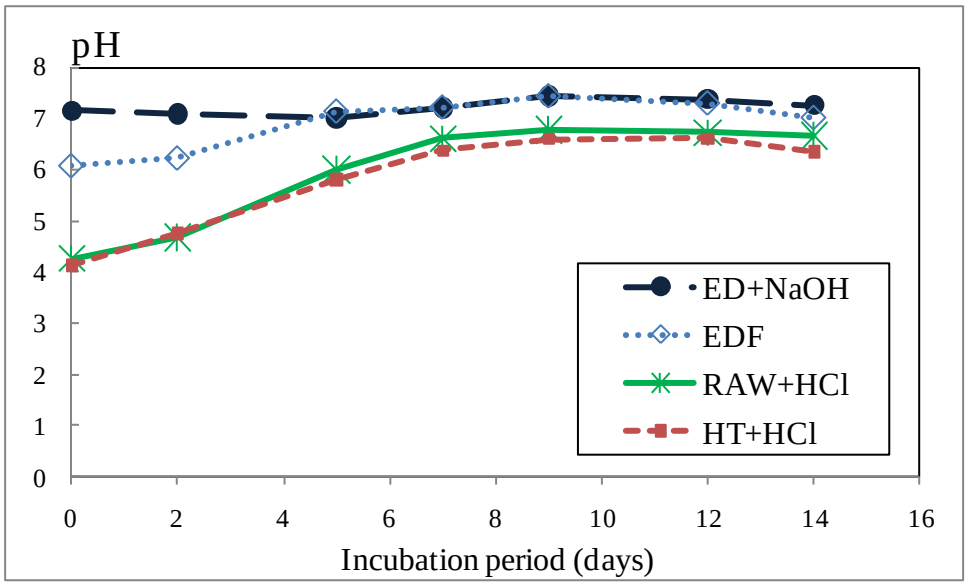


Figure 4-7: Biosolids pH of electro-dewatered added filtrate (EDF), electro-dewatered added NaOH (ED+NaOH), raw added acid (RAW+HCl) and heat-treated added acid (HT+HCl) samples over 14 days under anaerobic conditions. The ED+NaOH sample was not dryness adjusted.

However, the pHs of low pH adjusted samples (RAW+HCl and HT+HCl) gradually increased until it reached a plateau of 6.4 at day 7 and remained there for the rest of the incubation time (*Figure 4-7*). The EDF sample also showed a small increase and stabilized at 6.9 from day 5. Similar results for samples of E2 are given in *Figure 4-8.* In E2 biosolids pH as well as dryness were adjusted as described in *Table 4-6.* Unlike E1, the low pH EDF+HCl sample pH remained constant at 4.2-4.4 for the incubation time.

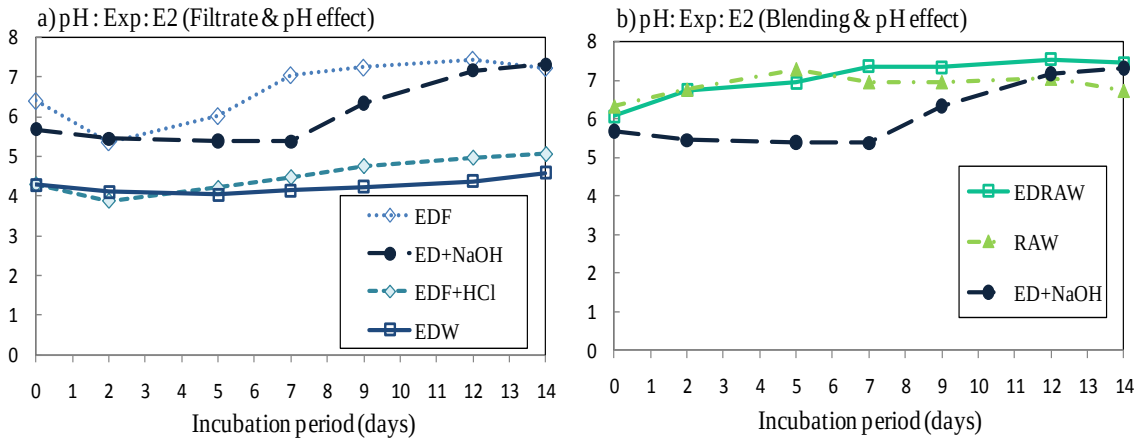


Figure 4-8: Biosolids pH for a) electro-dewatered filtrate added (EDF), electro-dewatered NaOH added (ED+NaOH), electro-dewatered filtrate and HCl added (EDF+HCl) and electro-dewatered distilled water added (EDW) b) biosolids pH for blended electro-dewatered and raw NaOH added (EDRAW), raw (RAW) and electro-dewatered NaOH added (ED+NaOH) samples over 14 days under anaerobic conditions. The ED+NaOH sample was dryness adjusted.

Protein concentrations for all the samples from experiment E1 and E2 at day zero are given in a bar chart in *Figure 4-9*. The RAW and the EDRAW had the lowest amounts (45 mg/g-TS and 39 mg/g-TS respectively) of extractable protein whereas the EDF had the highest value of 108 mg/g-TS.

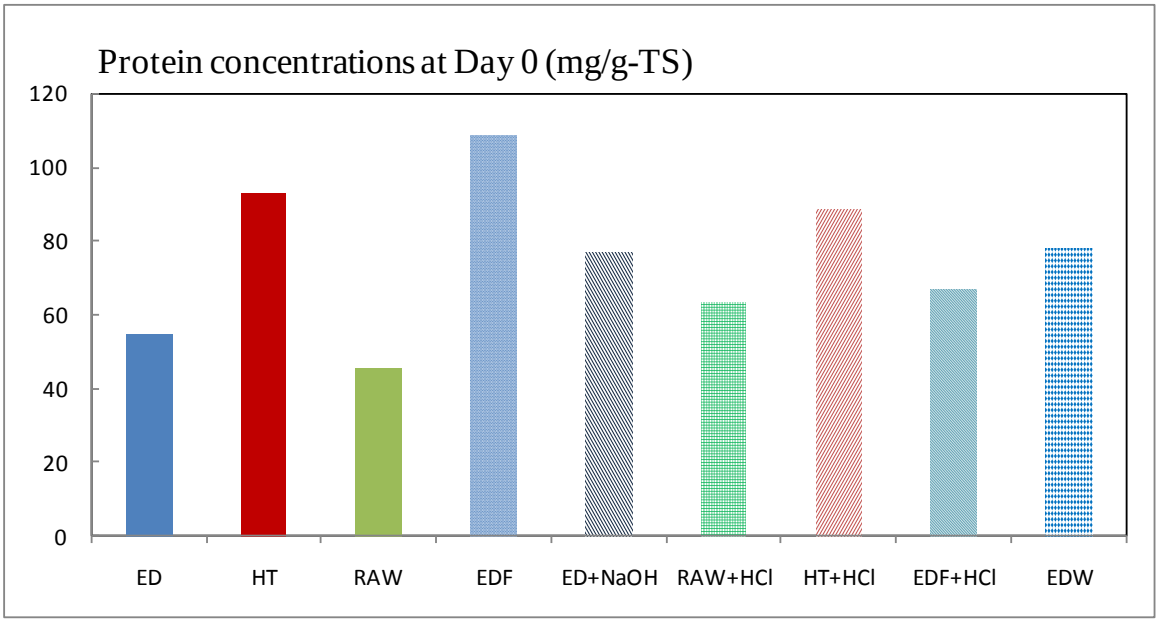


Figure 4-9: Day 0 protein concentration in mg/g-total solids for the samples, electro-dewatered (ED), heat treated (HT), raw (RAW), electro-dewatered filtrate added (EDF), electro-dewatered NaOH added (ED+NaOH), raw acid added (RAW+HCl), heat treated acid added (HT+HCl), electro-dewatered filtrate and HCl added (EDF+HCl), electro-dewatered distilled water added (EDW) and blended electro-dewatered and raw base added (EDRAW).

4.3.3 Microbial regrowth in biosolids samples

Microbial regrowth was measured during the limited sensorial analysis of the phase 3 of this study; results are in *Figure 4-10*. The figure shows that the *E. coli* counts in the treated samples (ED and HT) as well as those in the pH adjusted samples (ED+NaOH, EDF, HT+HCl) remained below the detection limit throughout the storage period. The RAW and the RAW+HCl samples showed a slight increase in *E. coli* counts from the initial 4.2 log and 2.9 log to 4.7 log and 4.2 log respectively. Total coliforms counts for these samples showed similar results (not shown).

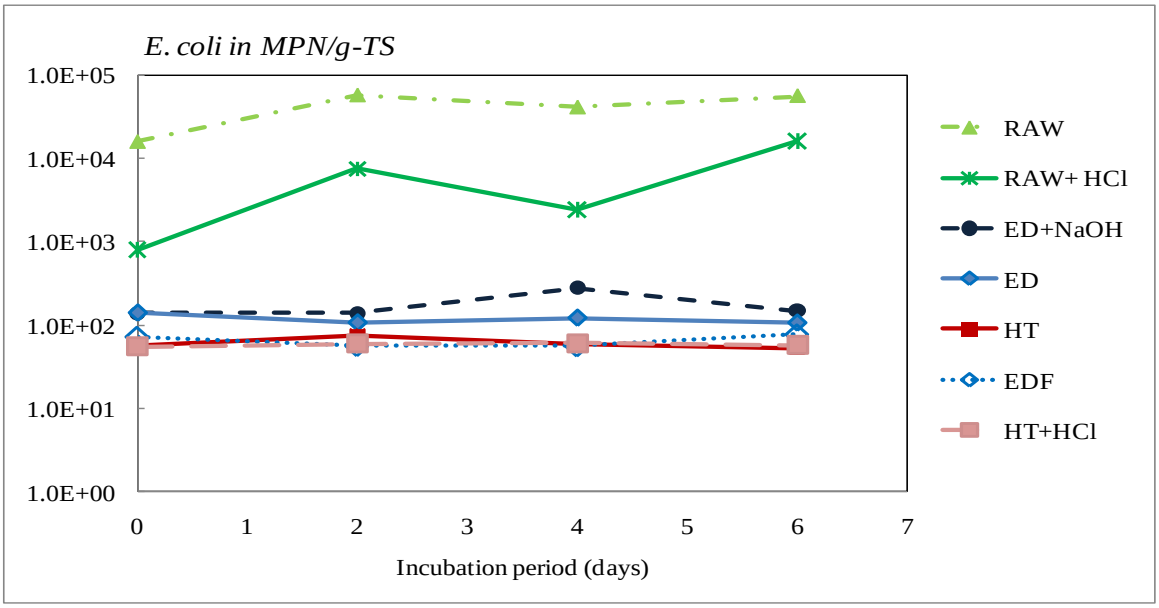


Figure 4-10: E. coli regrowth in biosolids samples raw (RAW), raw added acid (RAW+HCl) electro-dewatered added NaOH (ED+NaOH), electro-dewatered (ED), heat treated (HT), electro-dewatered added filtrate (EDF), heat treated added acid (HT+HCl) over 14 days of anaerobic incubation

4.3.4 Sensory evaluation

Limited sensory analyses by one analyst were first conducted before the precise analytical experiments. To examine the effect of pH on odours, the manipulated pH samples were analyzed for odours (*Table 4-7*). The raw biosolids was characterized by an intense and low rotten smell (IRS and LRS), the odours from the electro-dewatered biosolids were characterized by intense and low earthy smell (IES and LES) immediately after treatment. After 2 days of incubation the raw biosolids possessed an intense rotten smell while the odour for the same low-pH raw biosolids (RAW+HCl) was observed as a low intensity rotten smell. The HT+HCl sample's perceived odour was similar to the earthy smell of the ED sample, but the odour was identified as less objectionable as compared to the HT sample. At the end of the 6th day of incubation, the EDF odour was the most offensive. The low pH of the RAW+HCl and HT+HCl samples did not remain stable over 6 days of incubation; it started to increase after Day 4 and so did the intense rotten smell (*Table 4-7*).

Table 4-7: Limited sensory test results of pH-manipulated ED, HT and RAW samples

Days	ED	EDF[1]	ED+NaOH[2]	Raw	Raw+ HCl[3]	HT	HT+HCl[4]
0 (Measured pH)	4.6	5.7	7.4	7.3	4.4	6.6	4.8
2 (Measured pH)	4.4	5.6	7.1	7.1	4.8	7.2	5.0
2 (Odour descriptor)	LES[a]	LES	LES	IRS[a]	LRS[a]	LRS	LES
4 (Measured pH)	4.3	5.7	7.5	6.9	5.5	7.2	5.2
4 (Odour descriptor)	IES[a]	IRS	LES, LRS	IRS	IES, LRS	IRS	LES
6 (Measured pH)	4.3	6.3	7.5	6.8	6.4	7.4	6.1
6 (Odour descriptor)	IES	IRS	LRS	IRS	IRS	IRS	IRS, LES

[1]EDF: Electro-dewatered filtrate added
[2]ED+NaOH: Electro-dewatered NaOH added
[3]RAW+HCl: Raw acid added
[4]HT +HCl: Heat treated acid added
[a]LES: Low earthy-sweet, IES: Intense earthy-sweet, LRS: Low rotten biosolids, IRS: Intense rotten biosolids

Table 4-8: Sensory test results of odours produced by different mixtures of raw and electro-dewatered biosolids incubated anaerobically for 6 days.

Incubation Day	100% ED[a]	75% ED + 25% Raw	50% ED + 50% Raw	25% ED + 75% Raw	10% ED + 90% Raw	100% Raw
1	LES[b]	LES	LES, LRS	LES, LRS	LES, LRS	IRS
2	LES	LES	LES, LRS	LES, LRS	LES, IRS	IRS
3	LES	LES, LRS[b]	LES, LRS	LES, IRS	IRS	IRS
4	IES[b]	LES, LRS	LES, IRS[b]	IRS	IRS	LRS
5	IES	LES, LRS	IRS	IRS	IRS	LRS
6	IES	LES, IRS	IRS	IRS	IRS	LRS

[a]ED: Electro-dewatered biosolids
[b]LES: Low earthy-sweet, IES: Intense earthy-sweet, LRS: Low rotten biosolids, IRS: Intense rotten biosolids

In a separate sensory experiment, to investigate the inhibitory effect of the electro-dewatered biosolids, electro-dewatered and raw biosolids were blended at different percentages with the same mass of raw biosolids in each bottle and incubated as a separate experiment. Results are shown in *Table 4-8.* The rotten odours of the raw

biosolids decreased with an increase in the percentage of electro-dewatered biosolids. In addition, the intensity of the rotten odours of the raw biosolids decreased after 3 days, but the intensity of the earthy sweet smell of the ED biosolids increased after the same period.

