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252

Jenni Lehtinen

Odorous Volatile Organic Compounds in Waste and Wastewater Management

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ABSTRACT

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The odour emission from waste and wastewater management is experienced as very unpleasant and life quality diminishing factor. The odorous compounds and their possible risks for employees health in three municipal wastewater plants, in pulp mill effluent plant and in two waste management plants were determined in this thesis. Correlation between odorous compounds and odour concentrations was determined. In wastewater treatment the odorous compounds were dimethyl sulphide (DMS), dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS), hydrogen sulphide (H_2S), limonene, toluene, heptanal and octanal. In some cases carboxylic acids were determined. In most cases the incoming wastewaters already had an important role in defining the character of wastewater odour. In pulp mill wastewater treatment the odorous compounds were alpha-pinene, DMS, DMDS, toluene and p-cymene. In composting plant the odorous compounds were acetic acid, butanoic acid, 2,3-butanedione, 3-hydroxy-2-butanone, ethyl acetate, 2-butanol and limonene. The odorous compounds in the optic sorting of municipal waste were 2,3-butanedione, 3-hydroxy-2-butanone, ethyl acetate, ethyl benzene and p-cymene. As a difference from composting, aromatic and aliphatic hydrocarbons were abundantly present. Concentrations of VOCs in waste and wastewater treatment did not exceed the Finnish occupational exposure limits. Still some remarks were made from the results; 1,2-dichloroethane and styrene were determined in high concentrations being close to the WHO recommendation limits in one wastewater treatment plant. In waste management the concentrations of 2,3-butanedione exceeded the limit proposals given by US NIOSH. TVOC concentrations were in the range of 232-2300 $\mu g/m^3$ in waste management and in the range of 100-7719 $\mu g/m^3$ in municipal wastewater management. Total sum of odorous compounds seemed to correlate with the measured odour concentration. When comparing the TVOC concentration with OU/m^3 results, correlation between them was not determined.

Keywords: Odour; TD-GC-MS-sniff; VOCs; wastewater and waste treatment.

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CONTENTS

LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following original papers, which will be referred to in the text by their Roman numerals I-V. I have planned all the studies with my supervisors and co-authors and I have done all the experimental work considering VOCs including the field sampling and laboratory analysis of samples and also done all the data analyses and the discussion of results. I have been the corresponding author in publications I, II, III and V. In Publication IV I have been the corresponding author considering the parts of VOC emissions and in publication V I have been the corresponding author considering the VOC study of optic sorting plant.

I Lehtinen J. & Veijanen A. 2011. Determination of odorous VOCs and the risk of occupational exposure to airborne compounds at the wastewater treatment plants. *Water Science and Technology* 63 (10): 2183–2192.

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

III Lehtinen J & Veijanen A. 2012. Characterization of odorous VOCs at the Kraft pulp mill wastewater treatment by simultaneous instrumental and sensory method. Manuscript.

IV Tolvanen O., Nykänen J., Nivukoski U., Himanen M., Veijanen A. & Hänninen K. 2005. Occupational hygiene in a Finnish Drum composting plant. *Waste Management* 25 (4): 427–433.

V Lehtinen J., Tolvanen O., Nivukoski U., Veijanen A. & Hänninen K. 2012. Occupational hygiene in terms of volatile organic compounds and bioaerosols on two solid waste management plants in Finland. Submitted manuscript.

ABBREVIATIONS

bdl	below detection limit
bql	below quantification limit
BF	biofilter
BOD	biological oxygen demand
COD	chemical oxygen demand
CP	composting plant
DMDS	dimethyl disulphide
DMS	dimethyl sulphide
DMTS	dimethyl trisulphide
FID	flame ionization detector
FTIR	fourier transform infrared analyser
GC-MS	gas chromatography - mass spectrometry
GC-MS-O	gas chormatography - mass spectrometry - olfactometry
GC-PID	gas chromatograph - photo ionization detector
GR	grit removal
MeSH	methane thiol
NIOSH	National Institute of Occupational Safety and Health
OEL	occupational exposure limit
OSP	optic sorting plant
OU	odour unit
PT	purge and trap
RSD	relative standard deviation
SD	sludge dewatering
ST	sludge thickening
SVOC	semi volatile organic compound
TD-GC-MS	thermal desorption - gas chromatography - mass spectrometry
TR	trash rakes
TVOC	total volatile organic compounds
VOC	volatile organic compound
VVOC	very volatile organic compound
WHO	World Health Organization
WWTP	waste water treatment plant

1 INTRODUCTION

1.1 Waste and wastewater treatment in Finland

In Finland the sorting and managing of waste by the best available technology (BAT) is regulated by the environmental law (86/2000). Also the waste directive of EU (2006/12/EC) defines the direction of Finnish waste management. The main focus of the law and directive is the diminishing of the amount of waste and thereafter the reduction of emissions. The separate collection of waste fractions and efficient recycling of waste are the most important objectives of waste management nowadays.

Solid waste was collected over 1 500 000 tonnes in Finland in year 2010 from which 1 100 000 tonnes ended up to the landfills. The amount of deposit of waste to landfills has decreased and the energy use of waste has grown in recent years. Also utilization of biowaste has grown: biowaste was collected 300 000 tonnes in 2010 from which circa 295 000 tonnes were recycled (Official Statistics of Finland 2011). Biowaste and sludge is usually treated by composting with peat or wood chips as the additive in open fields in windrows or nowadays more and more in tunnel or drum composting plants.

In Finland communities and industry are obligated to process the wastewater according the environmental law and the wastewater enactment by using the BAT. The regulations are plant specific and defined in environmental licenses. The majority of wastewaters are treated in plants that use activated sludge process, which reduces the amount of organic matter in the effluent very efficiently. Wastewater processing methods and parameters are plant specific but many plants use primary and secondary wastewater treatment (Finland’s environmental administration 2010). Depending on the Finnish communal structure, there is quite a lot of dispersed settlement in the countryside where the separated household based wastewater treatment is in use (Government decree 542/2003).

1.2 Odour perception and odour-structure-relationships

Sense of smell is very important tool to assess quality of goods or environment and it is very strongly linked to our emotions and aesthetics (Brattoli et al. 2011). Odours evoke associations and emotions, even memories from for example childhood and from very important occasions in people´s live in which the odour is associated (Willander & Larsson 2006). It has been very important tool in past days in terms of surviving by keeping people avoiding anything harmful or hazardous like rotten food or toxic air (Doty 2007).

Odour perception and its stages can be presented as follows (Frechen 1994, Fig. 1): first is the odorant, reception that is a physical phenomenon. Then comes the interpretation of odours in neural system which is a pshycological process. Third part is the odour impression which can be effected by social and environmental factors (Arnold 1995). Sense of smell and the odour perception is very subjective matter and people's reactions are dependent for example on their background and home environment, education, cultural aspects etc. (Cheremisinoff 1988, Larsson et al. 2000). Furthermore, people's tolerance to annoying odours vary and different people find different odours offensive and at different concentrations. Odour thresholds that people have for odorous compounds vary widely due to the chemical nature of compounds and between persons depending on age, gender and state of health (Wysocki & Pelchat 1989, Bliss et al. 1996, Griep et al. 1997, Stuetz et al. 2001, Knaapila 2008).