4.3.5 Analytical experimentation

Phase 3 analytical experiments were conducted on the pH-manipulated and blended sample as well as on the original samples. The GC/MS analysis was conducted for quantification of methethiol (MT), dimethyl sulphide (DMS), dimethyl disulphide (DMDS) and trimethyl ammine (TMA). Unlike phase 2 of the study, in this phase only the MT could be quantified, and DMS, DMDS were not detected under the conditions of the

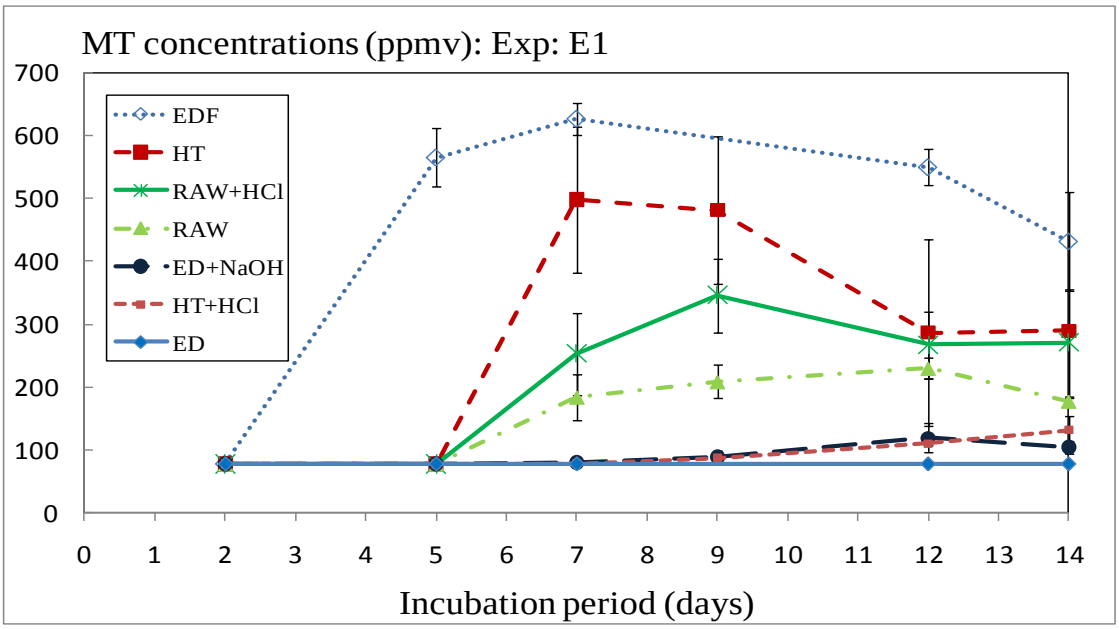


Figure 4-11: Methanethiol (MT) concentrations in ppmv of the electro-dewatered added filtrate (EDF), heat-treated (HT), raw acid added (RAW+HCl), raw (RAW), electro-dewatered NaOH added (ED+NaOH), heat-treated acid added (HT+HCl) and electro-dewatered (ED) for 14 days of anaerobic incubation. Error bars show ranges of two replicates.

experiment. The MT concentrations for the original and the pH adjusted samples are shown in *Figure 4-11*. The HT sample showed the highest MT production compared to the raw and ED samples. MT was below the detection limit in the ED sample (78 ppmv

detection limit). Average concentrations of MT for the HT sample increased and peaked on Day 7, with an average concentration of 498 ppmv; after that it decreased to 300 ppmv on Day 14. The raw sample followed the same trend as HT. Among all the samples, EDF possessed the highest concentration of MT on all days. The MT concentration reached the peak for EDF at Day 7 and decreased slightly afterwards. The concentration of this gas for the RAW+HCl sample showed a gradual increase after Day 5 and peaked at Day 9 at 346 ppmv. For the ED+NaOH and the HT+HCl sample the MT values were slightly above the detection limit at 104 ppmv and 131 ppmv respectively after 14 days of anaerobic incubation. Results for E2 are given in *Figure 4-12*. The RAW and the EDRAW samples' MT concentrations peaked at Day 10 and then decreased. Among all the samples, EDRAW had the highest amount of MT on any of the days of incubation, viz. 3,566 ppmv on Day 10. The concentration of MT in the ED, EDW and EDF+HCl samples remained below the detection limit for the length of the experiment. The ED+NaOH and the EDF biosolids started producing MT after Day 10 and increased to 2,335 ppmv and 2,441 ppmv respectively by Day 14.

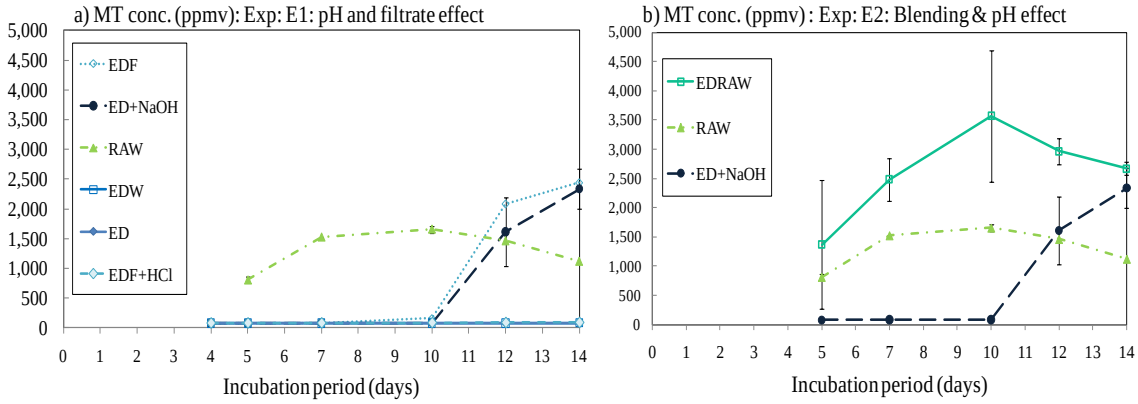


Figure 4-12: Methanethiol (MT) concentrations in ppmv for a) electro-dewatered filtrate added (EDF), electro-dewatered NaOH added (ED+NaOH), raw (RAW), electro-dewatered (ED), electro-dewatered filtrate and acid added (EDF+HCl) and electro-dewatered distilled water added (EDW) b) biosolids pH for blended electro-dewatered and raw added base (EDRAW), raw (RAW) and electro-dewatered base added (ED+NaOH) samples for 14 days of anaerobic incubation. Error bars represents ranges of two replicates. The ED+NaOH sample was dryness adjusted.

Chapter 5. Discussion

5.1 **Phase 1: Preliminary experiments: Dräger tube tests**

Tables 4-1 & 4-2 showed that the ammines, ammonia, methanethiol (MT) and dimethyl sulphide (DMS) concentrations in the electro-dewatered samples were consistently lower than those in the raw and HT samples. Moreover, all aerobically incubated samples showed higher concentrations than those which had been incubated anaerobically. These tests clearly demonstrated that sulphur compounds (MT and DMS) dominated compared to nitrogen compounds (ammines and ammonia) in the headspace of all the biosolids samples under anaerobic conditions. Hydrogen sulphide (H_2S) in this study was only detected twice in the raw aerobic samples but not in any other anaerobic samples, even though H_2S would be expected to occur under anaerobic conditions rather than under aerobic conditions (Gostelow et al. 2001). The reason of the absence of H_2S in most of the samples could be the binding of H_2S with metals, such as iron or aluminum (Novak et al. 2006), however, the detailed electro-chemical mechanisms behind the removal of ammines, ammonia, MT and DMS in ED biosolids cannot be explained within the scope of the study.

5.2 **Phase 2: Detailed analysis of Raw, ED and HT samples**

In phase 1, all the analyses were conducted under aerobic and anaerobic conditions. Typically, however, biosolids after the final stage of dewatering or treatment are piled in large containers. The surface of the pile is exposed to air and can be considered aerobic, but most of these storage piles are devoid of oxygen and are as assumed to be anaerobic. Lukicheva et al. (2012) showed that only the top 0.15 m of a biosolids pile is aerobic; the layers below are anaerobic. Therefore, for further analysis, only anaerobic incubation was used.

5.2.1 Total solids and pH

Electro-dewatered biosolids differed in several ways compared to the untreated-raw or the heat-treated biosolids, as shown in *Figure 4-1*. The dryness of the ED biosolids was much higher (30%-40%) than the raw and HT biosolids (14%-18%). [It is noted that the total solids for the ED samples decreased from 41% to 35% on Day 14; this was unexpected and possibly due to experimental error]. The increase in total solids was attributed to the key mechanisms governing this technology, electrophoresis and electro-osmosis. A negligible impact could also be accredited to the evaporation factor which was inevitable at the end of the cycle when the sludge temperature increases to about 100 ^{o}C due to joule heating. The ED sample's pH was 2.5 units lower than that of the HT or the raw samples (7.1 ± 0.2 in the raw and HT biosolids and 4.6 ± 0.1 in the ED samples). The reduction of pH during ED treatment along with the increase in temperature (>100 ^{o}C) was also reported previously (Saveyn et al. 2006; Tuan et al. 2012). As explained by Mahmoud et al. (2010), when an electrical field is applied to an aqueous media, electrolysis occurs to equilibrate the charges. As a result of electrolysis, oxygen gas and protons are generated near the anode, hydrogen gas and hydroxyl ions are produced near the cathode. Consequently, the biosolids pH close to the cathode increases and near the anode it decreases; on average the pH decreases compared to the untreated biosolids due to continuous production of chemical oxidants.

5.2.2 Regrowth of indicator organism

The ED and HT biosolids showed no regrowth of *E. coli* and total coliforms, after they had been inactivated initially to below the detection limits; the plate counts for the raw (untreated samples) decreased by 1 log after 14 days of incubation (*Figure 4-3).* According to a detailed study by Navab-Daneshmand et al. (2012) the inactivation of bacterial pathogen indicators was primarily due to joule heating during the electro-dewatering treatment. No inactivation was observed when applying same current but controlling the temperature to below 35 ^{o}C. As per USEPA regulations for biosolids land application, the pathogen requirement for class A biosolids is 1,000 MPN/ g-TS. In this

study, both the ED and HT samples achieved class A standard after treatment and maintained this even after 14 days of incubation under anaerobic conditions.

5.2.3 Sensory evaluation

Olfactometry evaluations of the raw, ED and HT samples showed that the ED sample had an approximately 50% lower detection and recognition threshold compared to the raw sample (*Table 4-3*). The HT samples' detection and recognition thresholds were between those of the raw and ED samples. The blank sample (nitrogen gas in the same bottles as the biosolids samples) had a 36 to 69 times lower detection threshold compared to the ED and raw samples respectively, indicating that the incubation system, the purged nitrogen, the bottle and the septa had a negligible effect on the odour produced by the biosolids sample. The average hedonic tones of all the samples had the same value and the primary odour descriptor in all cases was "offensive". However, the selective odour character relative intensity scale shown in *Table 4-4* (offensive, earthy, fishy....etc.) suggests that the HT sample had the highest value in the "offensive character" descriptor whereas the ED sample had the highest value in the "earthy odour" descriptor. Overall, the commonly selected specific descriptors for the ED sample were "musty" and "sewer", and for the raw sample it was "garbage", "musty", "sewer" and "rancid". Briefly, therefore, in this study, the ED biosolids possessed lower intensity odours in terms of odour concentrations which were also described as less offensive compared to the other two samples (raw and HT), even after 7-days of incubation.

These results are consistent with others in terms of the odour descriptors. In one study of odours from centrifuged and limed combined primary and waste activated biosolids, after 7 days of storage the hedonic tone (pH 8.4 at Day 7) was about - 6 (in this study, the average hedonic tone after Day 7 for all the samples was -3), and the odour was described as "fishy, putrid and rotten". After 15 days of storage the detection threshold value was recorded to be 17,000 (Krach et al. 2008b). Along with these sensory characterizations, they also found MT and DMS throughout the storage time of 29 days. (Murthy et al. 2003b) described odours from undigested dewatered heat-dried biosolids as "earthy and

sour" with a hedonic tone of - 4.9, which is close to the range of hedonic tones for the HT sample in this study.

5.2.4 Selection of compounds

The major odour producing gases associated with biosolids are volatile organic sulphur compounds (VOSCs) with a characteristic sewer odour (Murthy et al. 2003b; Krach et al. 2008b). Other significant classes of odorants are ammines and ammonia, volatile fatty acids (Rosenfeld et al. 2001b; Murthy et al. 2003b). Chang et al. (2005) showed that a high pH (>9) is usually required for sufficient volatilisation of ammines and ammonia, but in this study, the pH of all the samples was lower than 8, hence ammonia odours were not a priority. Besides, in phase 1 of our study, at least 10 times higher concentrations were detected for MT and DMS (*Table 4-2*) compared to the ammines and ammonia (*Table 4-1*). Furthermore, as indicated by the sensory evaluation, the most common offensive secondary descriptor used for all three samples was sewer odour (*Table 4-4*), therefore VOCSs were selected as the key compounds for further quantification by GC/MS.

5.2.5 Analytical experiments

The heat-treated (HT) sample produced the highest concentrations of MT and DMDS compared to the other two (raw and electro-dewatered (ED)) samples, but raw biosolids was the highest DMS producer as shown in *Figure 4-4*. The total volatile organic sulphur compounds (VOSC) production was the highest for the HT samples. This is in agreement with the sensory analysis, HT samples being the most offensive amongst the three samples. Glindemann et al. (2006) and Novak et al. (2006) showed that MT peaked earlier than DMS or DMDS during the storage period of anaerobically digested biosolids. In our study, MT peaked on Day 10 while the DMS and DMDS both peaked on Day 7. Some studies have shown that DMDS formation was the result of abiotic oxidation of MT in the presence of molecular oxygen (Higgins et al. 2006), but the occurrence of DMDS under strictly anaerobic conditions has also been reported (Turkmen et al. 2004b). In our study DMDS was detected only in the HT samples, and was barely detected in the raw

samples. It could be possible that some oxygen was introduced by the gas sampling procedure which oxidized some MT to DMDS. As shown in *Figure 4-3,* the raw sample had a higher respiration activity and this small amount of oxygen might have been consumed rapidly, but for the HT sample the oxygen remained longer. It should be noted here that MT was consistently detected in the later experiments of phase 3, but in those the DMS and DMDS were not detected.

To explain the odour behaviour of the Raw, ED and HT biosolids, the bacterial action as measured by *E. coli* or total coliforms and the readily extractable proteins from the biosolids samples were compared to the odorous gas production, as previous other studies showed a correlation between pathogen indicator regrowth or readily extractable protein concentration, and odour production (Higgins et al. 2008; Chen et al. 2011). In this study, neither *E. coli* nor total coliforms in the HT and ED samples grew after 14 days of anaerobic incubation. This may explain why VOCSs production from the ED sample was at or below the detection limit. Also, for the raw sample, where the *E. coli* and total coliform counts decreased after 14 days, VOCS production can be correlated to bacterial counts. The absence of any bacterial regrowth in the HT samples then does not explain the odour production from HT biosolids. Therefore bacterial action can not be correlated with the odour production, as although *E. coli* are known to be amongst the odour producing bacteria, and they could be responsible for odour production, odour could also be produced in the absence of *E. coli* or other bacteria (Chen et al. 2011).

The protein extraction method used in this study is a colourimetric method, and amino acids (tyrosine, tryptophan, cyctine, cysteine and histidine) are responsible for colour development. Sulphur-containing amino acids are considered to be the main precursors of odours (Higgins et al. 2008). The higher concentrations of VOSCs for HT than for raw and ED biosolids correspond to higher concentrations of readily extractable proteins in the HT biosolids (*Figure 4-2*). This is in agreement with Higgins et al.'s (2006) suggestion that high concentrations of readily extractable protein result in greater VOSCs production. In this study, ED biosolids did not produce detectable concentrations of

VOCSs but they contained higher concentrations of readily extractable proteins than the raw biosolids. Therefore, the proteins itself are not responsible for odour production.

5.3 **Phase 3: Manipulation of biosolids characteristics to explain ED effect on odour production**

Based on the results obtained from phases 1 & 2, three hypotheses were developed and tested in phase 3. As discussed earlier, the pH of ED biosolids was 2.5 units lower than that of the HT or raw samples. Thus the first hypothesis was that the low pH of the ED biosolids, compared that of the raw or HT biosolids, was responsible for the lower odour production. In addition, the ED technology produces a drier biosolids cake compared to the untreated and heat-treated biosolids, and a correspondingly higher amount of filtrate, hence the second hypothesis developed was that the water extracted during ED contained the odour precursors, whereas the untreated and the HT biosolids contained this water and adding this removed filtrate back to the ED biosolids could increase the production of VOCSs. Finally, ED treatment is known to produce chemical oxidants during treatment, and the application of an electrical current probably completely changes the biosolids structure. Thus it was speculated that ED may generate unknown `inhibitory compounds` which hinder the production of offensive odours even after days of incubation or storage. Based on that, our final hypothesis was that ED may produce odour-suppressing inhibitory compounds.

5.3.1 Total solids

The total solids concentration of the ED sample obtained in phase 1 of the study (41%) was the highest of all three phases as salt ($Ca(NO_3)_2$) had been used to facilitate the electro-osmosis process during ED. In phase 3, the average total solids achieved through electro-dewatering were 30% - 36% without adding any electrolyte. The total solids of the electro-dewatered biosolids to which filtrate had been added (EDF) were close to that of the raw biosolids, as all the filtrate removed by the ED process was added back. The total solids of other pH-adjusted samples in E1 did not change much, as a very small amount of acid or base was added to the samples (*Table 4-6*). However, to properly control the

dryness, the total solids of each sample was adjusted in E2 to the level similar to that of raw biosolids except for the unaltered ED sample. *Table 4-6* presents the total solids concentration. There were small differences between the total solids concentrations for these samples, which can be attributed to experimental errors.

5.3.2 pH & proteins

The pHs of the raw, HT and ED samples were consistent with the results of phase 2 (*Figure 4-6*). However the low pH adjusted samples except for the EDF+HCl (electro-dewatered filtrate and acid added) showed an increase and stabilized at pH 6.8 - 7.5 (*Figures 4-7 & 4-8*). The reason behind this increase could be because the effect of the added HCl was neutralized by basic ions from the biosolids being released during incubation.

The protein concentrations of the ED+NaOH, EDF+HCl, EDW and EDF samples were higher than the original ED sample, probably due to increased handling and mixing of the biosolids, as Forbes et al. (2004) showed that increased handling of biosolids resulted in the release of proteins (*Figure 4-9*). The HCl-added raw sample also showed /higher concentration of protein than the raw sample, but the HT+HCl sample showed slightly lower concentration than the HT sample.

The *E. coli* and the total coliforms, shown in *Figure 4-10* remained below the detection limit for 6 days of incubation for the ED, EDF, HT+HCl and the HT samples. HCl addition to the raw biosolids resulted in a 1 log reduction in *E. coli* MPN counts on Day 0.

5.3.3 Sensory evaluation

As shown in *Table 4-7*, a limited sensory analysis of the manipulated biosolids samples was carried out. The intense rotten smell was associated with the high pH samples, and when the pH of the raw and HT samples was lowered to obtain a pH similar to the original ED biosolids, the odours were perceived as less pronounced or intense than the original raw and HT samples. Similar to the results of phase 2 (*Figure 4-8*), the pH did

not remain constant during the incubation period and it started increasing gradually after Day 2, and the odour became similar and intense rotten for all the samples except for the ED+ NaOH and ED after the 6th day of incubation. These limited sensory test results were important as they revealed the correlation of pH and generation of odours qualitatively.

The blending test described in *Table 4-8* shows that there was a delay in the production of more offensive odours as the percentages of ED biosolids in the blend increased. This could have been due to a masking or dilution effect of the two different odours blended together, which could only be indentified by analytical experiments, i.e. by GC/MS.

5.3.4 Analytical experiments

The higher concentrations of MT produced by the EDF sample (*Figure 4-11*) demonstrated that the filtrate had a major impact on the odours; therefore it appeared that the second hypothesis (odour precursors removed by the filtrate) should be the correct one. Adding the filtrate back to the ED biosolids, however, produced higher odours than that of the raw sample. It is pertinent to mention here that the filtrate pH was very high (12.8). The mixture of the filtrate and the ED biosolids also had an elevated pH (6.8-7.2). Comparing the HT+HCl and the HT samples, the HT+HCl had the lower MT production, which was in agreement with our limited sensory test results presented in *Table 4-7* and discussed in the previous section (*5.3.3*). On the other hand, the MT concentrations were lower in the raw sample than in the RAW+HCl sample. This could be explained by the *E. coli* profile of the RAW+HCl sample. Unlike HT+HCl or HT sample, the RAW and RAW+HCl samples had higher *E. coli* counts above the detection limits (*Figure 4-10*) and because of this the odour behaviour can be changed. The high pH ED sample (ED+NaOH) showed only marginal concentrations of MT on Day 12. It would be difficult to explain the MT production in relation to pH after the 7th day of incubation for the raw and HT samples, because the pH of these samples stabilizes at their original pH after Day 7 (*Figure 4-7*), yet, the odour profile is different (*Figure 4-11*). However, in E2, pH change could be clearly correlated with MT production, because for the EDF and the ED+NaOH samples, MT was produced only after Day 10, when the pH (6.8-7.2)

increased to the level found in the raw (*Figures 4-8 & 4-12*). Therefore the low pH of biosolids before incubation likely leads to odour reduction. Thus the first hypothesis (that low pH is responsible for lower odour production) is also reasonable.

The second hypothesis (removed filtrate contains the precursors) was accepted based on the previous (E1) results, nonetheless the filtrate also increased the pH of the ED sample and only this high pH could be responsible for producing MT. In the next experiment (E2), an additional sample, which is the ED, added filtrate and acid (EDF+HCl, pH 4.5-4.8) was incubated along with the EDF and ED samples. Interestingly, there was no detectable gas production in the EDF+HCl sample, indicating that the second hypothesis could not be consistently defended, and only the first hypothesis (low pH) remained.

The third hypothesis (inhibitory effect of the ED sample) was tested analytically, and the blended sample showed higher MT production than the raw or the ED+NaOH sample. This result indicates that the delay observed in the limited sensory test was due to dilution or masking of the odorous raw sample with the less odorous ED sample or as a result of stabilizing the pH of the raw sample to a lower value by the ED biosolids, and was not caused by the ‘inhibitory effect’ of the ED biosolids.

Chapter 6. Summary and Conclusions

Electro-dewatering (ED) technology has been recently developed to enhance the dewatering of biosolids and to reduce their handling costs, with the added benefit of producing Class A biosolids. In this study, the major odour-causing compounds in ED biosolids were identified and quantified and compared with the untreated or HT biosolids. Finally, the mechanisms leading to a reduction of odour production by electro-dewatered biosolids were also examined.

The study was conducted in three distinct phases. In phases 1 & 2, preliminary detection of the odorous gases (ammines and ammonia, and volatile reduced sulphur compounds) and olfactometric analyses indentified reduced sulphur compounds as the major odour-causing compounds in ED, untreated, and HT (control) biosolids. Reduced sulphur compounds have odour threshold typically 1-2 orders of magnitude higher than those of ammines, and their concentrations were also at least 10× higher. Furthermore, the principal descriptors used by the olfactometric panel were those associated with reduced sulphur compounds. In phase 2, analytical evaluations using GC/MS measurements of the odorous gas emitted by untreated, ED and HT samples over 14 days under anaerobic conditions were conducted. ED biosolids had higher dryness (30-40%) and lower pH (4.5-4.8) than the untreated and the HT biosolids (dryness 16-18%, pH 6.8-7.2). Results from this phase demonstrated a clear difference in odour production between the ED and the raw or HT samples. Sensory test results showed approximately 50% lower odour concentrations in terms of detection and recognition thresholds in the ED samples compared to the two other treatments after 7-days of anaerobic incubation. Reduced sulphur compounds (mathanethiol, dimethyl sulphide and dimethyl disulphide) were detected at very high values (>830 ppmv of total sulphur) in the untreated and HT biosolids, but they remained below or at the detection limit in the ED biosolids (detection limit 179 ppmv) for the duration of the experiment.

In phase 3, several hypotheses to explain the odour production were developed and tested. Important factors such as low pH of the ED biosolids, odour precursors removed by the filtrate, and an unknown "inhibitory factor" were studied in detail.

To test the pH hypothesis, sodium hydroxide was added to raise the pH of the ED biosolids to reach the pH level of the raw biosolids (6.8 – 7.5) and hydrochloric acid was added to lower the pH of the HT sample to the level similar to that of the ED biosolids (4.5 - 4.8); both were incubated separately with the original ED and HT biosolids and analyzed for reduced sulphur gases. After 7 days, all samples at higher pH generated more MT than those at lower pH.

For the hypothesis that ED filtrate may contain the odour precursors, ED filtrate (at pH 12.8) which was removed during the process was added back to the ED biosolids (pH 4.5-4.8) and mixed. The pH of this mixed sample was also increased to 6.8-7.5o the addition of high pH filtrate. After 7 days the mixed sample produced more MT than the raw biosolids. To separate the pH and filtrate factors, the pH of the mixed ED and filtrate sample was reduced to the level of the ED biosolids immediately after treatment by adding hydrochloric acid. The odorous gas emission (MT) from this low pH mixed ED and filtrate sample was at the detection limit of the GC/MS method. The odour production from this sample was similar to that of the original ED sample, which indicates that low pH was the leading factor responsible for reduced odours in the ED biosolids.

To test the inhibitory hypothesis, raw and ED biosolids were blended at different percentages. Limited sensory test results showed that there was a delay in the production of more offensive odours as the ED percentage increased. However, the GC/MS analysis of the blended raw and NaOH added ED sample (50% /50%, pH 6.8-7.0) showed higher MT production than the raw or the base added ED (pH 6.8-7.0) samples individually (3,600 ppmv in the blended sample compared to 1,700 ppmv in the raw sample at day 10 under anaerobic conditions). This result suggests that the delay observed in the limited sensory test was due to dilution or masking of odorous raw sample with less odorous ED

sample or lowering of the pH of the raw sample by the low pH ED biosolids, and not caused by the inhibitory effect of the ED biosolids

In conclusion, ED technology not only produces biosolids with high solids content and achieves inactivation of pathogen within a very short time (10 minutes), but it produces less odorous biosolids cakes as well. Moreover, the inactivation of bacterial pathogen indicators remains irreversible and the bacterial counts remain below the detection limits even after 14 days of incubation under anaerobic conditions; furthermore the odours remain stabilized at the detection limit throughout the incubation period. Finally, low pH was identified as the major odour reduction mechanism of ED biosolids, although conventionally high pH treatments have been used for stabilizing biosolids pathogens and odour emissions.

Future directions: The main objective of this study was to determine the principal mechanisms whereby electro-dewatering treatment reduced odours from biosolids; this objective was achieved to a large extent. Nevertheless more questions need to be answered: first, to evaluate the detailed mechanisms which form, alter and destroy odour producing gases. Second, it would be interesting to observe the effect on odour production when the factors of applied current and the heat produced are separated, because in a previous study on the pathogen inactivation mechanism of ED treatment (Navab-Daneshmand et al. 2012), it was observed that pathogen inactivation was primarily due to the high temperature caused by joule heating and the application of current itself had no effect. Finally, the effect of coating the anode with a metal oxide should be studies, as many researchers have found that such coating helps to reduce odorous compounds, as the metal oxide reacts with chlorides found in the biosolids, producing chlorine gas which eventually oxidizes ammonium or ammines to nitrogen gas.

References:

Ábalos, M., Prieto, X. & Bayona, J.M. 2002 Determination of volatile alkyl sulfides in wastewater by headspace solid-phase microextraction followed by gas chromatography–mass spectrometry. *J. Chromat. A* **963** (1), 249-257.

Abu-Orf, M., Dentel, S.K., Chang, J.-S., Hepner, S., Turkmen, M. & Fagerstrom, A. 2005 Odor reduction using alternative polymers and dewatering equipment. In: *Proceedings of the WEFTEC 2005*, Washington D.C., United States.

Adams, G., Witherspoon, J., Card, T., Erdal, Z., Forbes, B., Geselbracht, J., Glindemann, D., Hargreaves, R., Hentz, L. & Higgins, M. 2003 *Identifying and Controlling the Municipal Wastewater Odor Environment Phase II: Impacts of In-plant Operational Parameters on Biosolids Odor Quality.* Report no. 00-HHE-5T. Water Environment Research Foundation (WERF), Alexandria, VA, United States.

Adams, G., Witherspoon, J., Erdal, Z., Forbes, R., Hargreaves, J., Higgins, M., McEwen, D. & Novak, J. 2008 *Identifying and Controlling the Municipal Wastewater Odor Environment Phase 3: Biosolids Processing Modifications for Cake Odor Reduction.* Report no. 03-CTS-9T. Water Environment Research Foundation (WERF), Alexandria, VA, United States.

Amoore, J.E. & Hautala, E. 1983 Odor as an aid to chemical safety: Odor thresholds compared with threshold limit values and volatilities for 214 industrial chemicals in air and water dilution. *J. Appl. Toxicol.* **3** (6), 272-290.

APHA, AWWA & WEF 2012 *Standard Methods for Examination of Water and Wastewater, 20th Edition.* American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.

ASTM 1992 *Atlas of Odor Character Profiles.* ASTM-DS61, American Society for Testing and Materials (ASTM) International, West Conshohocken, PA, United States.

ASTM 2011 *Standard Practice for Determination of Odor and Taste Thresholds by a Forced-Choice Ascending Concentration Series Method of Limits.* ASTM E679-

04, American Society for Testing and Materials (ASTM) International, West Conshohocken, PA, United States.

Banwart, W. & Bremner, J. 1976 Evolution of volatile sulfur compounds from soils treated with sulfur-containing organic materials. *Soil Bio. Biochem.* **8** (5), 439-443.

Bentley, R. & Chasteen, T.G. 2004 Environmental VOSCs–formation and degradation of dimethyl sulfide, methanethiol and related materials. *Chemosphere* **55** (3), 291-317.

BSI 2003 *Air Quality: Determination of Odour Concentration by Dynamic Olfactometry.* BS EN 13725;2003, The British Standard Institution, London, United Kingdom.

Bureau, M.A., Drogui, P., Sellamuthu, B., Blais, J.F. & Mercier, G. 2012 Municipal wastewater sludge stabilization and treatment using electrochemical oxidation technique. *J. Environ. Eng.* **138** (7), 743-751.

CCME 2010 *A Review of the Current Canadian Legislative Framework for Wastewater Biosolids.* Report no. PN 1446. Canadian Council of Ministers of the Environment, Ontario, Canada.

CCME 2012 *Canada Wide Approach for the Management of Wastewater Biosolids.* Report no. PN 1477. Canadian Council of the Ministers of the Environment, Ontario, Canada.

Chang, J.S., Abu-Orf, M. & Dentel, S.K. 2005 Alkylamine odors from degradation of flocculant polymers in sludges. *Water Res.* **39** (14), 3369-3375.

Chen, G., Lock Yue, P. & Mujumdar, A.S. 2002 Sludge dewatering and drying. *Dry. Technol.* **20** (4-5), 883-916.

Chen, Y., Higgins, M.J., Maas, N.A., Murthy, S.N., Toffey, W.E. & Foster, D.J. 2005 Roles of methanogens on volatile organic sulfur compound production in anaerobically digested wastewater biosolids. *Water Sci. Technol.* **52** (1/2), 67-72.

Chen, Y., Higgins, M.J., Murthy, S.N., Maas, N.A., Covert, K.J. & Toffey, W.E. 2006a Mechanisms for the production of odorous volatile aromatic compounds in wastewater biosolids. *J. Res. Sci. Technol.* **3** (4), 193-202.

Chen, Y.C., Higgins, M., Murthy, S., Maas, N., Covert, K. & Toffey, W. 2006b Production of odorous indole, skatole, p-cresol, toluene, styrene, and ethylbenzene in biosolids. *J. Res. Sci. Technol.* **3** (4), 193-202.

Chen, Y.C., Higgins, M.J., Beightol, S.M., Murthy, S.N. & Toffey, W.E. 2011 Anaerobically digested biosolids odor generation and pathogen indicator regrowth after dewatering. *Water Res.* **45** (8), 2616-2626.

Chun, H., XiangZhong, L., Sharma, V. & ShiYu, L. 2009 Elimination of sludge odor by oxidizing sulfur-containing compounds with ferrate (VI). *Environ. Sci. Technol.* **43** (15), 5890-5895.

Citeau, M., Larue, O. & Vorobiev, E. 2011 Influence of salt, pH and polyelectrolyte on the pressure electro-dewatering of sewage sludge. *Water Res.* **45** (6), 2167-2180.

Cooper, C.D. & Alley, F. 1994 *Air Pollution Control: A Design Approach*. Waveland Press Prospect Heights, IL, United States.

Curiale, M. 2004 *MPN Calculator, Build 24.* http://www.i2workout.com/mcuriale/mpn/index.html

Dewulf, J., Van Langenhove, H. & Wittmann, G. 2002 Analysis of volatile organic compounds using gas chromatography. *TrAC Trends in Analytical Chemistry* **21** (9), 637-646.

Dhar, B.R., Youssef, E., Nakhla, G. & Ray, M.B. 2011 Pretreatment of municipal waste activated sludge for volatile sulfur compounds control in anaerobic digestion. *Bioresour. Technol.* **102** (4), 3776-3782.

Dräger Safety AG & Co KGaA 2008 *Dräger-Tube/CMS Handbook: Handbook for Short Term Measurements in Soil, Water and Air Investigations as well as Technical Gas Analysis, 15th Edition.* Dräger Safety AG & Co KGaA, Lübeck, Germany.

Drogui, P., Blais, J.-F. & Mercier, G. 2007 Review of electrochemical technologies for environmental applications. *Recent Patents on Engineering* **1** (3), 257-272.

Drogui, P., Bureau, M.-A., Mercier, G. & Blais, J.F. 2013 Effectiveness of electrooxidation process for stabilizing and conditioning of urban and industrial wastewater sludge. *Water Environ. Res.* **85** (1), 35-43.

Du, W. & Parker, W. 2012 Modeling volatile organic sulfur compounds in mesophilic and thermophilic anaerobic digestion of methionine. *Water Res.* **46** (2), 539-546.

Elektorowicz, M., Hasan, S.W. & Oleszkiewicz, J.A. 2011 Pilot studies of a novel submerged membrane electro-bioreactor (SMEBR). In: *Proceedings of the WEFTEC 2011*, LA, United States.

Elektorowicz, M. & Oleszkiewicz, J., 2012. Method of treating sludge material using electrokinetics. US Patent 8,329,042.