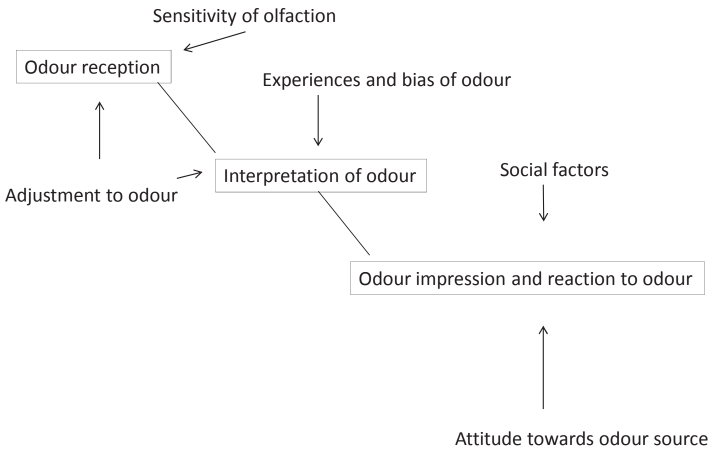


FIGURE 1 Stages of odour perception and factors effecting on the impression of odour (Arnold 1995, Frechen 1994).

Chemical structure of a compound has a strong effect on the odour characteristics and the intensity of odour. Different substituent groups and their positions in the carbon chain, the stereochemical structure of a compound, length of carbon chain, double bonds in the structure etc. all have influence on the type and strength of the odour (Ohloff et al. 2011). For example the neighbouring substances in homologous series of organic compounds have the greatest similarity in odour descriptions than those widely separated in chain length (Döving 1966). In addition, chirality of a compound is an important factor in differences of odour descriptions. Well known cases of chirality and odour is for example limonene and its D- and L- enantiomers (optical isomers). The D (+)-form is described to smell citrus, orange-like but the L (-)-form smells like harsh, turpentine (Brenna et al. 2003).

1.3 Odorous compounds in waste and wastewater management

1.3.1 Volatile Organic Compounds (VOCs)

Odorous compounds in waste and wastewater treatment are different organic compounds, especially volatile organic compounds (VOCs) and some inorganic compounds of which the most important are hydrogen sulphide (H_2S) and ammonia (NH_3).

Volatile organic compounds (VOCs) are a great variety of odourless, odorous and even toxic organic compounds (Hunter & Oyama 2000). According to EU Solvent Emissions Directive (EC Directive 1999/13/EC), Volatile Organic Compounds (VOCs) are defined as organic compounds having at 293.15 K (20 °C) a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under particular conditions of use. An organic compound is defined as a compound containing at least the element carbon and one or more of hydrogen, halogens (e.g., chlorine, fluorine or bromine), oxygen, sulphur, phosphorus, silicon, or nitrogen. However, carbon oxides and inorganic carbonates and bicarbonates are not included in to the definition. In addition, methane, ethane, organometallic compounds and organic acids are excluded from this definition. Furthermore, by the definition made by World Health Organization (WHO) in 1989, organic compounds that have boiling points in a range of below zero to 400 °C, are considered as VOCs and they are divided into three different subcategories (Table 1).

TABLE 1 Categorization of VOCs by their boiling points (modified from WHO 1989).

Category and abbreviation	Boiling point range (°C)
Very volatile organic compounds (VVOC)	<0-50…100
Volatile organic compounds (VOC)	50-100...240-260
Semi volatile organic compounds (SVOC)	240-260…380-400

The chemical and physical properties of VOCs have a very important role in understanding the behaviour of odour in different sources, predicting what compounds are to be evaporated and in what rate, and also in the planning of best available odour emission abatement methods. These properties include compound´s polarity, vapour pressure and Henry´s law constant, chemical and biological reactivity, ionization and sorption (Card 1998).

1.3.2 Hydrogen sulphide (H_2S)

Hydrogen sulphide (H_2S) has been very common odorant in waste and wastewater treatment and it is associated with anaerobic conditions (Gostelow & Parsons 2001). The formation of H_2S under anaerobic conditions is also studied widely because of its toxicity and corrosive properties. H_2S has a very low odour threshold concentration so it does not have to exist in high concentration to cause odour problems. Odour threshold concentration for hydrogen sulphide is 0.0001 mg/m^3. Odour characteristic of H_2S is rotten eggs (Ruth 1986).

H_2S is a weak dibasic acid and it dissociates depending on the prevailing pH value. In pH 7, 50 % of the hydrogen sulphide is present at the molecular form and 50% as a dissociated form (HS^-). Only molecular H_2S cause odour and this fact has been utilized in odour control (Hunter & Oyama 2000).

1.3.3 Ammonia (NH_3)

Ammonia (NH_3) is a weak base. NH_3 is common odorant in agriculture and can be detected also in waste and wastewater processing (Rappert & Muller 2005). Odour character of NH_3 is pungent, very distinctive. It has a rather high odour threshold concentration, 3.6-36 mg/m^3 (Finnish Institute of Occupational Health 2012) but it is harmful for health in rather low concentration (14 mg/m^3) and therefore it is important to recognize in waste and wastewater management. It is formed under either anaerobic or aerobic conditions, when proteins and amino acids degrade. Carbon/nitrogen ratio has an effect on formation of NH_3 so that the lower the C/N-ratio, more easily the NH_3 is formed and released from example biowaste or wastewater sludge (Epstein 1997).

1.4 Odour and VOCs as an environmental problem

The emissions of industry, traffic, agriculture and waste management are a growing global problem. Parts of this problem are the volatile organic compounds (VOCs), hydrogen sulfide and ammonia. In Finland, the amount of VOCs emitted to the atmosphere from waste management was 0.47 tonnes in year 2006 (Finland's Environmental Administration 2006). The known anthropogenic sources of VOCs in waste management are landfilling, incineration, composting and landspreading of sludges or compost (Giusti 2009).

VOCs contribute to the ozone formation in the lower troposphere and thus to the generation of smog. VOCs also participate in the stratospheric ozone depletion and therefore they are considered as an environmental issue (Derwent 1995). Furthermore, most of the VOCs are also odorous compounds (Hunter & Oyama 2000). The odour emission especially from waste and wastewater management is experienced as very unpleasant and life quality diminishing factor (Arnold 1995). In addition, the unpleasant odour emission may raise a concern about possible health threats the odorous emission may cause (Rosenkranz & Cunningham 2003). People's prejudices and attitude towards the emission from waste management effect strongly on the perception of odour and its possible psychosocial effects on humans (Dalton 2003).