Eschborn, R., Abu-Orf, M. & Sarrazin-Sullivan, D. 2011 Integrating electro-dewatering into advanced biosolids processing where does it make sense? In: *Proceedings of the Water Environment Federation: Adapting Residuals Management to a Changing Climate*, Sacramento, CA, United States.

Esmaeily, A., Elektorowicz, M., Habibi, S. & Oleszkiewicz, J.A. 2006 Dewatering and coliform inactivation in biosolids using electrokinetic phenomena. *J. Environ. Eng. Sci.* **5** (3), 197-202.

Fang, J.-J., Yang, N., Cen, D.-Y., Shao, L.-M. & He, P.-J. 2012 Odor compounds from different sources of landfill: Characterization and source identification. *Waste Manage.* **32** (7), 1401-1410.

Feinbaum, R. 2000 *Odor Control: Going the Extra Mile.* Journal for Municipal Solid Waste Professional. Santa Barbara, CA, United States. http://www.forestermedia.net/MSW/Articles/Odor_Control_Going_the_Extra_Mile_4447.aspx

Forbes, B., Adams, G., Hargreaves, R., Witherspoon, J., McEwen, D., Erdal, Z., Hentz, L., Murthy, S., Card, T., Glindemann, D. & Higgins, M. 2004 Impacts of the in-plant operational parameters on biosolids odor quality- final results of WERF odor project phase 2 field and laboratory study. In: *Proceedings of the Water Environment Federation, WEF/A&WMA Odors and Air Emissions*, Bellevue, WA, United States.

Frolund, B., Griebe, T. & Nielsen, P. 1995 Enzymatic activity in the activated-sludge floc matrix. *Appl. Microb. Biotechnol.* **43** (4), 755-761.

Glindemann, D., Murthy, S.N., Higgins, M.J., Chen, Y. & Novak, J.T. 2006 Biosolids incubation method for odorous gas measurement from dewatered sludge cakes. *J. Residuals Sci. Technol* **3** (3), 153-160.

Gostelow, P., Parsons, S. & Stuetz, R. 2001 Odour measurements for sewage treatment works. *Water Res.* **35** (3), 579-597.

Gul-E-Hina 2011 *Regrowth of Bacterial Pathogen Indicators in Electro-Dewatered Biosolids.* MEng Thesis, Department of Civil Engineering and Applied Mechanics, McGill University, Montreal, Quebec, Canada.

Hasan, S. 2012 *Design and Performance of a Pilot Submerged Membrane Electro-Bioreactor (SMEBR) for Wastewater Treatment.* PhD thesis, Department of Building, Civil, and Environmental Engineering, Concordia University, Montreal, Quebec.

Hébert, M. 2008 *Guidelines for the Beneficial Use of Fertilising Residuals: Reference Criteria and Regulatory Standards.* Développement durable, Environnement et Parcs, Québec, Canada.

Hébert, M. 2012 *Boues Municipales: Politiques de Recyclage et Évaluation des Émissions de GES.* Ministère du Développement Durable, de l'Environnement, Québec, Canada.

Held, J. & Chauhan, S.P., 2002. Method and apparatus for the molecular destruction of waste-activated sludge using high electrical voltage. US patent number: US20020036175-A1.

Higgins, M.J., Adams, G., Chen, Y.C., Erdal, Z., Forbes, R.H., Glindemann, D., Ronald Hargreaves, J., McEwen, D., Murthy, S.N. & Novak, J.T. 2008 Role of protein, amino acids, and enzyme activity on odor production from anaerobically digested and dewatered biosolids. *Water Environ. Res.* **80** (2), 127-135.

Higgins, M.J., Chen, Y.C., Yarosz, D.P., Murthy, S.N., Maas, N.A., Glindemann, D. & Novak, J.T. 2006 Cycling of volatile organic sulfur compounds in anaerobically digested biosolids and its implications for odors. *Water Environ. Res.* **78** (3), 243-252.

Hua, R., Wang, J., Kong, H., Liu, J., Lu, X. & Xu, G. 2004 Analysis of sulfur-containing compounds in crude oils by comprehensive two-dimensional gas chromatography with sulfur chemiluminescence detection. *J. Separation Sci.* **27** (9), 691-698.

Iranpour, R., Cox, H., Kearney, R., Clark, J., Pincince, A. & Daigger, G. 2004 Regulations for biosolids land application in US and European Union. *J. Res. Sci. Technol.* **1** 209-222.

Kadota, H. & Ishida, Y. 1972 Production of volatile sulfur compounds by microorganisms. *Ann. Rev. Microbiol.* **26** (1), 127-138.

Kim, H., Murthy, S., Peot, C., Ramirez, M., Strawn, M., Park, C.H. & McConnell, L.L. 2003 Examination of mechanisms for odor compound generation during lime stabilization. *Water Environ. Res.* **75** (2), 121-125.

Kim, H., Nochetto, C. & McConnell, L.L. 2002 Gas-phase analysis of trimethylamine, propionic and butyric acids and sulfur compounds using solid-phase microextraction. *Anal. Chem.* **74** (5), 1054-1060.

Krach, K.R., Burns, B.R., Li, B., Shuler, A., Cole, C. & Xie, Y. 2008a Odor control for land application of lime stabilized biosolids. *Water Air Soil Poll.* **8** (3-4), 369-378.

Krach, K.R., Li, B., Burns, B.R., Mangus, J., Butler, H.G. & Cole, C. 2008b Bench and full-scale studies for odor control from lime stabilized biosolids: the effect of mixing on odor generation. *Bioresource Technology* **99** (14), 6446-6455.

Lehtinen, J. & Veijanen, A. 2011a Determination of odorous VOCs and the risk of occupational exposure to airborne compounds at the waste water treatment plants. *Water Sci. Technol.* **63** (10), 2183-2192.

Lehtinen, J. & Veijanen, A. 2011b Odour monitoring by combined TD-GC-MS-sniff technique and dynamic olfactometry at the wastewater treatment plant of low H_2S concentration. *Water Air Soil Poll.* **218** (1-4), 185-196.

Liu, H. & Fang, H.H.P. 2002 Extraction of extracellular polymeric substances (EPS) of sludges. *J. Biotechnol.* **95** (3), 249-256.

Lowry, O.H., Rosebrough, N.J., Farr, A.L. & Randall, R.J. 1951 Protein measurement with the Folin phenol reagent. *J. Bio. Chem.* **193** (1), 265-275.

Lue-Hing, C., Zenz, D. & Kuchenrither, R. 1992 *Municipal Sewage Sludge Management: Processing, Utilization, and Disposal*. Water Quality Management Library, V 4, Technomic Pub. Co., Lancaster, PA, United States.

Lukicheva, I., Tian, G., Cox, A., Granato, T. & Pagilla, K. 2012 Anaerobic and aerobic transformations affecting stability of dewatered sludge during long-term storage in a lagoon. *Water Environ. Res.* **84** (1), 17-24.

Mahmoud, A., Olivier, J., Vaxelaire, J. & Hoadley, A.F.A. 2010 Electrical field: A historical review of its application and contributions in wastewater sludge dewatering. *Water Res.* **44** (8), 2381-2407.

McGinley, C.M. & McGinley, M.A. 2000 Odor Intensity Scales for Enforcement, Monitoring, and Testing. In: *Proceedings of the Air and Waste Management Association- Annual Conference*, Stillwater, MN, United states.

McGinley, M.A. & McGinley, C.M. 2006 *Performance Verification of Air Freshener Products and Other Odour Control Devices for Indoor Air Quality Malodours.* St. Croix Sensory Inc., Lake Elmo, MN, USA.

McKay, S.F., Paradis, R. & Blanchette, M. 2007 Reducing Disposal Costs through Advanced Electro-dewatering. In: *Proceedings of the WEFTEC 2007*, San Diego, CA, United States.

McTavish, V. 2008 *Green Box Envy.* Bcliving. BC, Canada. http://www.bcliving.ca/home/green-box-envy

MDDEP, Agricultural Utilization of Fertilizing Residual Materials: Questions and Answers. Residual Materials. Ministère du Développement durable, de l'Environnement et des Parcs, Quebec, Canada.

Metcalf & Eddy Inc. 2003 *Wastewater Engineering Treatment, Disposal and Reuse*. 4th edition, revised by George Tchobanoglous. McGraw-Hill, Inc., New York, United States.

Munoz, R., Sivret, E.C., Parcsi, G., Lebrero, R., Wang, X., Suffet, I. & Stuetz, R.M. 2010 Monitoring techniques for odour abatement assessment. *Water Res.* **44** (18), 5129-5149.

Murthy, S., Higgins, M., Chen, Y.C., Peot, C. & Toffey, W. 2006 High-solids centrifuge is a boon and a curse for managing anaerobically digested biosolids. *Water Sci. Technol.* **53** (3), 245-253.

Murthy, S., Kim, H., Peot, C., McConnell, L., Strawn, M., Sadick, T. & Dolak, I. 2003a Evaluation of odor characteristics of heat-dried biosolids product. *Water Environ. Res.* 523-531.

Murthy, S., Kim, H., Peot, C., McConnell, L.L., Strawn, M., Sadick, T. & Dolak, I. 2003b Evaluation of odor characteristics of heat-dried biosolids product. *Water Environ. Res.* **75** (6), 523-531.

Navab-Daneshmand, T., Beton, R., Hill, R.J., Gehr, R. & Frigon, D. 2012 Inactivation mechanisms of bacterial pathogen indicators during electro-dewatering of activated sludge biosolids. *Water Res.* **46** (13), 3999-4008.

Newbold, A. & Schici, R. 2011 Enhanced sludge reduction using external bioaugmentation at a full-scale municipal wastewater treatment plant. In: *Proceedings of the NSTI Nanotechnology Conference and Expo*, Boston, MA.

NIST 2005 *Mass Spectral Library Version 2 d.* Standard Reference Data Program, National Institute of Standards and Technology, United States.

Novak, J.T., Adams, G., Chen, Y.C., Erdal, Z., Forbes, R.H., Glindemann, D., Hargreaves, J.R., Hentz, L., Higgins, M.J. & Murthy, S.N. 2006 Generation pattern of sulfur containing gases from anaerobically digested sludge cakes. *Water Environ. Res.* **78** (8), 821-827.

Oleszkiewicz, J. & Mavinic, D. 2002 Wastewater biosolids: An overview of processing, treatment and management. *J. Environ. Eng. Sci.* **1** (2), 75-88.

Orzi, V., Cadena, E., D'Imporzano, G., Artola, A., Davoli, E., Crivelli, M. & Adani, F. 2010 Potential odour emission measurement in organic fraction of municipal solid waste during anaerobic digestion: Relationship with process and biological stability parameters. *Bioresour. Technol.* **101** (19), 7330-7337.

Paradis, R., Dermoune, A., McKay, S.F. & Sullivan, D.S. 2008 Electro-dewatering waste activated sludge: Lessons learned from real world cases. In: *Proceedings of the WEFTEC 2008*, Chicago, IL, United States.

Qi, Y., Dentel, S.K. & Herson, D.S. 2008 Effect of total solids on fecal coliform regrowth in anaerobically digested biosolids. *Water Res.* **42** (14), 3817-3825.

Raats, M.H.M., van Diemen, A.J.G., Lavèn, J. & Stein, H.N. 2002 Full scale electrokinetic dewatering of waste sludge. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **210** (2–3), 231-241.

Ras, M., Girbal-Neuhauser, E., Paul, E., Spérandio, M. & Lefebvre, D. 2008 Protein extraction from activated sludge: An analytical approach. *Water Res.* **42** (8–9), 1867-1878.

Raunkjær, K., Hvitved-Jacobsen, T. & Nielsen, P.H. 1994 Measurement of pools of protein, carbohydrate and lipid in domestic wastewater. *Water Res.* **28** (2), 251-262.

Rosenfeld, P.E., Henry, C.L., Dills, R.L. & Harrison, R.B. 2001a Comparison of odor emissions from three different biosolids applied to forest soil. *Water Air Soil Poll.* **127** (1), 173-191.

Rosenfeld, P.E., Henry, C.L., Dills, R.L. & Harrison, R.B. 2001b Comparison of odor emissions from three different biosolids applied to forest soil. *Water Air Soil Pollut.* **127** (1-4), 173-191.

Rosenfeld, P.E. & Suffet, I.H. 2004 Understanding odorants associated with compost, biomass facilities, and the land application of biosolids. *Water Sci. Technol.* **49** (9), 193-199.

Ruth, J.H. 1986 Odor thresholds and irritation levels of several chemical substances: A review. *American Industrial Hygiene Association Journal* **47** (3), 142-151.

Sander, R. 1999 *Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry*. Max-Planck Institute of Chemistry, Air Chemistry Department, Mainz, Germany.

Saveyn, H., Van Der Meeren, P., Pauwels, G. & Timmerman, R. 2006 Bench-and pilot-scale sludge electrodewatering in a diaphragm filter press. *Water Sci. Technol.* **54** (9), 53-60.

Sekyiamah, K., Kim, H., McConnell, L.L., Torrents, A. & Ramirez, M. 2008 Identification of seasonal variations in volatile sulfur compound formation and

release from the secondary treatment system at a large wastewater treatment plant. *Water Environ. Res.* **80** (12), 2261-2267.

Sparkman, O.D., Penton, Z. & Kitson, F.G. 2011 *Gas Chromatography and Mass Spectrometry: A Practical Guide*. 2nd Edition. Elsevier Inc., Oxford, United Kingdom.

St. Croix Sensory Inc 2005 *A Review of The Science and Technology of Odor Measurement.* Prepared for the Air Quality Bureau of the Iowa Department of Natural Resources, St. Croix Sensory Inc., Lake Elmo, MN, United States.

Sunesson, A., Vaes, W., Nilsson, C., Blomquist, G., Andersson, B. & Carlson, R. 1995 Identification of volatile metabolites from five fungal species cultivated on two media. *Appl. Environ. Microb.* **61** (8), 2911-2918.

Tomita, B., Inoue, H., Chaya, K., Nakamura, A., Hamamura, N., Ueno, K., Watanabe, K. & Ose, Y. 1987 Identification of dimethyl disulfide-forming bacteria isolated from activated sludge. *Appl. Environ. Microb.* **53** (7), 1541-1547.

Tsang, K. & Vesilind, P. 1990 Moisture distribution in sludges. *Water Sci. Technol.* **22** (12), 135-142.

Tuan, P.-A., Mika, S. & Pirjo, I. 2012 Sewage sludge electro-dewatering treatment- a review. *Dry. Technol.* **30** (7), 691-706.

Tuan, P.A., Jurate, V. & Mika, S. 2008 Electro-dewatering of sludge under pressure and non-pressure conditions. *Environ. Technol.* **29** (10), 1075-1084.

Turkmen, M., Dentel, S., Chiu, P. & Hepner, S. 2004a Analysis of sulfur and nitrogen odorants using solid-phase microextraction and GC-MS. *Water Sci. Technol.* **50** (4), 115.

Turkmen, M., Dentel, S.K., Chiu, P.C. & Hepner, S. 2004b Analysis of sulfur and nitrogen odorants using solid-phase microextraction and GC-MS. *Water Sci. Technol.* **50** (4), 115-120.

Urbain, V., Block, J.C. & Manem, J. 1993 Bioflocculation in activated sludge: An analytic approach. *Water Res.* **27** (5), 829-838.

US-EPA 1993 *Standards for the Use and Disposal of Sewage Sludge: Final rules.* Report no. 40 CFR Part 257. United States Environmental Protection Agency, Cincinnati, OH, United States.

US-EPA 2003 *Environmental Regulations and Technology: Control of Pathogens and Vector Attraction in Sewage Sludge (under 40 CFR Part 503).* Report no. EPA/625/R-92/013. United States Environmental Protection Agency, Cincinnati, OH, United States.

van Leerdam, R.C., de Bok, F.A.M., Lomans, B.P., Stams, A.J.M., Lens, P.N.L. & Janssen, A.J.H. 2006 Volatile organic sulfur compounds in anaerobic sludge and sediments: Biodegradation and toxicity. *Environ. Toxicol. Chem.* **25** (12), 3101-3109.

Vesilind, P.A. 1994 The role of water in sludge dewatering. *Water Environment Research* 4-11.

Vesilind, P.A. & Hsu, C.-C. 1997 Limits of sludge dewaterability. *Water Sci. Technol.* **36** (11), 87-91.

Zitomer, D., Owens, D. & Speece, R. 2000 Methanethiol production as an indicator of toxicity in anaerobic treatment. *Water Sci. Technol.* **42** (5-6), 231-235.

Appendix A: Preliminary experiment: Dräger tube test

The dilution factor with each stroke was calculated and given below. For each stroke, 100 mL of gas is sucked, and 100 mL of atmospheric gas enters through the open needle to maintain the pressure. Hence in the 2^{nd} stroke, the gas will be diluted and so on for the subsequent strokes. One needs to calculate that factor for each stroke.

Assuming that the concentration does not change within a stroke; it only changes after a stroke:
The density of the biosolids is 1.27 g/mL
68 g sludge occupies approximately 54 mL volume, so the headspace for 1 L jar is 1000-54=946 mL, assuming 11 mL reduction for socket, so headspace volume is 935 mL

It is assumed that the 1^{st} stroke is undiluted. So before sampling there is x_o g of gas. Initial or original concentration is $C_o = x_o$ g/ 935 mL

With the 1^{st} stroke 100 mL gas was extracted, $x_e = 100 * C_o$

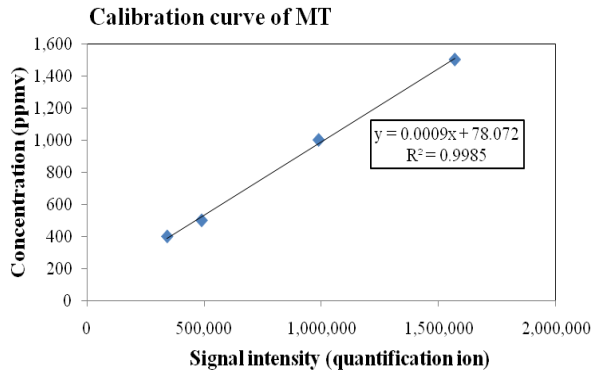
Hence amount of gas remaining after 1^{st} stroke, $X_{r1} = (935C_o - 100C_o) = 835\ C_o$
Concentration after 1^{st} stroke is $C_1 = 835\ C_o / 935 = 0.893\ C_0$

Similarly,
Concentration after 2^{nd} stroke= $0.80\ C_0$
Concentration after 3^{rd} stroke= $0.71\ C_0$
Concentration after 4^{th} stroke= $0.64\ C_0$
Concentration after 5^{th} stroke= $0.57\ C_0$
Concentration after 6^{th} stroke= $0.51\ C_0$
Concentration after 7^{th} stroke= $0.45\ C_0$
Concentration after 8^{th} stroke= $0.41\ C_0$
Concentration after 9^{th} stroke= $0.36\ C_0$

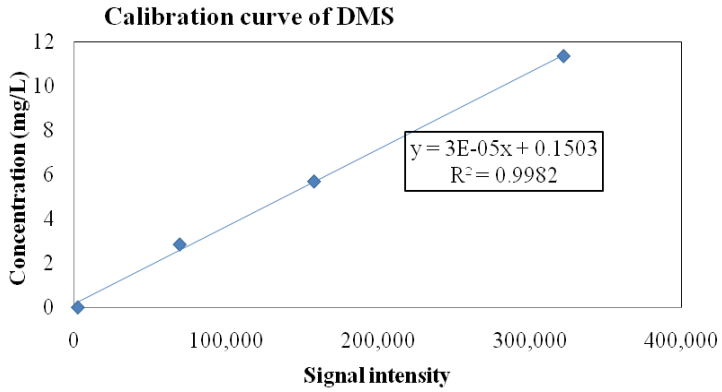
For this experiment, for the sampling with ammine and ammonia tubes two stokes were performed and noted the specific stroke (e.g. 2^{nd} and 3^{rd} or 5^{th} and 6^{th}), so that the dilution factor can be applied.

Example:
For raw aerobic amine, in 1^{st} two strokes the discolouration length was 4 mm. As a result, the concentration is, $C_0 + 0.89\ C_0 = 4$, so $C_0 = 2.12$ mm

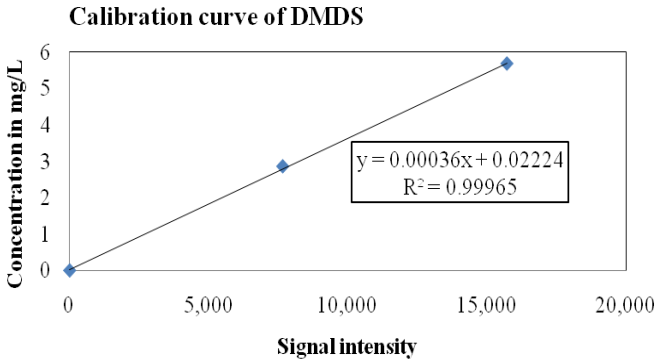
Appendix B: Calibration of MT, DMS and DMDS



Sample	Injected volume of 2000 ppmv MT (mL)	Concentration (ppmv)	Signal intensity: quantification ion (47)	Confirmation ion (48)
Blank	0	0	25	125
MT01	0.2	400	341,598	276,424
MT02	0.25	500	488,479	401,897
MT03	0.5	1,000	988,010	806,358
MT04	0.75	1,500	1,568,997	1,308,030



Head space concentration (mg/L)	Signal intensity: Quantification ion (62)
0	2,125
2.84	69,300
5.68	157,825
11.34	322,327



Headspace concentration (mg/L)	Signal Intensity: Quantification ion (94)
0	25
2.86	7,675
5.68	15,725

Conversion equation from mg/L to ppmv (DMS and DMDS)

$$ppmV = \frac{mg}{L} \times \left(10^3\right) \times \frac{l}{Molecular\ Weight_{contaminant}\ [g/mole]} \times 8.3144 \left[\frac{L \cdot kPa}{mol \cdot K}\right] \times T_{air}[K] \times \frac{1}{P_{air}[kPa]}$$

Appendix C: Odour evaluation report

PINCHIN
ENVIRONMENTAL

Odour Evaluation Report

McGill University
845 Sherbrooke Street West
Montreal, Quebec
H3A 0G4

Attention: Samia Enayet

July 25, 2013

Pinchin File: 85308-072513

2470 MILLTOWER COURT, MISSISSAUGA, ONTARIO L5N 7W5 PHONE: (905) 363-0678 FAX: (905) 363-0681
ENVIRONMENTAL HEALTH & SAFETY MANAGEMENT SERVICES FROM OFFICES ACROSS CANADA
www.pinchin.com • 1-888-767-3330

1.0 EVALUATION SAMPLE & TIMING SUMMARY

Pinchin Environmental (Pinchin) was contracted to determine the detection threshold (DT), recognition threshold (RT), hedonic tone (HT) and character of air samples submitted to Pinchin's Odour Laboratory located in Mississauga, Ontario. The particulars of the odour panel were as follows:

Client Name:	McGill University
No. of Samples Delivered:	Four (4)
Date Samples Received:	July 25, 2013
Condition of the Sample Bags on Arrival:	No leaks or condensation was detected
No. of Samples Analyzed:	Four (4)
Date of Odour Panel Analysis:	July 25, 2013
Time of Odour Panel Analysis:	9:21 – 11:18 AM

2.0 METHODOLOGY

2.1 Laboratory Methodology

All samples were evaluated in accordance with British Standard, BS EN 13725:2003, "Air quality – Determination of odour concentration by dynamic olfactometry", using an AC'SCENT International triangular forced-choice, ascending concentration, dynamic dilution Olfactometer. A listing of Standard Practices to which the evaluations conform is provided in Appendix II.

The AC'SCENT Olfactometer was calibrated according to the manufacturer's guidelines on the day of sample evaluation. The CHEMFLUOR® PTFE tubing through which the odour sample is presented to the panellists was replaced prior to the assessment session. All sample delivery lines were purged continuously with odour free air between sample presentations.

A panel of five trained assessors was employed in the evaluation of the odour samples. Each panel is screened for accuracy and repeatability following the procedures outlined in BS EN 13725:2003, utilizing 50 ppm n-butanol calibration gas prior to sample evaluation. The geometric mean of the individual threshold estimates for 50 ppm n-butanol was determined to be between 20 and 80 ppb/v.

The odour samples were presented to the panellists using the "triangular forced-choice" method, described by ASTM E679-04, "Standard Practice for Determination of Odor and Taste

Thresholds By a Forced-Choice Ascending Concentration Series Method of Limits". Each panellist evaluated the odour by "sniffing" the diluted odour samples presented by the Olfactometer. At each dilution level, the panellist "sniffed" three sample presentations, two of which were blank, odour free samples and one that contained the odorous air. The panellist was then asked to identify which of the three presentations was different from the other two by recording a "guess", "detect" or "recognize" response as defined by ASTM E679-04.

A "guess" response was recorded when the assessor could not distinguish between any of the presentations. A "detect" response was recorded when the assessor could differentiate the odorous sample from the two blanks, and "recognize" was recorded when the assessor could identify and describe the odorous sample.

As per BS EN 13725:2003, each sample assessment began with the Olfactometer diluting the odorous sample to sub-detection levels. The odour sample and two blanks were then presented to one panellist, who "sniffed" the three presentations and recorded their response. The concentration of odorous gas was then doubled and re-presented to the same assessor with two blanks. Again, the assessor "sniffed" the three presentations and recorded their response. The process continued with the concentration of odorous gas increasing until the panellist had correctly detected the odour in at least two consecutive presentations as described by BS EN 13725:2003. The process was repeated for each panellist until all samples were evaluated.

Sample analysis was conducted "blind"; neither the panellist nor the test administrator knew which port would deliver the odour sample. Panellist's results were recorded and analyzed using AC'SCENT DataSense Olfactometry software integrated with the Olfactometer. The software incorporates an Access database program designed specifically for olfactometry laboratories and is compatible with international olfactometry standards including BS EN 13725:2003 and ASTM E679-04.

As part of laboratory Quality Assurance and Quality Control (QAQC), test results were retrospectively screened in accordance with BS EN 13725:2003. As the standard requires, each assessor's individual threshold estimate (Z_{ITE}) was compared to the panel's average threshold, with the ratio between the individual threshold estimate and the panel average threshold represented as ΔZ. Assessors having a ΔZ greater than 5.0 or lower than -5.0, were eliminated from the results. The purpose was to exclude panel members that showed deviant responses due to health factors or specific hypersomia or ansomia for the odour of the analyzed sample. Where screening was required, both the screened and unscreened results were provided.

2.2 Odour Evaluation Parameters

2.2.1 Odour Threshold Values – Detection Threshold (DT)

The detection threshold (DT) is the dilution ratio at which 50% of the panellists correctly detected the odour. DT, as defined by ASTM E679-04, is synonymous with the MOE Draft definition of an odour threshold value (ED_{50}) and the BS EN 13725:2003 definition of odour concentration (C_{OD}). That is, the DT represents the amount of dilution required for the odour to be just detectable. Since DT values are dimensionless, pseudo-dimensions of odour units per unit volume (i.e. odour units per cubic metre (ou/m^3)) are often used for reporting purposes.

In accordance with BS EN 13725:2003, individual threshold estimates (Z_{ITE}) were calculated as the geometric mean of the lowest dilution ratio where the odour could not be detected and the dilution ratio at which the panellist correctly detected the odour. Where a detection response could not be established at the Olfactometer's dilution limit, it was assumed that the panellist would have detected the odour at a dilution ratio half that of the limit, and the Z_{ITE} was calculated. The sample odour concentration (C_{OD}) was then calculated as the geometric mean of the Z_{ITE} values.

2.2.2 Odour Threshold Values – Recognition Threshold (RT)

The recognition threshold (RT), as defined by ASTM E679-04 is the dilution ratio at which the assessor first detects the odour's character (i.e. the odour "smells like…") or the dilution level at which 50% of the panellists correctly recognized the odour.

RT was evaluated following the same procedure as outlined for DT except once the assessor correctly detected the odour, the process continued with the concentration of odorous gas increasing until the panellist had correctly recognized the odour in at least two consecutive presentations. The process was repeated for each panellist until all samples were evaluated.

Calculations for RT were based on the BS EN 13725:2003 procedures for the determination of odour concentration (C_{OD}) where the individual recognition threshold estimates were calculated as the geometric mean of the lowest dilution ratio where the odour could not be recognized and the dilution ratio at which the panellist correctly recognized the odour. Where a recognition response could not be established at the Olfactometer's dilution limit, it was assumed that the panellist would have recognized the odour at a dilution ratio half that of the limit, and the individual recognition threshold estimate was calculated. The sample RT was then calculated as the geometric mean of the individual recognition threshold estimates.

2.2.3 Hedonic Tone (HT)

Hedonic tone (HT) is a measure of the pleasantness or unpleasantness of an odour sample and is independent of its character. Odours are commonly ranked by hedonic tone using the following 21 point scale:

+10	Most Pleasant
0	Neutral
-10	Least Pleasant

Prior to evaluating a sample for HT, each panellist was provided with a copy of an odour descriptor data collection form. For each sample requiring HT, the recognition threshold (RT) was determined by following the procedures outlined above. Once the panellist had correctly recognized the odour in two consecutive responses, the panellist was asked to mark the box corresponding to the point on the 21 point scale which best described the "pleasantness" of the odour. HT evaluation is done independently by each panellist without the consultation of the other panel members or the test administrator.

The average of the individual HT values was reported as the HT for the sample. If the panellist was unable to recognize the odour at the Olfactometer's dilution limit, that panellist was eliminated from the calculation of the sample HT.

2.2.4 Odour Character

There are numerous odour wheels available for use as a referencing vocabulary when describing an odour's character. The eight recognized odour categories include "Vegetable", "Fruity", "Floral", "Medicinal", "Chemical", "Fishy", "Offensive" and "Earthy". Each of the eight odour categories includes a list of specific descriptors to be used for further odour character analysis. The odour wheel currently used as Pinchin is shown in the figure below (Figure 1).

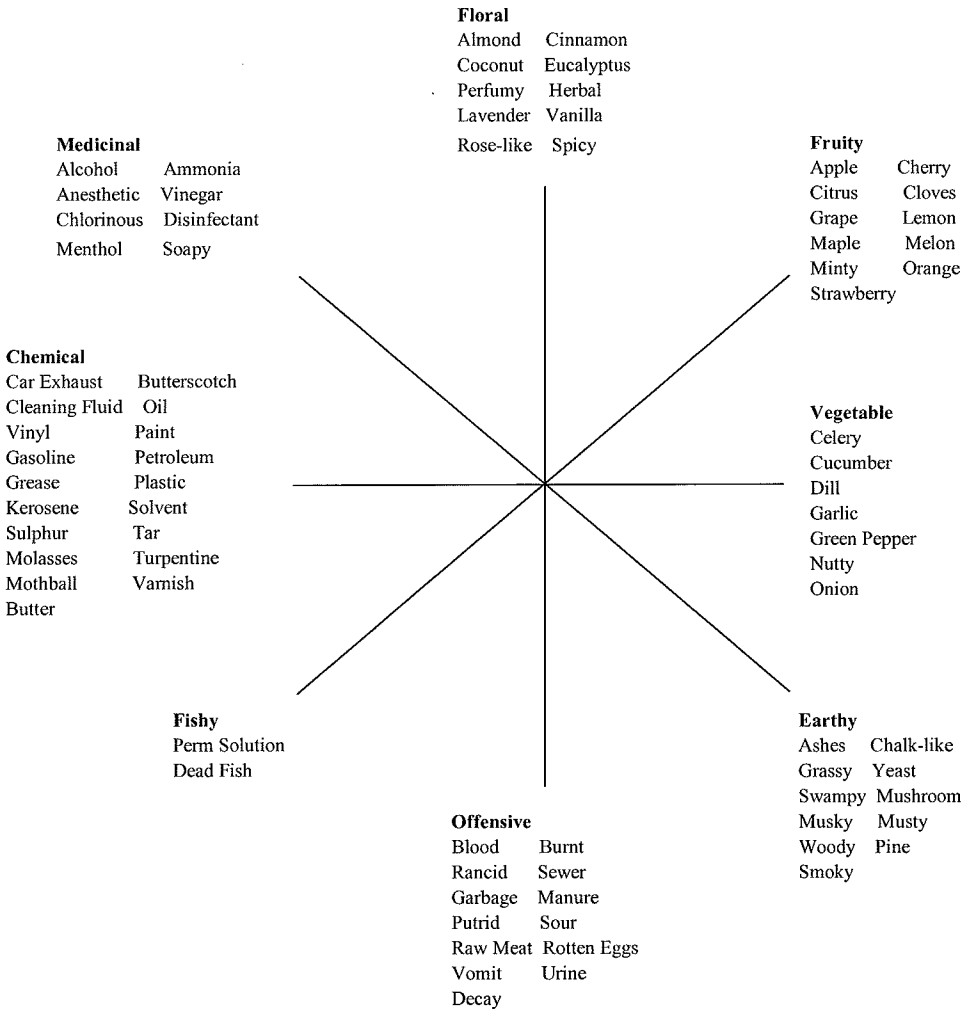


Figure 1: Odour Character Reference Vocabulary Wheel

Prior to evaluating a sample for odour character, each panellist was provided with a copy of an odour descriptor data collection form. For each sample requiring characterization, the recognition threshold (RT) was determined by following the procedures outlined above. If a panellist was unable to recognize the odour at the Olfactometer's dilution limit, that panellist was eliminated from odour character evaluations. Once the panellist had correctly recognized the odour in two consecutive responses, the panellist was asked to indicate which of the eight general odour categories best described the odour. In addition, the assessor was asked to mark the box corresponding to the strength of the odour within that general category. The odour strength is referred to as the relative odour intensity.