1.5 VOCs, odour and health

The role of odours as the cause of health effects is nowadays still unclear and the potential patophysiological mechanisms of symptoms possibly associated with odour are insufficiently understood. However, it is suggested that some of the odorous VOCs may also have a considerable toxic potential (Domingo & Nadal 2009). Impact of waste and wastewater management to the environment and employees is nowadays recognised as a growing environmental and public health-related concern (Giusti 2009). In the last decade and especially in the last few years the interest considering occupational health issues and odour in waste management has grown in Europe because of the rapid increase of the mechanical-biological treatment (Biasioli et al. 2004). Several studies concerning the VOCs as the odour source and VOC and bioaerosols emissions from landfills and composting as the health affecting factors are conducted all over Europe (Pierucci et al. 2005, Chiriac et al. 2007, Persoons et al. 2010, Scaglia et al. 2011, Vilavert et al. 2012) and in Asia (Zou et al. 2003, Majumdar & Srivastava 2012).

In addition to the direct sensory irritation of high concentration of odorous VOCs there are several non-sensory factors like mental models, bias, psychosocial factors and personality variables that influence odour and irritation perception (Schusterman et al. 1991, Smeets & Dalton 2005). In research considering odour as the health hazard, Schiffman et al. (2005) have described three different mechanisms how odour can be a health effecting factor. In the first mechanism type odorous VOCs occur in concentrations above the irritation levels and so the health effects are caused by direct irritation, not especially the odour. In the second mechanism odorous VOCs are present in concentrations that are clearly below irritation threshold concentrations but still above the odour threshold concentrations. In this case the health threat is connected with genetic heritage and making the brains react very differently on good or foul odours (Schiffman et al. 1995). Several other studies suggest also that the odour annoyance itself may lead to the symptoms like shortness of breath, eye irritation, dry throat, unusual tiredness, joint pain etc. (Cavalini 1994, Steinheider et al. 1998, Aatamila et al. 2011). The third type of mechanism is that odour is connected to some other factor that person is exposed to, like dust or endotoxins that are the real causes of health effects, not necessarily the odour (Schiffman et al. 2005).

The source and type of odour have an impact on the odour perception and the elicited worry about health hazard; for example unpleasant odours from waste management are more easily perceived as threatening. Increase in symptom reporting from odour exposure is reported in cases of increased dissatisfaction or annoyance of unpleasant odour (Sucker et al. 2009). However, it has not been indicated, that chemicals that have an unpleasant odour, may cause health hazards as the concentration or the odour intensity rises. On the contrary, it has been indicated, that odourless and non volatile compounds have more systematic connection with health effects than the odorous compounds have (Rosenkranz & Cunningham 2003).

Health effects of VOCs are studied widely, but the concentration range where symptoms have occurred is very broad. There are still contradictory impressions whether the moderately low concentrations of VOCs effect to people’s health and this subject has been studied in indoor air and occupational health exposure cases. Some studies show that moderately large concentrations of several VOCs may cause symptoms like headache, eye and skin irritation in a range of 0.3-3.0 mg/m^3 (Mölhave et al. 1991) but in other studies (Fiedler et al. 2005) the exposure to VOC mixture of concentration range of 2.5–26 mg/m^3, did not seem to cause significant acute changes in symptoms.

High concentrations of VOCs are known to be harmful to human health but synergetic effects and their relevance in working environments is still insufficiently studied (Ten Brinke et al. 1998, Fischer & Dott 2003, Smeets & Dalton 2005). Mölhave et al. (1991) have reported total volatile organic compound (TVOC) concentrations of 0.3-3.0 mg/m^3 to be the multifactor exposure range in which the VOC concentrations are low but still cause health problems depending on interactions with other exposure factors such as bioaerosols and dust particles. They also reported that simultaneous exposure to several common VOCs that are not very harmful by definition may be a health risk even if the total concentration is quite low; 8 mg/m^3. In higher TVOC concentrations – 25 mg/m^3 – Pappas et al. (2000) have showed that four hour exposure caused several upper and lower respiratory symptoms. Bioaerosols such as the fungal spores and bacteria found at the waste water handling sites together with VOCs may also increase the risk of health problems. Mesophilic heterotrophic bacteria moulds and yeasts, fecal coliforms and fungi, have been detected in the different stages of waste water handling (Pascual et al. 2003). In composting and waste management in general, bioaerosol concentrations may be abundant as determined in studies by Tolvanen (2001), Tolvanen & Hänninen (2007), Persoons et al. (2010) and Vilavert et al. (2012) and they may be causing the health effects especially in the upper airways (Bunger et al. 2002, Heldal et al. 2003).

Health risk of VOCs is based on the fact that VOCs most directly affects the skin, the exposed mucous membranes in the eyes and nose, as well as the lungs causing irritation effects and respiratory problems (Ware et al. 1993). In Finland, health problems caused by exposure to low concentrations of odorous sulphurous compounds emitted from pulp mills were studied and the results showed that even low concentrations of sulphurous compounds cause symptoms such as respiratory problems and eye irritation. This was especially true among children (Haahtela et al. 1992, Marttila et al. 1994).

1.6 Sources of odorous emissions in waste and wastewater management

1.6.1 Municipal wastewater treatment

Odour at the wastewater treatment plants is a combination of dozens of odorous volatile organic compounds. Some of the compounds are present in the incoming wastewater and others may be generated during the transport or the treatment processes at a facility (van Durme 1998). Odorous compounds present in fresh wastewater are different kinds of oxygen, sulphur and nitrogen containing compounds, aliphatic, aromatic and chlorinated hydrocarbons. They are derived from cleaning agents used in households, solvents and petrol derivatives, and compounds associated with human waste such as urea, ammonia, scatole and indole (Hwang et al. 1995, Vincent 2001). Some compounds are also formed due to the microbial degradation of organic matter (Hvitved-Jacobsen & Vollertsen 2001). Different chemical and biological processes and processing conditions like pH, temperature, retention time etc. have a great effect on the odour characteristics during the different stages of the treatment process (Bonanni 1998, van Durme 1998). For example, anaerobic conditions or low oxygen levels in the wastewater and long retention times in the sewers favour the formation of malodorous sulphur compounds and carboxylic acids. Furthermore, the physico-chemical properties of volatile odorous compounds such as polarity, solubility in water, vapour pressure and sorption define the compounds tendency to either volatilize into the air from the liquid phase or adsorb/absorb to the organic particulate material present in effluents, and therefore have a great impact on the overall odour composition (Chao et al. 1998, Tansel & Eyma 1999). Emissions of organic compounds can occur by diffusive or convective methods from the surface of effluent ponds. Diffusion occurs when the concentrations at the surface are higher than in the ambient air and the compounds attempt to reach equilibrium between aqueous and gaseous phases. Convection occurs by air flow sweeping compounds from the surface to the air (Capelli et al. 2009). One mechanism for VOC emissions is also gas stripping that happens from ponds that are aerated. In gas stripping the gas (usually air) is entrained in wastewater and thus the VOCs are transferred from the wastewater by mass transfer laws (Tchobanoglous & Burton 1991).