The relative odour intensity was determined using a 5 point scale. The number "1" corresponds to a mild odour and "5" corresponds to a strong odour. Assessors were given the option to choose as many general categories as required to describe the odour. The eight general odour

categories were presented on a spider graph with each extension representing a scale of 0 to 5, referencing relative intensity (mild to strong). The intensity is the average of the individual intensity scores reported for that category. General odour categories showing a "0" were not used by the panellists in the odour's general character description.

Once the general odour character section was complete, the assessors were asked to indicate specific odour descriptors. Assessors were given the option to choose as many specific descriptors as required to describe the odour and to add their own descriptions as required. A histogram was used to present the percentage of assessors that assigned specific descriptors to the odour sample.

All odour character evaluation is done independently by each panellist without the consultation of the remainder of the panel or the test administrator.

3.0 RESULTS

3.1 Odour Threshold Values – Detection Threshold (DT) & Recognition Threshold (RT)

The odour threshold value results for detection threshold (DT) and recognition threshold (RT) are presented in Table 1. Where appropriate, the DT and RT values have been adjusted for field pre-dilution reported by the client. The adjusted DT and RT values are recorded as DT_{NET} and RT_{NET}, respectively. Datasheets are provided in Appendix I.

Table 1. Odour Threshold Value Results

Odour Evaluation Results

Client: McGill University **Test Reference No.:** 85308-072513

Pinchin Project No.: 85308 **Evaluation Date:** 25-Jul-13

Client Project No.:

Lab No.	Field Number/ Description	Dilution Factor	Evaluation Time	Detection		Recognition		Comments
				DT	DT_{NET}	RT	RT_{NET}	
PO13-85308-A0535	Blank 01	2.3 :1	9:21 - 9:41 AM	121	282	69	161	
				155	361	92	214	E
PO13-85308-A0536	Raw 02	2.3 :1	9:42 - 10:20 AM	7321	17058	3411	7948	
				10005	23312	4582	10676	E
PO13-85308-A0537	ED 03	2.3 :1	10:21 - 10:46 AM	5544	12918	2411	5618	
PO13-85308-A0538	HT 04	2.3 :1	10:47 - 11:18 AM	8410	19595	3919	9131	

Odour Evaluation Report Nomenclature

DT Detection Threshold
RT Recognition Threshold
DT_{NET} Detection Threshold adjusted for field dilution
RT_{NET} Recognition Threshold adjusted for field dilution

Comments

E Result has been retrospectively screened

3.2 Hedonic Tone (HT) & Odour Character

The hedonic tone (HT) values are presented in Table 2. The relative odour intensities and corresponding general odour character for each sample are represented in the spider graphs attached as Appendix II.

Specific descriptors were the second part of the odour character evaluation. The histograms found in Appendix III present the percentage of assessors that assigned specific descriptors to the odour sample. The results summary is provided in Table 2.

Table 2. Hedonic Tone & Odour Character Results

Odour Characterization Results

Client: McGill University
Test Reference No.: 85308-072513
Pinchin Project No.: 85308
Evaluation Date: 25-Jul-13
Client Project No.:
Evaluation Time: 9:21 - 11:18 AM

Lab No.	Field No. Description	Average HT	Range HT	Primary Descriptor	Specific Descriptors[1]
PO13-85308-A0535	Blank 01	-5	-2 to -9	Fishy	Dead fish, *fishy,* garbage, musty, offensive, perm solution, raw meat, raw fish, salted cod, sour
PO13-85308-A0536	Raw 02	-3	-5 to -2	Offensive	Chemical, chlorinus, fruity, *garbage,* lemon, manure, maple, medicinal, *musty,* offensive, orange, *rancid,* raw meat, *sewer,* sour, vinegar
PO13-85308-A0537	ED 03	-3	-4 to -2	Offensive	Anesthetic, blood, cloves, disinfectant, earthy, fruity, garbage, manure, medicinal, melon, *musty,* offensive, raw meat, *sewer,* sour, swampy
PO13-85308-A0538	HT 04	-3	-7 to -2	Offensive	Earthy, eucalyptus, garbage, manure, mushroom, musty, *offensive,* pine, raw meat, rose-like, rotten eggs, sewer, sour, swampy, urine, yeast

Odour Evaluation Report Nomenclature

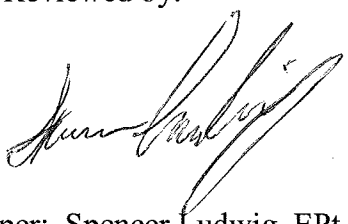
HT Hedonic Tone
Note 1 – The most commonly selected specific descriptor(s) for a sample are presented in *italics*.

Pinchin Environmental Ltd.

Prepared by:

per: Andrew Eldebs
Project Technologist
Emissions Reduction & Compliance
aeldebs@pinchin.com

Reviewed by:



per: Spencer Ludwig, EPt
Project Technologist
Emissions Reduction & Compliance
sludwig@pinchin.com

Pinchin Master Report Guide, Ver. 1, May 2007

J:\85000s\85308 McGillU,845SherbrookW,Montreal,ODPNL\July 25, 2013\85308-072513 Odour Lab Report.docx

APPENDIX I
ODOUR EVALUATION DATA SHEETS
PINCHIN FILE: 85308-072513
(6 PAGES)

Olfactometer Evaluation Results
AC'SCENT International Olfactometer

Test Name : McGill **Test No. :** 85308-072513 **Test Date :** 7/25/2013

Test Administrator : Andrew Eldebs **Test Method :** Triangular Forced Choice

Flow Rate (lpm) : 20 **Sniff Time (sec) :** 3

Sample Information

Lab No. : PO13-85308-A0535 **Field No. :** Blank 01 **Sampling Date :** 7/24/2013

Sampling Time :

Description : 2.3:1 **Sample Collector :** McGill

Sample Source : unknown

Dilution Level	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sample Volume	0.34	0.60	1.21	2.42	4.84	9.7	19.4	38.9	77.7	156	317	635	1268	2516
Total Volume	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350
Dilution Ratio	59,853	33,917	16,818	8,409	4,205	2,096	1,048	524	262	130	64.2	32.0	16.0	8.1
Geometric Mean	84,645	45,056	23,883	11,892	5,946	2,968	1,482	741	370	185	92	45.4	22.7	11.4
Log (Geo. Mean)	4.93	4.65	4.38	4.08	3.77	3.47	3.17	2.87	2.57	2.27	1.96	1.66	1.36	1.06

Calibration Date : 7/25/2013

THRESHOLDS
G = Guess
D = Detection
R = Recognition

Assessor/Round															Log G	Log D	Log R
000300	1										8	8				2.27	2.27	2.27
000300	2										8	8				2.27	2.27	2.27
14853-665	1										1	1	2	6	8	1.66	1.36	1.06
14853-665	2										2	6	8	8		2.27	1.96	1.66
14853-671	1										2	6	8	8		2.27	1.96	1.66
14853-671	2										1	6	8	8		1.96	1.96	1.66
14853-675	1										6	8	8			2.27	2.27	1.96
14853-675	2										6	8	8			2.27	2.27	1.96
000100	1										6	8	8			2.27	2.27	1.96
000100	2										6	8	8			2.27	2.27	1.96

Sample Comments :

Specific Chemical Concentration Data

Chemical : N/A

Concentration (ppm) :

Response Key:
1 = Incorrect Guess
2 = Correct Guess
5 = Incorrect Detection
6 = Correct Detection
7 = Incorrect Recognition
8 = Correct Recognition

Final Results

	G	D	R
Avg. Log Value	2.18	2.08	1.84
Std. Dev.	0.21	0.29	0.36
Threshold	150	121	69

Olfactometer Evaluation Results
AC'SCENT International Olfactometer

Test Name : McGill **Test No. :** 85308-072513 **Test Date :** 7/25/2013

Test Administrator : Andrew Eldebs **Test Method :** Triangular Forced Choice

Flow Rate (lpm) : 20 **Sniff Time (sec) :** 3

Sample Information

Lab No. : PO13-85308-A0535 **Field No. :** Blank 01 **Sampling Date :** 7/24/2013

Sampling Time :

Description : 2.3:1 **Sample Collector :** McGill

Sample Source : unknown

Dilution Level	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sample Volume	0.34	0.60	1.21	2.42	4.84	9.7	19.4	38.9	77.7	156	317	635	1268	2516
Total Volume	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350
Dilution Ratio	59,853	33,917	16,818	8,409	4,205	2,096	1,048	524	262	130	64.2	32.0	16.0	8.1
Geometric Mean	84,645	45,056	23,883	11,892	5,946	2,968	1,482	741	370	185	92	45.4	22.7	11.4
Log (Geo. Mean)	4.93	4.65	4.38	4.08	3.77	3.47	3.17	2.87	2.57	2.27	1.96	1.66	1.36	1.06

Calibration Date : 7/25/2013

THRESHOLDS
G = Guess
D = Detection
R = Recognition

Assessor/Round															Log G	Log D	Log R
000300	1										8	8				2.27	2.27	2.27
000300	2										8	8				2.27	2.27	2.27
14853-665	1										1	1	2	6	8			
14853-665	2										2	6	8	8				
14853-671	1										2	6	8	8		2.27	1.96	1.66
14853-671	2										1	6	8	8		1.96	1.96	1.66
14853-675	1										6	8	8			2.27	2.27	1.96
14853-675	2										6	8	8			2.27	2.27	1.96
000100	1										6	8	8			2.27	2.27	1.96
000100	2										6	8	8			2.27	2.27	1.96

NOTE : This Report represents data which includes any Retrospective Screening of data.

Sample Comments :

Specific Chemical Concentration Data

Chemical : N/A

Concentration (ppm) :

Response Key:
1 = Incorrect Guess
2 = Correct Guess
5 = Incorrect Detection
6 = Correct Detection
7 = Incorrect Recognition
8 = Correct Recognition

Final Results

	G	D	R
Avg. Log Value	2.23	2.19	1.96
Std. Dev.	0.11	0.14	0.23
Threshold	169	155	92

Olfactometer Evaluation Results
AC'SCENT International Olfactometer

Test Name : McGill **Test No. :** 85308-072513 **Test Date :** 7/25/2013

Test Administrator : Andrew Eldebs **Test Method :** Triangular Forced Choice

Flow Rate (lpm) : 20 **Sniff Time (sec) :** 3

Sample Information

Lab No. : PO13-85308-A0536 **Field No. :** Raw 02 **Sampling Date :** 7/24/2013

Sampling Time :

Description : 2.3:1 **Sample Collector :** McGill

Sample Source : unknown

Dilution Level	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sample Volume	0.34	0.60	1.21	2.42	4.84	9.7	19.4	38.9	77.7	156	317	635	1268	2516
Total Volume	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350
Dilution Ratio	59,853	33,917	16,818	8,409	4,205	2,096	1,048	524	262	130	64.2	32.0	16.0	8.1
Geometric Mean	84,645	45,056	23,883	11,892	5,946	2,968	1,482	741	370	185	92	45.4	22.7	11.4
Log (Geo. Mean)	4.93	4.65	4.38	4.08	3.77	3.47	3.17	2.87	2.57	2.27	1.96	1.66	1.36	1.06

Calibration Date : 7/25/2013

THRESHOLDS
G = Guess
D = Detection
R = Recognition

Assessor/Round															Log G	Log D	Log R
000300	1		2	2	1	6	8	8							3.77	3.77	3.47
000300	2		1	2	2	6	8	8							4.38	3.77	3.47
14853-665	1			1	1	1	1	2	6	8	8				3.17	2.87	2.57
14853-665	2		1	1	1	6	8	8							3.77	3.77	3.47
14853-671	1			1	6	6	8	8							4.08	4.08	3.47
14853-671	2		1	1	5	6	8	8							3.77	3.77	3.47
14853-675	1			2	6	8	8								4.38	4.08	3.77
14853-675	2		2	6	8	8									4.65	4.38	4.08
000100	1		1	1	6	8	8								4.08	4.08	3.77
000100	2		1	2	6	8	8								4.38	4.08	3.77

Sample Comments :

Specific Chemical Concentration Data

Chemical : N/A

Concentration (ppm) :

Response Key:
1 = Incorrect Guess
2 = Correct Guess
5 = Incorrect Detection
6 = Correct Detection
7 = Incorrect Recognition
8 = Correct Recognition

Final Results

	G	D	R
Avg. Log Value	4.04	3.86	3.53
Std. Dev.	0.43	0.40	0.40
Threshold	11,046	7,321	3,411

Olfactometer Evaluation Results
AC'SCENT International Olfactometer

Test Name : McGill **Test No. :** 85308-072513 **Test Date :** 7/25/2013

Test Administrator : Andrew Eldebs **Test Method :** Triangular Forced Choice

Flow Rate (lpm) : 20 **Sniff Time (sec) :** 3

Sample Information

Lab No. : PO13-85308-A0536 **Field No. :** Raw 02 **Sampling Date :** 7/24/2013

Description : 2.3:1 **Sampling Time :**

Sample Collector : McGill

Sample Source : unknown

Dilution Level	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sample Volume	0.34	0.60	1.21	2.42	4.84	9.7	19.4	38.9	77.7	156	317	635	1268	2516
Total Volume	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350
Dilution Ratio	59,853	33,917	16,818	8,409	4,205	2,096	1,048	524	262	130	64.2	32.0	16.0	8.1
Geometric Mean	84,645	45,056	23,883	11,892	5,946	2,968	1,482	741	370	185	92	45.4	22.7	11.4
Log (Geo. Mean)	4.93	4.65	4.38	4.08	3.77	3.47	3.17	2.87	2.57	2.27	1.96	1.66	1.36	1.06

Calibration Date : 7/25/2013

THRESHOLDS
G = Guess
D = Detection
R = Recognition

Assessor/Round															Log G	Log D	Log R
000300	1		2	2	1	6	8	8							3.77	3.77	3.47
000300	2		1	2	2	6	8	8							4.38	3.77	3.47
14853-665	1			1	1	1	1	2	6	8	8						
14853-665	2		1	1	1	6	8	8									
14853-671	1			1	6	6	8	8							4.08	4.08	3.47
14853-671	2		1	1	5	6	8	8							3.77	3.77	3.47
14853-675	1			2	6	8	8								4.38	4.08	3.77
14853-675	2		2	6	8	8									4.65	4.38	4.08
000100	1		1	1	6	8	8								4.08	4.08	3.77
000100	2		1	2	6	8	8								4.38	4.08	3.77

NOTE : This Report represents data which includes any Retrospective Screening of data.