1.6.2 Pulp and paper industry effluent treatment

Kraft pulping process consists of chemical removal of lignin from the polysaccharide fibres of wood or other raw material. Pulping is carried out by sodium sulphate ($NaSO_4$) and sodium hydroxide (NaOH) in high temperature (170 ºC). Thereupon, a large number of low molecular weight and volatile compounds are formed from lignin and polysaccharides as they decompose and/or react with pulping chemicals (Álen 2000). As a result of the pulping process, pulp mill effluent consists of parts of wood chips, pieces of bark, dissolved sugars, smaller organic and inorganic molecules like acids and alcohols and lignin (Joutsenoja 2002). In the digester, main volatile compounds are known to be methanol, ethanol, acetone, sulphur compounds and terpenes (Karnofski 1975). Bleaching removes the residuals of lignin and is done by several sequential chemical operations with chlorine dioxide followed by washing.

Odorous compounds are formed during the kraft pulping process or are due to the biochemical changes in the wastewater treatment processes. The amount of odorous compounds released during the kraft process depends largely on the wood species, condition of the wood and conditions used in subsequent processing of pulp and black liquor. Odorous sulphur compounds are formed due to the sulphate pulping process and odorous terpenes are released from the wood tissue structures during pulping (Álen 2000). Wood species have a great effect of released terpenes, as some woods such as pines contain a much higher concentration of extractives.

In Finland, many pulp mills use primary and secondary wastewater treatment (Hynninen & Laine 1998). Especially biological activated sludge ponds are highly aerated and the stripping of volatile compounds is increased due to elevated turbulence and interfacial contact of air and water (Lange & Christensen 2004). In addition, volatilisation of many VOCs typical for pulping effluents is very high from the open surface of aerated pond because of their physico-chemical properties like solubility in water and boiling point and therefore they are more easily released to the atmosphere than consumed by microbes.

1.6.3 Composting

Composting is an efficient method to treat biological waste but the disadvantage of the method is the fairly strong odour emissions produced during the process (Haug 1993). Composting is a very complicated biochemical process in which the organic matter, eg. proteins, fats and carbohydrates are converted into water, carbon dioxide, and humus (Epstein 1997). Many parameters have an effect on the function of compost and compost odours. These are oxygen content, pH, temperature, moisture content and the amount of nutrients available (Hentz et al. 1996).

Alongside the degradation process the intermediate products like low weight volatile molecules are released as a result of the microbiological metabolism (Fischer et al. 1999). Odorous gaseous emissions from compost include usually different organic sulphur containing, oxygen containing and nitrogen based compounds. VOCs in composting are typically reduced sulphur compounds, alcohols, aldehydes, ketones, esters, some terpenes and carboxylic acids (Wilkins 1994, Imppola et al. 2003, Schlegelmilch et al. 2005, Mao et al. 2006, Lasaridi et al. 2010) and they are a result of incomplete aerobic degradation process (Mao et al. 2006). The most odorous compounds like sulphur based compounds are released especially when the aeration of the compost mass is incomplete or insufficient (Wilber & Murray 1990, Krzymien et al. 1999). In studies considering the odour emission from compost, most of the VOCs have been noticed to be released at the early stages of the process; as in the tipping floors, the shredder and during the initial forced aeration composting period (Eitzer et al. 1995).

Ammonia, among other nitrogen based compounds, is also produced during composting. The origin of ammonia is the degradation of urea, proteins and amino acids (Pagans et al. 2006, Cadena et al. 2009, Lasaridi et al. 2010).

1.6.4 Solid waste handling

Handling and management of solid waste offer a potential emission route for VOCs because they are emitted from waste material as such or as metabolic products of microbial activity during the aerobic or anaerobic decomposition processes (Leach et al. 1999). Odour problems are more likely to occur if residues of biowaste are accompanied in the waste management process.

Major compound groups are determined as ketones, alcohols, esters, aliphatic and aromatic hydrocarbons and terpenes, especially limonene (Davoli et al. 2003, Chiriac et al. 2011). Limonene is detected particularly in fresh waste analyses (Davoli et al. 2003). P-cymene is considered to be a tracer of biogas, meaning that the decomposition of solid waste and possibly the accompanied biowaste has already happened and the waste is aged (Termonia 1999). In some studies made by Chiriac et al. (2007) also chlorinated hydrocarbons, especially trichloroethene and tetrachloroethene, were found to be released in the early stages of handling the solid waste in the landfills. Strongest waste odours are generated during discharge and compaction of waste. Also mixing of wastes creates strong odour emissions (Chiriac et al. 2011).

1.7 Contemporary VOC and odour measurement techniques

1.7.1 Gas chromatography-mass spectrometry (GC-MS)

Odours are traditionally measured either analytically by different instruments or by sensorial methods. Instrumental methods allow getting information on the existing compounds and their concentrations, but do not gather information on the odour characteristics or the induced annoyance level (Zarra et al. 2009). On the other hand, odour analyses conducted by sensorial methods such as dynamic olfactometry, sociological surveys and field panels give information on the intensity and temporal and spatial occurrence of the overall odour annoyance, but leave out the information on single chemical compounds people might be exposed to. Furthermore, odour abatement methods in plants are more difficult to apply without knowing the chemical composition of odour emission.

Odour is a result of a mixture of hundreds of compounds present in air. Instrumental approaches to characterize odour are based on the evaluation of the chemical composition of odorous air (Brattoli et al. 2011). The quantification of odorous and polar VOCs has been challenging because of the highly reactive nature of compounds and their presence in complex matrices and in very different concentrations. The best analytical technology for identifying and measuring individual compounds in very complex mixture of organic compounds, that can be hundreds in one sample, is gas chromatography-mass spectrometry, GC-MS (Hobbs 2001, Su et al. 2008, Woolfenden 2010a & 2010b). Although FID is the most representative method in organic analysis, mass spectroscopy offers better sensitivity and the possibility to identify the unknown compounds in the mixture (Pandey & Kim 2009). GC-MS has been recently used widely in analyzing the air from landfills and composting plants, as well as in the wastewater treatment and animal rendering plants (Defoer et al. 2002, Davoli et al. 2003, Dincer et al. 2006, Zarra et al. 2008, Cadena et al. 2009).

The sample injection and concentration techniques are usually headspace based methods, either dynamic or static, and it has been in use since the 1960´s (Cronin 1982). Also cryogenic trapping and purging and trapping are used in order to pre-concentrate the sample before injection to the GC.

The limits of traditional instrumental techniques have directed the attention to odour measurement procedures that relies on the use of human nose as a detector (Brattoli et al. 2011). The most sensitive and broad range odour detector is undoubtedly the mammalian olfactory system that has millions of years of experience and it has been developed during the evolution. Therefore, in odour determination, the combined GC-MS-olfaction (GC-MS-O) has been also introduced in recent years, especially in food and aroma chemistry research (Plutowska & Wardencki 2008). GC-MS-O allows a deeper comprehension about the odour composition and about the individual separated compounds odour characteristics (Veijanen 1990, Friedrich & Acree 1998, van Ruth 2001, Lo et al. 2008). The methodological problems can arise from the subjective nature of odour assessment, decreasing alertness of assessors or from the non-random sequence in which the compounds elute. Decreasing alertness will be important factor if there is only a few compounds to perceive or they show only low odour intensity, when the stimulus is brief or the session is long and if the assessor is not motivated (van Ruth 2001).

1.7.2 Sampling methods for odour and VOC analysis

Odour measurements can be made from point sources, area sources with outward flow and area sources without an outward flow (Jiang & Kaye 2001). Sampling is the critical phase in measuring odours and VOCs. Often the odorous compounds are found at very low concentrations and the adsorption onto surfaces becomes significant (Hobbs 2001). Also the sample storage is critical because the sample degrades or alters over the time. Furthermore, the sampling materials like containers or sampling lines have to be odourless, undergo minimal physical or chemical reactions with the sample and have a low permeability in order to minimize the sample losses through diffusion (Brattoli et al. 2011). The main materials used in bag sampling of odour or VOCs have been stainless steel, tetrafluoroethylene hexafluoropropylene copolymer (Teflon™), polyvinyl fluoride (Tedlar™), glass and polytereftalic ester copolymer (Nalophan NA™). When sampling into canisters or bags, the disadvantages are that the reactivity among the different compounds could compromise sample stability and cause artefacts. Also the longer the time of a sample is in a bag, the lower the recovery of compounds or odour is or there can be sample losses. In addition, backround odour is determined in sampling bags and Trabue et al. have shown, that Tedlar™ bags, for instance emit acetic acid and phenol (Trabue et al. 2006).

The chemical composition or the concentration of certain odorous compounds can be in the ppt range or below and direct injection to the GC-MS is not possible in most of the cases and the pre-concentration of sample is needed (Bruno et al. 2007). Therefore, sorbent-based sampling method and thermal desorption or extraction from adsorbents is usually linked with the analysis of VOCs (Kleeberg et al. 2005, Pandey & Kim 2009, Woolfenden 2010a, Gallego et al. 2012, Rodriquez-Navas et al. 2012). The most used sampling methods for VOCs are presented in Fig. 2.

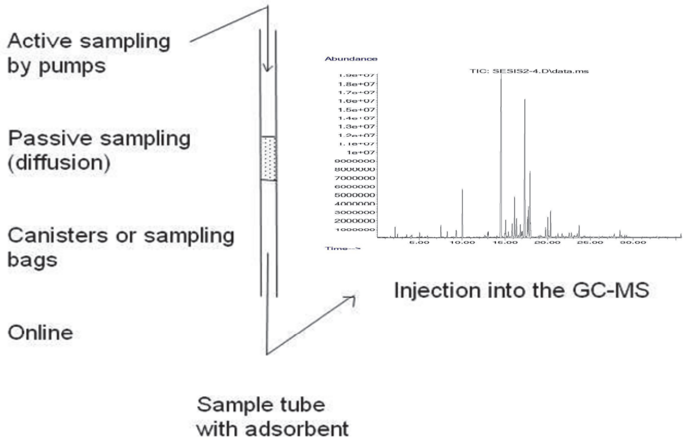


FIGURE 2 Overview of the most used sampling procedures in sorbent based air sampling (modified from Woolfenden 2010a).

Different adsorbents have a range of specific properties in VOC collection (Hobbs 2001). Adsorbents can be very selective to certain chemical groups or molecule sizes. Generally, the larger is the adsorbent surface area, the greater is the adsorption capacity for the smaller molecules. In choosing the sorbent for analysis, several factors should be considered. Important features of the sorbent are the strength of sorbent–sorbate interaction, artefacts, hydrofobicity, inertness and mechanical strength (Woolfenden 2010a). Nowadays, if a wide volatility range of compounds is to be monitored, multi-sorbent tubes are possible to use (Woolfenden 2010b).

Once the analytes are trapped to the sorbent, they must be released for analysis. The solvent desorption is the best technique for thermally labile compounds. Analytes are extracted from the sorbent with a low boiling solvent, for example carbon disulphide (CS_2). Most widely used desorption method is thermal desorption (TD), that is used for VOC analysis in urban and indoor air. Advantages for TD are that it is solvent free, offers lower LODs, and lower risks for contamination by solvents (Ras et al. 2009).

1.7.3 Fourier transform infrared analyser (FTIR)

Fourier transform Infrared (FTIR) analyser is equipment that can be used in different gaseous sample measurements. It is based on differentiation of compounds' infra red spectrums from each other in gaseous mixtures. It measures the gas concentration in stack and does not extract the samples for analysis. Therefore, it can be used in situ monitoring and the analysis is rather rapid compared to the extractive methods like TD-GC-MS (Ojala et al. 2006).

FTIR has been used for VOC analysis for example in paint manufactories (Lin et al. 2008).

1.7.4 Olfactometry

Odour concentration can be measured by olfactometry, which is nowadays a standardized analysis method. Concentration presented in OU/m^3 (odour unit per cubic meter) is a measure of the concentration of overall odour. It represents the number of dilutions required to bring the odour concentration of the sample to its odour threshold. One odour unit is thereby the amount of odorants present in one cubic metre of odorous gas at the panel threshold (SFS-EN 13725).

Three different choice modes are in use in olfactometry. In the yes/no mode, a panellist is asked to evaluate the gas presented from a single port and to indicate if the odour is detected (yes/no). Other form of olfactometry is the forced choice method, where a person has to decide between the odorous sample air and the reference air. In this mode the panellist is also asked to indicate whether their choice was a guess, whether they had inkling or whether they were certain to have chosen the correct port. The third mode is a forced choice/probability mode, where three or more ports are used. In this mode the dilution factor at the individual thresholds are estimated first and then the series of dilutions calculated from the individual threshold estimate are presented to the panellist (Sneath 2001). Olfactometry is widely used in assessing the odour emissions from different types of waste or wastewater handling processes (Defoer et al. 2002).

1.7.5 Electronic noses

In odour analysis problems arise from the subjectivity of the perception of odour between different persons. Attempt to solve this problem is the development of electronic noses that may offer an objective instrument for analysing odours (Stuetz & Fenner 2001). Sensor array systems such as electronic noses are systems that can characterize odour without reference to its chemical composition. The odour analysis is based on the pattern recognition technique, like a fingerprint technique. Materials used in sensors are chemically sensitive materials like thin metal film oxides, conducting polymers, supramolecular materials, functional inorganic materials like Pt, Au, nanomaterials etc. The signal from chemically sensitive material is transduced in various methods that are for example conductometric, optical, electrochemical, mechanical/acoustic, and thermal (DÁmico & Di Natale 2001).

2 OBJECTIVES

The main purpose of the study was to characterize odour and odour causing components, especially VOCs, in modern Finnish wastewater and waste treatment for future need to assess the possible odour reducing methods. Also measurement of inorganic compounds such as hydrogen sulphide and ammonia due to their important role as odorants was included in the measurements although the main focus of the study was to determine VOCs. Furthermore, the aim was to determine whether the emissions contained some health threatening components that employees have to be aware of. This is important especially in cases where the treatment processes have moved indoors in modernized plants. In these cases the VOC emissions may be concentrated and people still are working in these areas.