Sample Comments :

Specific Chemical Concentration Data

Chemical : N/A

Concentration (ppm) :

Response Key:
1 = Incorrect Guess
2 = Correct Guess
5 = Incorrect Detection
6 = Correct Detection
7 = Incorrect Recognition
8 = Correct Recognition

Final Results

	G	D	R
Avg. Log Value	4.19	4.00	3.66
Std. Dev.	0.31	0.21	0.22
Threshold	15,342	10,005	4,582

Olfactometer Evaluation Results
AC'SCENT International Olfactometer

Test Name : McGill **Test No. :** 85308-072513 **Test Date :** 7/25/2013

Test Administrator : Andrew Eldebs **Test Method :** Triangular Forced Choice

Flow Rate (lpm) : 20 **Sniff Time (sec) :** 3

Sample Information

Lab No. : PO13-85308-A0537 **Field No. :** ED 03

Description : 2.3:1

Sampling Date : 7/24/2013

Sampling Time :

Sample Collector : McGill

Sample Source : unknown

Dilution Level	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sample Volume	0.34	0.60	1.21	2.42	4.84	9.7	19.4	38.9	77.7	156	317	635	1268	2516
Total Volume	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350
Dilution Ratio	59,853	33,917	16,818	8,409	4,205	2,096	1,048	524	262	130	64.2	32.0	16.0	8.1
Geometric Mean	84,645	45,056	23,883	11,892	5,946	2,968	1,482	741	370	185	92	45.4	22.7	11.4
Log (Geo. Mean)	4.93	4.65	4.38	4.08	3.77	3.47	3.17	2.87	2.57	2.27	1.96	1.66	1.36	1.06

Calibration Date : 7/25/2013

THRESHOLDS
G = Guess
D = Detection
R = Recognition

Assessor/Round															Log G	Log D	Log R
000300	1			1	2	6	8	8								4.08	3.77	3.47
000300	2			1	6	8	8									4.08	4.08	3.77
14853-665	1		2	1	1	1	6	6	8	8						3.47	3.47	2.87
14853-665	2			1	1	1	6	6	8	8						3.47	3.47	2.87
14853-671	1			1	2	2	6	8	8							4.08	3.47	3.17
14853-671	2			2	1	1	6	8	8							3.47	3.47	3.17
14853-675	1		1	2	6	8	8									4.38	4.08	3.77
14853-675	2			2	1	6	8	8								3.77	3.77	3.47
000100	1			2	1	6	8	8								3.77	3.77	3.47
000100	2		2	1	6	8	8									4.08	4.08	3.77

Sample Comments :

Specific Chemical Concentration Data

Chemical : N/A

Concentration (ppm) :

Response Key:
1 = Incorrect Guess
2 = Correct Guess
5 = Incorrect Detection
6 = Correct Detection
7 = Incorrect Recognition
8 = Correct Recognition

Final Results

	G	D	R
Avg. Log Value	3.86	3.74	3.38
Std. Dev.	0.32	0.26	0.35
Threshold	7,320	5,544	2,411

Olfactometer Evaluation Results
AC'SCENT International Olfactometer

Test Name : McGill **Test No. :** 85308-072513 **Test Date :** 7/25/2013

Test Administrator : Andrew Eldebs **Test Method :** Triangular Forced Choice

Flow Rate (lpm) : 20 **Sniff Time (sec) :** 3

Sample Information

Lab No. : PO13-85308-A0538 **Field No. :** HT 04 **Sampling Date :** 7/24/2013

Sampling Time :

Description : 2.3:1 **Sample Collector :** McGill

Sample Source : unknown

Dilution Level	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sample Volume	0.34	0.60	1.21	2.42	4.84	9.7	19.4	38.9	77.7	156	317	635	1268	2516
Total Volume	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350	20,350
Dilution Ratio	59,853	33,917	16,818	8,409	4,205	2,096	1,048	524	262	130	64.2	32.0	16.0	8.1
Geometric Mean	84,645	45,056	23,883	11,892	5,946	2,968	1,482	741	370	185	92	45.4	22.7	11.4
Log (Geo. Mean)	4.93	4.65	4.38	4.08	3.77	3.47	3.17	2.87	2.57	2.27	1.96	1.66	1.36	1.06

Calibration Date : 7/25/2013

THRESHOLDS
G = Guess
D = Detection
R = Recognition

Assessor/Round															Log G	Log D	Log R
000300	1		1	1	6	8	8								4.08	4.08	3.77
000300	2		1	1	1	2	8	8							3.77	3.47	3.47
14853-665	1		1	1	2	2	6	8	8						4.08	3.47	3.17
14853-665	2		1	1	2	6	8	8							4.08	3.77	3.47
14853-671	1		1	5	6	6	8	8							4.08	4.08	3.47
14853-671	2		1	2	2	6	6	8	8						4.38	3.77	3.17
14853-675	1		1	1	6	8	8								4.08	4.08	3.77
14853-675	2		1	6	8	8									4.38	4.38	4.08
000100	1		1	2	6	8	8								4.38	4.08	3.77
000100	2		1	2	6	8	8								4.38	4.08	3.77

Sample Comments :

Specific Chemical Concentration Data

Chemical : N/A

Concentration (ppm) :

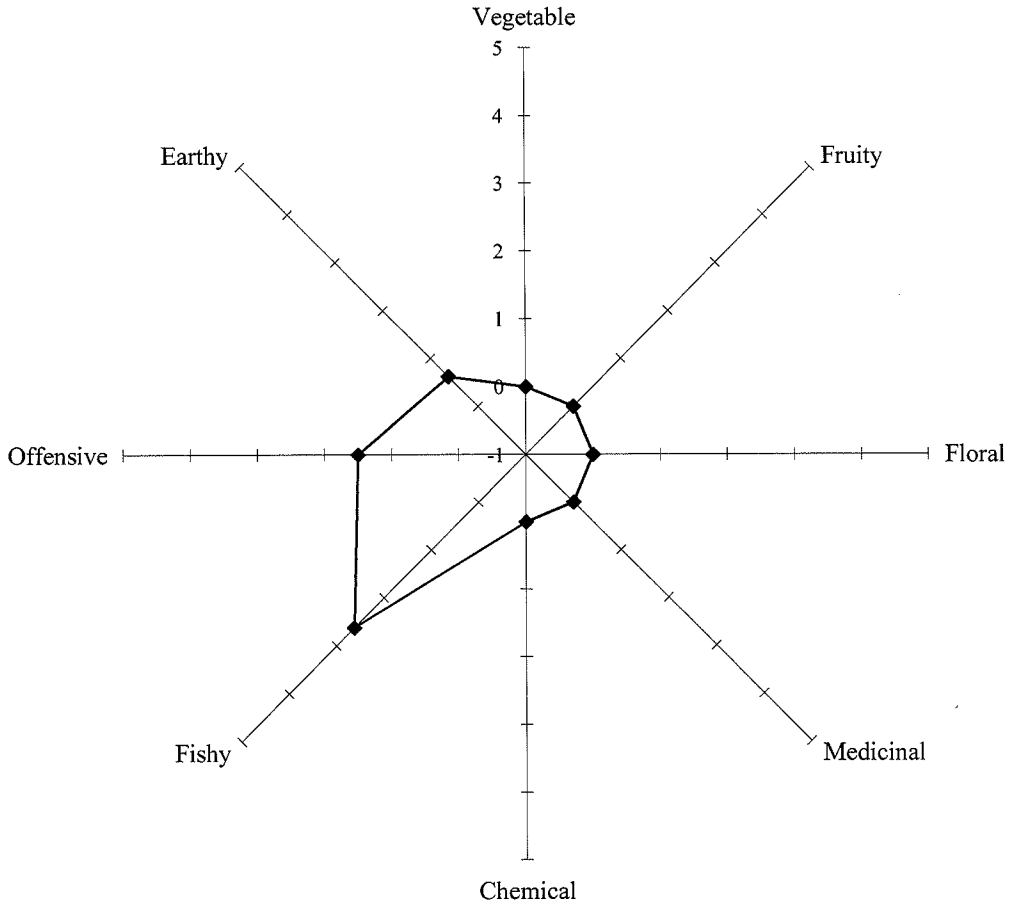
Response Key:
1 = Incorrect Guess
2 = Correct Guess
5 = Incorrect Detection
6 = Correct Detection
7 = Incorrect Recognition
8 = Correct Recognition

Final Results

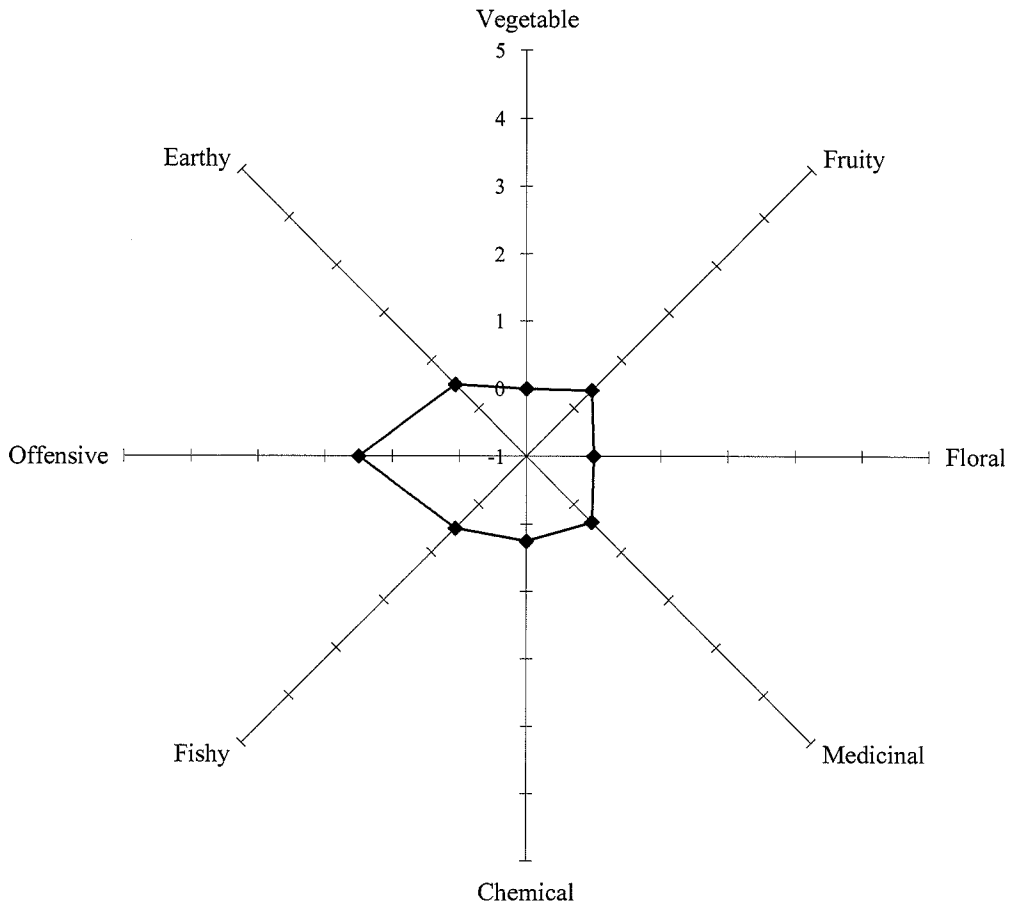
	G	D	R
Avg. Log Value	4.17	3.92	3.59
Std. Dev.	0.20	0.29	0.29
Threshold	14,665	8,410	3,919

APPENDIX II
RELATIVE ODOUR INTENSITY SPIDER GRAPHS
PINCHIN FILE: 85308-072513
(4 PAGES)

Odour Descriptor Graph
Blank 01

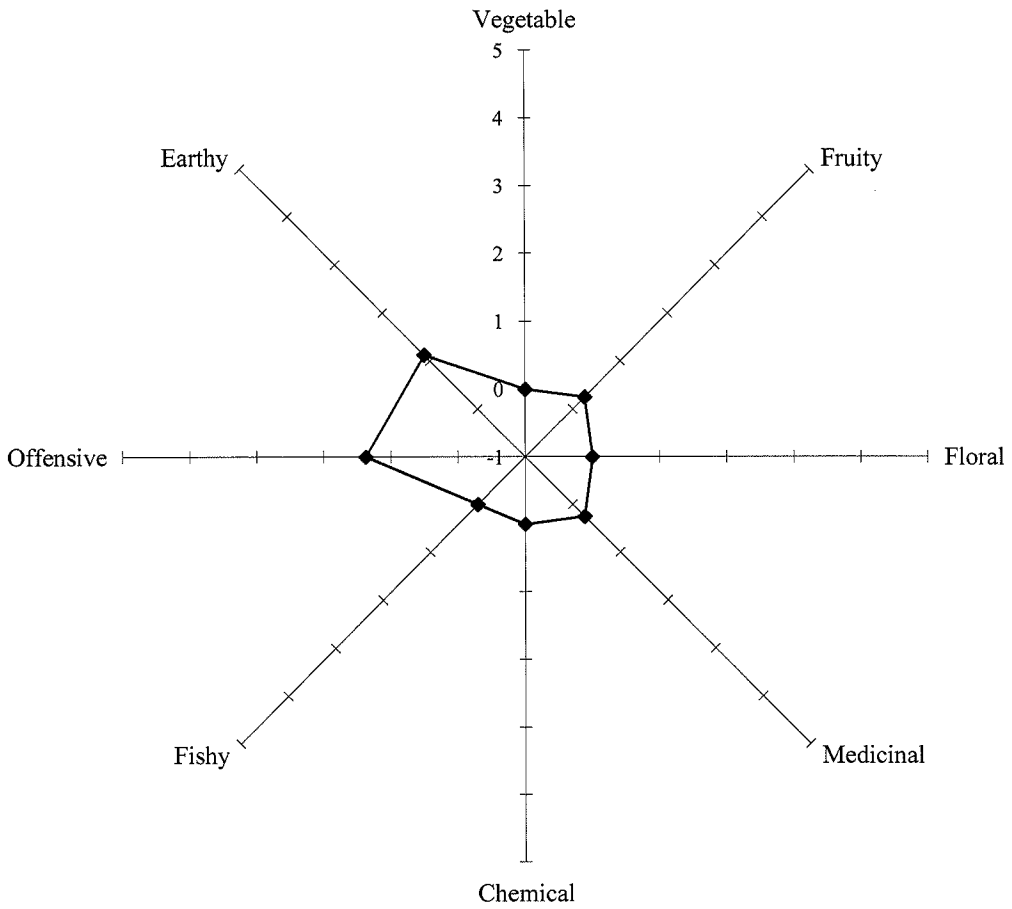


Odour Descriptor Graph
Raw 02

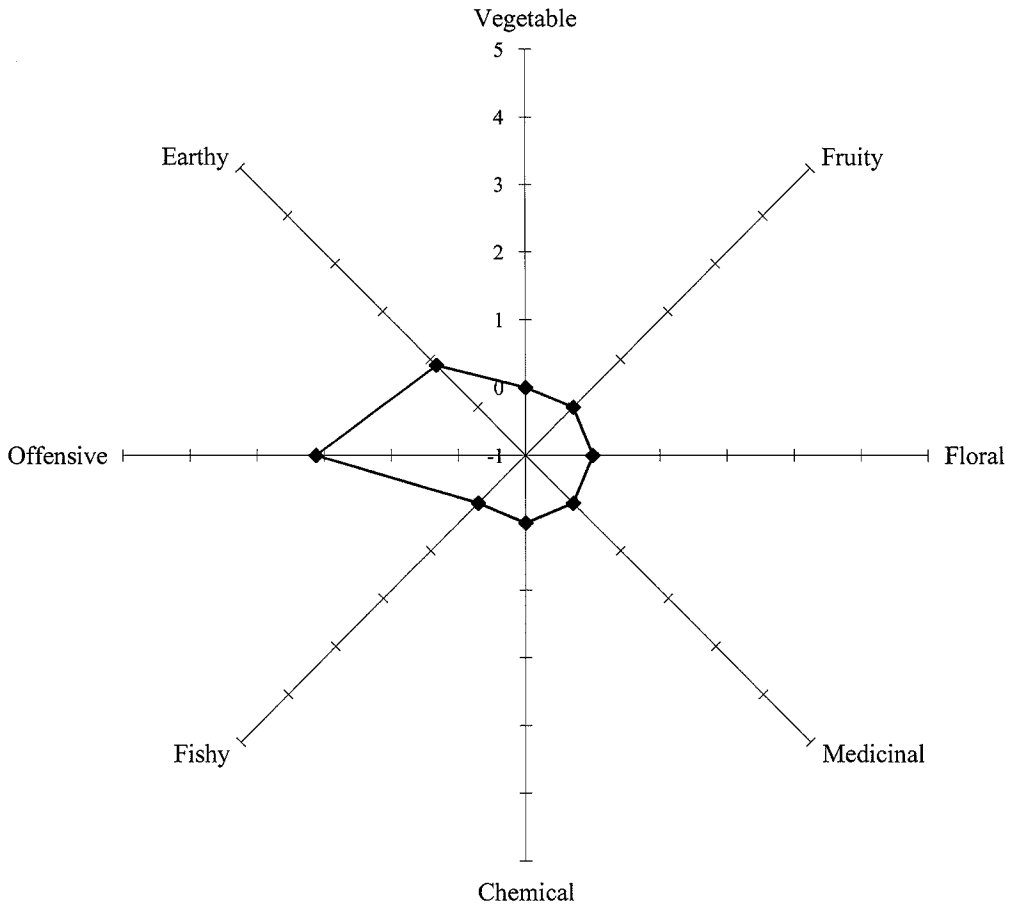


Pinchin Environmental

Odour Descriptor Graph
ED 03

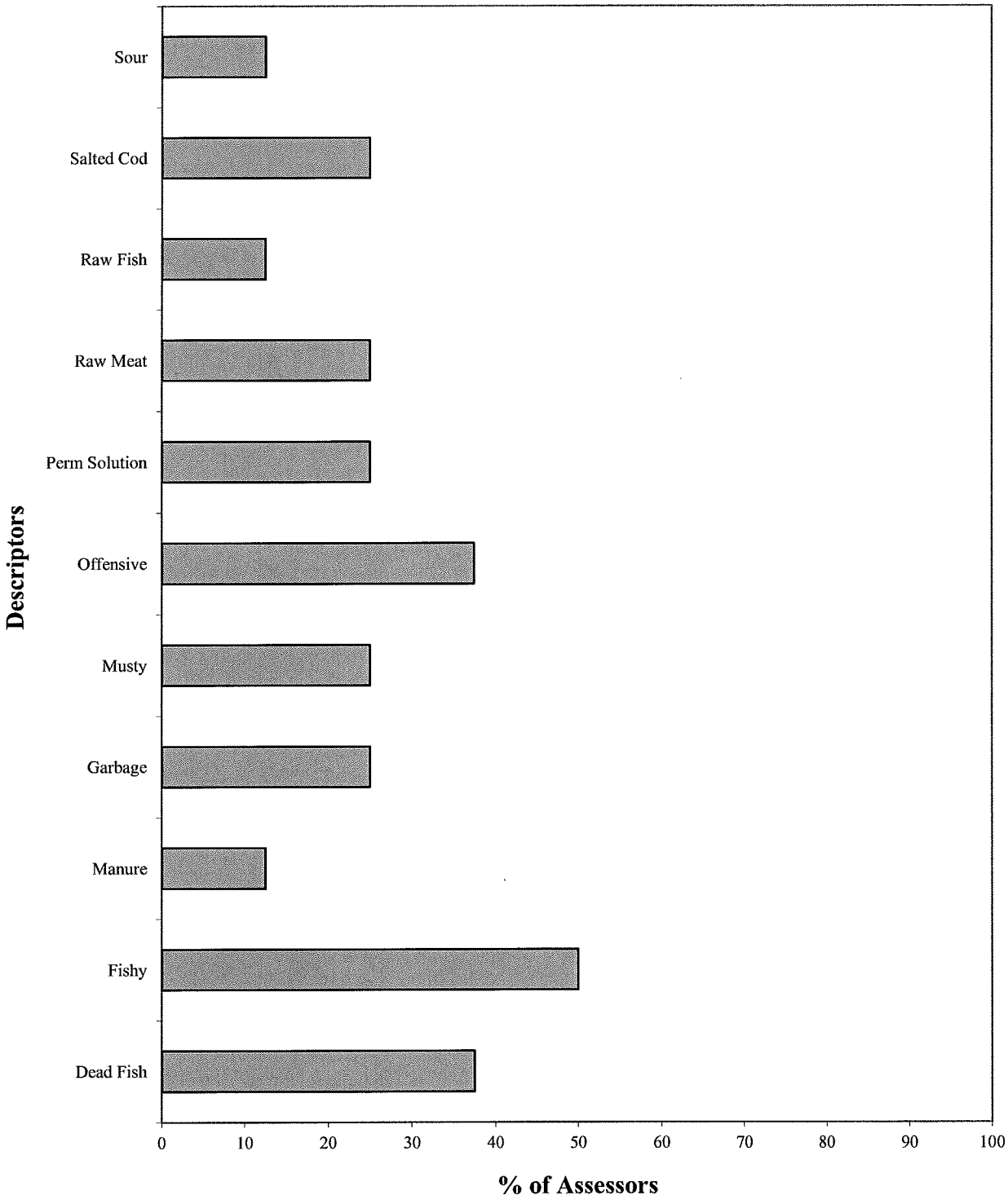


Odour Descriptor Graph
HT 04

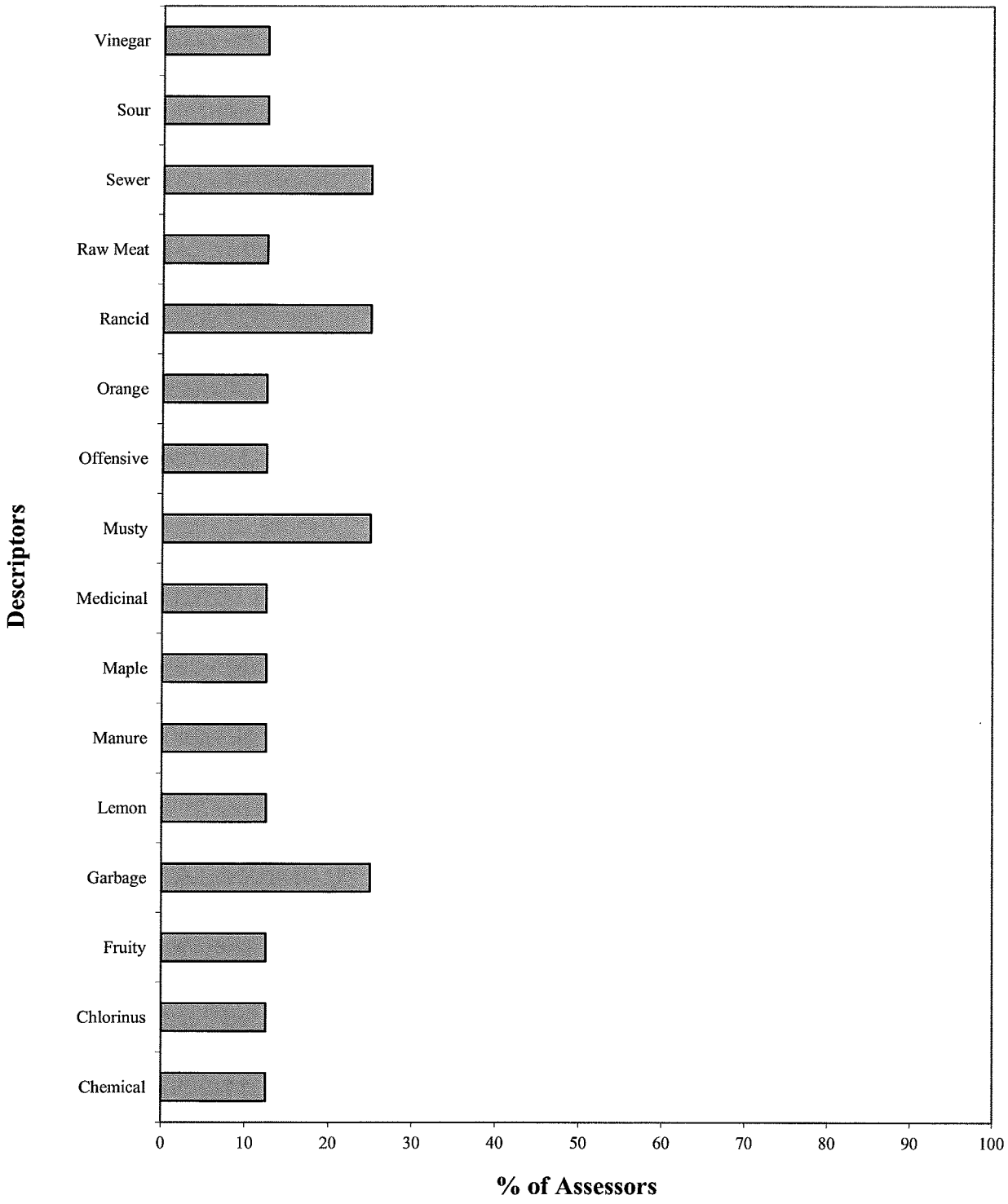


APPENDIX III
SPECIFIC DESCRIPTOR HISTORGRAMS
PINCHIN FILE: 85308-072513
(4 PAGES)

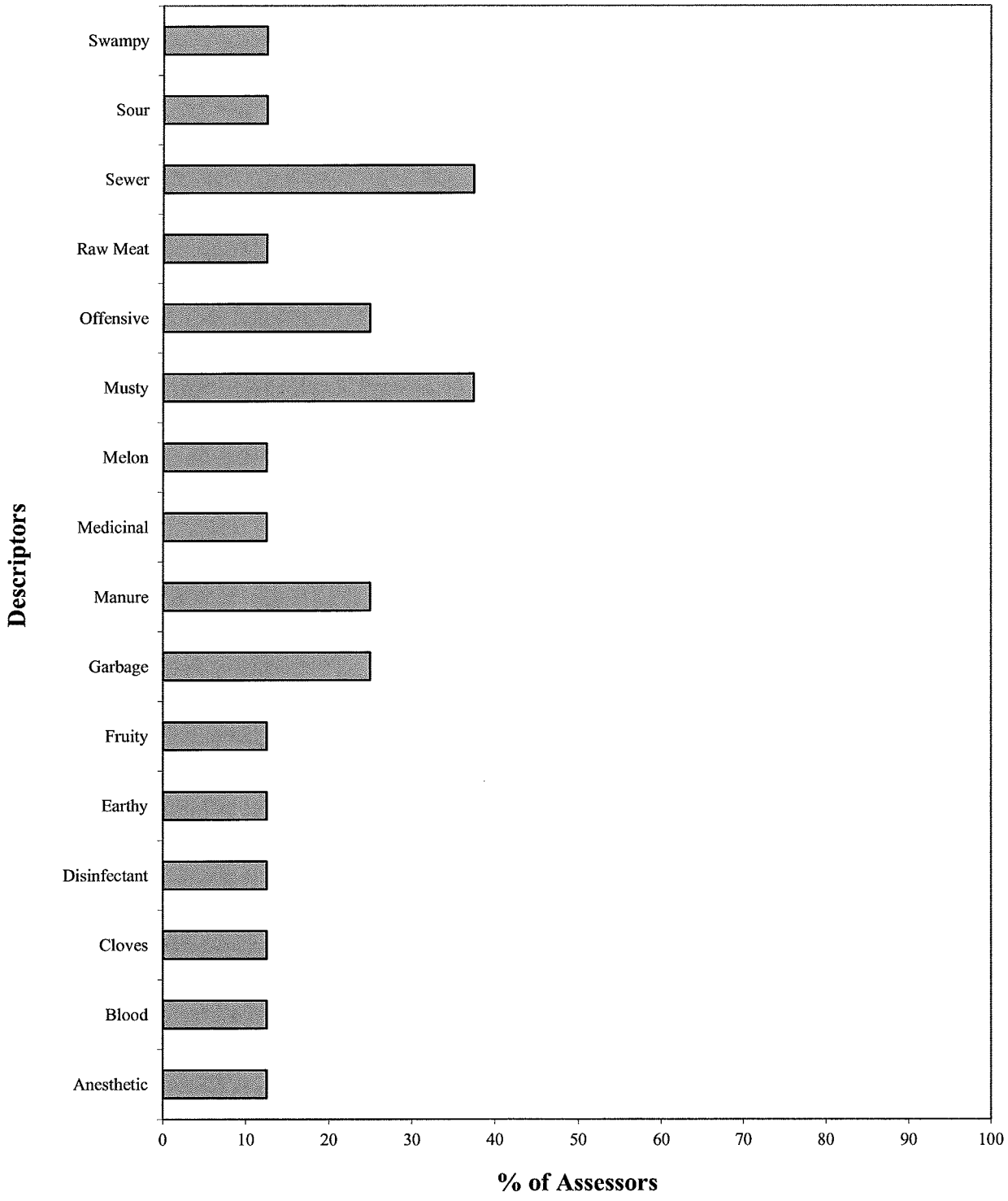
Odour Descriptors Histogram
Blank 01



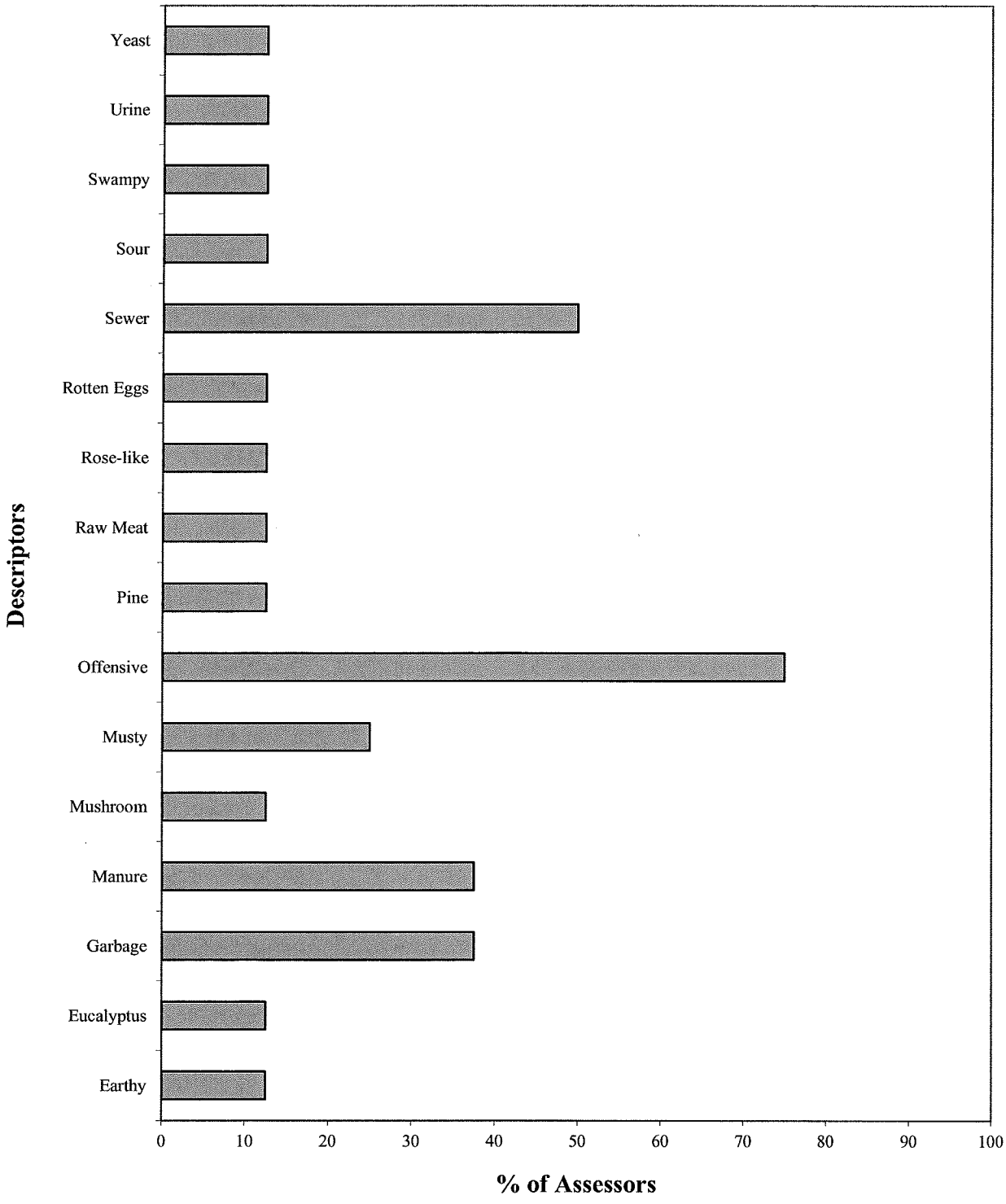
Odour Descriptors Histogram
Raw 02



Odour Descriptors Histogram
ED 03



Odour Descriptors Histogram
HT 04



APPENDIX IV
ODOUR EVALUATION QUALITY ASSURANCE
PINCHIN FILE: 85308-072513
(1 PAGE)

ODOUR EVALUATION QUALITY ASSURANCE

- Odour evaluations conducted at the Pinchin Environmental Odour Laboratory conform to the procedures outlined in the Ministry of the Environment "Ontario Source Testing Code" (OSTC), Version #3, June 2010 (Part G, Method ON-6) and are in accordance with ASTM (American Society for Testing and Materials) Standard Practice E679-04, Determination of Odour and Taste Thresholds by a Forced-Choice Ascending Concentration Series of Limits.
- The AC'SCENT® Dynamic Dilution Forced-Choice Triangle Olfactometer complies with all aspects of the ASTM E679-04 standard as well as the operational requirements of the British Standard, BS EN 13725:2003, "Air quality – Determination of odour concentration by dynamic olfactometry".
- The detection threshold values are reported as defined by ASTM E679-04 and BS EN 13725:2003.
- Assessors are selected and trained in accordance with BS EN 13725:2003.
- The Pinchin Environmental Odour Laboratory is managed based on the requirements of the International Organization for Standardization (ISO) International Standard ISO 17025:2005, "General requirements for the competence of testing and calibration laboratories".
- Samples are consumed during the evaluation and all sample bags are destroyed 48 hours after transmittal of the Preliminary Odour Evaluation Results, unless otherwise specified.