The specific objectives of the study were determined as follows:

1. To determine the odorous compounds in municipal and industrial wastewater treatment and to measure single VOC and TVOC concentrations (I, II, III).

2. To determine odorous compounds and single VOC and TVOC concentrations in municipal waste and biowaste treatment (IV and V).

3. To study the correlation between overall odour concentration and single odorous compounds in order to see if there are target compounds that can be used in predicting odour concentrations (II).

4. To estimate the exposure of employees to the possible harmful compounds according to received VOC results and comparing them with the occupational exposure limits and recommendations for indoor air quality (I, II, III, IV, V).

3 MATERIALS AND METHODS

3.1 Plant descriptions

3.1.1 Wastewater treatment plants (I, II, III)

The waste water treatment plants (WWTPs) examined in the study, referred to as A, B and C and pulp mill WWTP, all use the activated sludge biological treatment process. Basic information of the WWTP effluent parameters was received from the plants´ quality control (Table 2). In the plant C there is a biofilter that has a surface area of 60 m^2 and the filter material consists of sludge compost and woodchips. The detailed characteristics, sampling sites and analyses of these plants are presented in Table 3.

TABLE 2 Basic parameters for studied WWTP effluents.

WWTP	pH	Temperature (°C)	BOD$_7$ (influent) (mg/l)	COD (influent) (mg/l)
A	7.2	9-20	267	580
B	7.3	10-20	500	1633
C	7.3	8-20	450	857
Pulp mill	7.6	35-45	385	1935

3.1.2 Waste treatment plants (IV, V)

The city of Oulu composts its biowaste in a drum composting plant where the three drums (125 m^3) are placed inside a composting hall. The retention time of biowaste in the drum is one week and after that the biowaste is composted and cured in windrows outdoors. The bulking agent in Oulu drum composting is peat.

Sorting of solid waste and biowaste was required by households and restaurants, groceries etc. in Hämeenlinna at the time of measurements.

Separation in the source was managed by sorting the biowaste into black plastic bags. The separation process is based on the optic electronic surveillance that recognizes the black colored bags. Biowaste is collected and transported to a biowaste composting plant. Solid waste is deposited in to the bank in the waste disposal area. The detailed characteristics, sampling sites and analyses of these plants are presented in Table 3.

TABLE 3 Characteristics, sampling sites and analyses made in studied plants.

Site (Publication)	Treatment method	Influent flow (m^3/d) Air flow (m^3/d) Incoming waste (t/a)	Sampling sites in the plant (indoors (i)/outdoors (o)) From duct (du), Liquid sample (l)	Analyses from the sites
WWTP A Kotka (I)	Biological, activated sludge +$FeSO_4$	11600 m^3/d (91 % municipal, 9% industrial)	Bar screens (i), grit removal, (i) sludge dewatering (i)	VOCs, H_2S, NH_3
WWTP B Kotka (I)	Biological, activated sludge +$FeSO_4$	14 500 m^3/d (75% municipal, 25% industrial)	Bar screens (i), grit removal (i), sludge dewatering (i)	VOCs, H_2S, NH_3
WWTP C Jyväskylä (II)	Biological, activated sludge +$FeSO_4$	43 000 m^3/d	Bar screens (i), grit removal (i), primary clarifier (o), sludge thickening (o), sludge dewatering (i)	VOCs, OUs, H_2S, NH_3
WWTP C Biofilter Jyväskylä (II)	Biol. treatment of odour (sludge compost and wood chips)	310 500 m^3/d	Incoming gas (du), outgoing gas (du)	VOCs, OUs, H_2S, NH_3
Pulp mill WWTP (III)	Biological, activated sludge	30 000 m^3/d (95% pulping effluent, 5 % other industrial effluent)	Aeration pond (o), primary clarifier (o), fiber line control room (i), office (i) aeration pond (l), mixing pond (l), three influent fractions (Ef1, Ef2 and Ef3) (l)	VOCs, H_2S, NH_3
Oulu composting (IV)	Drum composting of municipal biowaste, three 125 m^3 drums	8 000 t/a	Process hall (i), control room (i)	VOCs, H_2S, NH_3
Hämeen-linna plant (V)	Optical sorting of municipal solid waste	23 000 t/a	Process hall (i), control room (i)	VOCs, H_2S, NH_3

3.2 Sampling (I, II, III, IV, V)

For VOC analyses duplicate air samples were collected in-situ to the adsorption tubes (Supelco 20920-U) filled with Tenax® GR adsorption resin (200 mg) by using an air pump (Gilian LFS-113DC, adjusted flow rate 0.1 litres per minute). The back-up tubes were connected to the first tubes to ensure capturing all compounds and to see the possible breakthrough of compounds. In addition, blank (zero) tubes were taken from every stack of sample tubes prepared and they were carried along in the sampling sites in order to see the possible background effect on sample tubes. The average sample volume was 4-10 litres in depending on the expected VOC concentrations. The process conditions at the plants were normal on the measurement days as recommended for this type of sampling (Albrecht et al. 2008). Liquid samples from mixing pond and aeration pond and from three different industrial effluent fractions, referred as Ef1, Ef2 and Ef3, at the pulp mill were taken from the ponds and ducts by the personnel of the plant.

Point source samples for olfactometric analyses were taken from the same sites as the VOC samples to ensure the comparability of olfactometry and VOC results. Sample air was collected into the Nalophan® sampling bags (7 litres) by Ecoma Vacuum Sampling device. In the biofilter the samples were collected to the sampling bags with the help of sampling hood of 1 m^2 area from four different points at the biofilter surface (surface area of 60 m^2), and the out coming flow velocity from the biofilter was measured (I). Detailed sampling sites are presented in Table 3. Sampling and measurements for this thesis were made in different seasons during years 2002-2007.

3.3 Combined instrumental and sensory analysis of VOCs (TD-GC-MS-Sniff-technique)

3.3.1 TD-GC-MS-sniff setup and analysis conditions (I, II, III, IV, V)

Laboratory analyses for VOC samples were performed by applying a thermal desorption or purge & trap-thermal desorption / gas chromatograph / mass spectrometer device (PT-TD-GC-MS) (Tekmar 3000 / Agilent 6890+ / 5973N MSD spectrometer), connected with simultaneous sniffing done by a professional assessor with odours and odorous compounds. Helium (Aga, 99.9996 % purity) was used as the carrier and purge gas. For liquid samples, suitable amount of sample (0.5–3 ml in this study) was set into the purge vial of the Tekmar 3000 system and the volatilized compounds were trapped into the adsorbent (Tenax GR®) during purging. Purge temperature was 40 °C and duration 12 minutes.

Thermal desorption, in which the compounds are transferred from the adsorbent to the GC column, was accomplished by purging the adsorbent with helium for 10 minutes at 250 °C and simultaneously collecting the desorbed compounds into a cooling trap at –120 °C (cooled by liquid nitrogen). After desorption, the cooling trap was heated very rapidly to 280 °C causing the trapped volatile compounds to be desorbed forward in the gas chromatograph columns. The GC oven program was as follows: at 40 °C for two min, after that ramping 5 °C/min up to 150 °C and from that ramping 15 °C/min up to 250 °C keeping that temperature for 5 min.

3.3.2 Sniff-technique (I, II, III, IV, V)

A double column system (HP-5, 30 m, 1 µm phase) in the GC-MS was used so that the one column led to the mass spectrometer and the other to a glass funnel attached to the GC. The separated compounds were sniffed in the funnel (Fig. 3). The retention time of odour, the odour intensity and its character was registered during the sniffing simultaneously with the GC-MS analysis. The type of detected odour was described and the intensity was rated in the scale of 1-4 in chromatograms in which the stage 1 was slight odour and stage 4 was very strong odour (Fig. 4).

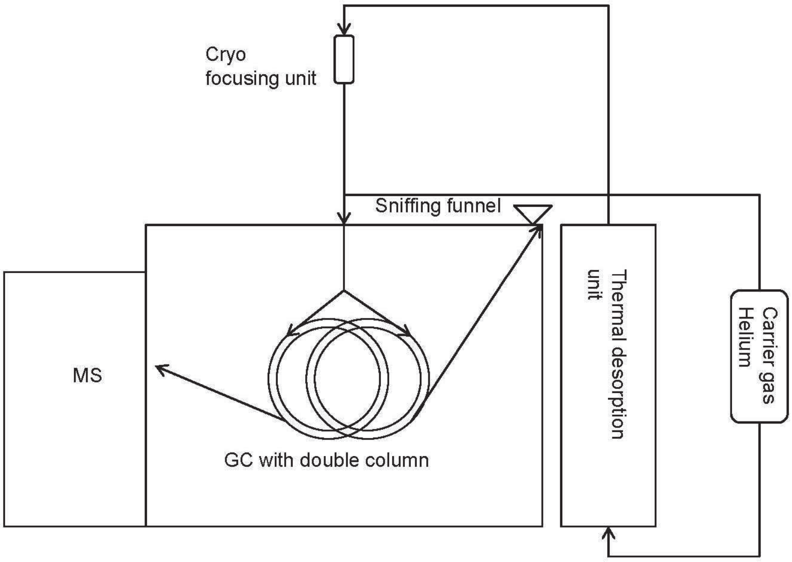


FIGURE 3 Simplified scheme of TD-GC-MS-Sniff equipment used in the study.

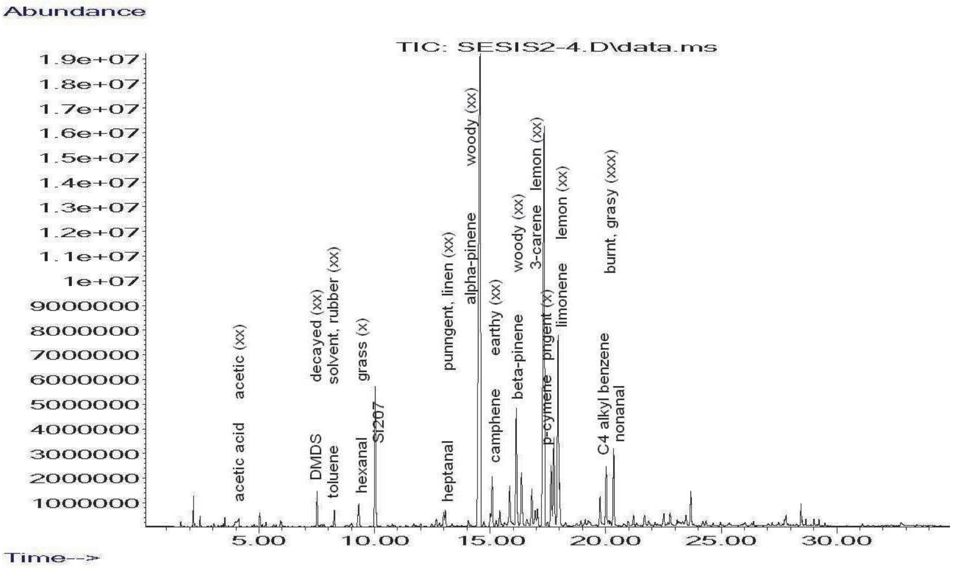


FIGURE 4 An example chromatogram with sniffing technique results. The compounds are identified by their retention times and/or their mass spectrum. Odour descriptions results acquired during the GC-MS analysis are marked on the chormatograms and the odour intensity is evaluated with x:s in a scale of x–xxxx (slight odour–very strong odour).

In order to combine the retention time of odours and the retention times of compounds in the GC-MS, the sniffing calibration curve was established from known odorous VOCs (Fig. 5). In sniffing, especially in the long time analysis, the humid, non-odorous air was added to the eluate coming to the nose in order to prevent the nasal mucous membrane drying and thus prevent nose losing its sensitivity to odours (Veijanen 1990, van Ruth 2001). RSD (%) for the repeatability of retention times was 0.6% at highest (for benzaldehyde) and RSD (%) for the repeatability of odour retention time was 1% at highest (for limonene).

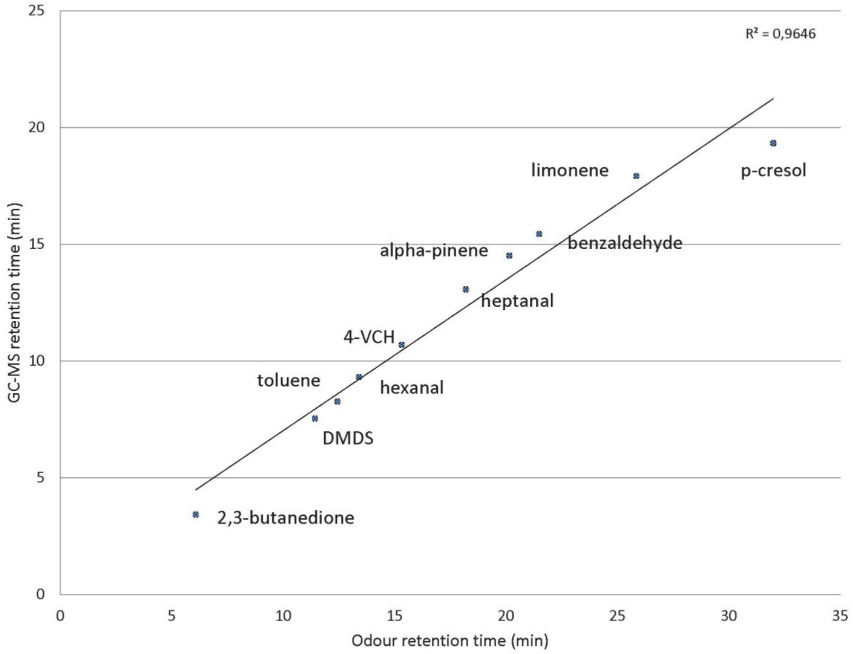


FIGURE 5 Odour curve for determining the odorous compounds from chromatogram. Curve can be used for determining the comparable retention time from the y-axis for the odour retention times (x-axis) acquired in the sniffing analysis.

3.3.3 Identification and quantification of VOCs and TVOCs (I, II, III, IV, V)

Mass spectral data was acquired over a mass range of 32-300 amu. Qualitative identification was based on the ion ratios from the mass spectrum compared to the spectrums of Nist spectrum library (Nist D.04.00) and on the retention times of compounds. Quantification was conducted via external standard. Standard compounds are presented in Tables 4 and 5. LODs (limits of detection) were determined by a signal to noise ratio of 3 ranging from 0.2 μg/m^3 to 2.8 μg/m^3. Analysis repeatability for different compounds varied from 3.2% (RSD) of toluene to 19.3% (RSD) for heptanal. Linearity for the standard compounds was also tested in a range of 10–1000 ng and the correlation coefficient was over 0.995 for all other compounds in the standard except for 2-hexanone (0.9872) and benzaldehyde (0.9869). TVOC (total volatile organic compounds) concentrations were calculated from hexane to hexadecane as a toluene equivalent including dimethyl sulphide, chloroform and diethyl ether outside the range because of their significance in TVOC concentration and odour.

TABLE 4 VOC standard compounds used in quantification and odour curve establishing. Retention times acquired by the HP-5 column.

Compound	Retention time (min)	Odour description	Manufacturer	Purity (%)	Quality
2,3-butanedione	3.99	butter, toffee	Fluka	>99	Puriss
2-methylfurane**	4.24	nutty	Fluka	-	-
1,1,1-trichloroethane	5.30	sweet, chlorine	Fluka	95	Prakt.
1-butanol	6.00	alcohol, sweet	Riedel-Haen	100	-
heptane	6.76	mild, sweet, gasoline	Baker	>97	-
methylcyclohexane**	8.47	solvent	Merck	-	Synth.
DMDS**	8.47	decayed cabbage	Merck	-	Synth.
toluene	9.25	paint, solvent	Riedel-Haen	100	-
2-hexanone	10.04	pungent, acetone-like	Fluka	98	Purum.
hexanal	10.41	grass	Merck	>98	-
buthyl acetate	10.91	sweet, fruity	Merck	98	-
4-ethenylcyclohexane*,**	11.79	pungent, rubbery	-	-	-
3-hexen-1-ol	12.51	grass	Aldrich	99	-
1-hexanol	12.92	grass	Fluka	98	Prakt.
styrene	14.00	rubber, solvent	Fluka	99	
o-xylene	14.06	sweet, rubber	Fluka	>99	Purum.
heptanal	14.11	pungent, linen	Merck	>97	-
alpha-pinene	15.69	pine	Fluka	>97	Purum.
benzaldehyde	16.67	bitter almond	Riedel-Haen	99	-
1,3,5-trimethylbenzene	16.94	sweet, aromatic	Fluka	97	-
1-octen-3-ol	17.17	musty, mushroom	Aldrich	98	-
decane	17.85	mild gasoline-like	Aldrich	99	-
limonene**	19.18	lemon	Sigma	-	-
p-cresol**	20.47	feces	Merck	-	-
2,6-nonadienal	23.36	cucumber, sweet	Aldrich	95	-
4-phenylcyclohexene*,**	28.32	plastic carpet	-	98	-

*from plastic manufacturer, **purity tested by GC-MS

TABLE 5 Carboxylic acid standard compounds used in quantification. Retention times acquired by HP-5 column.

Compound	Retention time (min)	Odour description	Manufacturer	Purity (%)	Quality
acetic acid	5.17	acetic	Bayer	100	-
propanoic acid	7.96	rancid, sour	Merck	99	synthesis
butanoic acid	11.12	rancid butter	Fluka	>99	puriss
pentanoic acid	13.72	rancid, sour	Fluka	98	purum

3.4 Ammonia and reduced sulphur compounds measurements (I, II, III, IV, V)

Ammonia was measured at every sampling site in-situ using detection tubes or diffusion tubes (Rae Systems and Dräger, range 0.86–25.8 mg/m^3). Perkin Elmer Portable gas chromatograph (Perkin Elmer Photovac Voyager) equipped with a photo ionization detector (GC/PID) was used for in-situ measurements of reduced sulphur compounds such as H_2S, methane thiol (MeSH), dimethyl sulphide (DMS) and dimethyl disulphide (DMDS). The measuring range for MeSH, DMS and DMDS was 0.13-25.8 mg/m^3 and for H_2S 0.15-14.5 mg/m^3. Hydrogen sulphide (H_2S) was analysed also in-situ by a portable infrared gas analyser GA 94 which has an external electrochemical cell for hydrogen sulphide analysis. The measuring range for H_2S was 1.45-290 mg/m^3.

3.5 Odour concentration measurements (II, IV)

The olfactometric analyses were conducted in the Olfactometric Laboratory of Jyväskylä University Department of Biological and Environmental Sciences by Ecoma TO7 olfactometer device. The odour analysis method was compatible to the European Standard EN 13725 (2003). Panellists were selected and their sense of smell was tested according to the guidelines presented in the European Standard EN 13725 (2003).

Odour concentration presented in OU/m^3 (odour unit per cubic meter) is a measure of the concentration of overall odour. It represents the number of dilutions required to bring the odour concentration of the sample to its odour threshold. One odour unit is thereby the amount of odorants present in one cubic metre of odorous gas at the panel threshold. The odour concentration analysis is performed by presenting the sample to four selected panellists at increasing concentrations via olfactometer instrument until they start to perceive the sample odour. The reporting of panellists in Olfactometer TO7 dilution system is based on the positive perception informing: a panellist pushes button in the instrument when he/she has noticed the sample odour, and a computer registers all panellists' answers. After three replicate analyses per sample, the odour concentration in OU/m^3 is calculated as the geometric mean of all panellists' results and then multiplied with sample pre-dilution factors, if they were used. When determining odour units, it is important to keep in mind the subjective nature of odour perception of different persons and therefore to consider the results as a directional, not explicit.

4 RESULTS

4.1 VOCs in municipal wastewater treatment plants (I, II)

4.1.1 WWTP A (I)

VOC results from the municipal wastewater treatment plant A are presented in Table 6. Compounds contribution to overall odour was determined by comparing the concentration to the threshold odour concentrations presented in scientific literature. The odour threshold concentrations and odour characteristics are presented in Appendix 1.

The odour threshold exceeding compounds at the plant A bar screens were dimethyl sulphide (DMS), dimethyl disulphide (DMDS), acetic acid, butanoic acid, limonene, toluene, styrene, heptanal, octanal and nonanal. In grit removal the odour threshold exceeding compounds were acetic acid, butanoic acid, DMS, DMDS, heptanal, octanal and nonanal. In sludge dewatering the odorous compounds according to their odour thresholds were methane thiol, DMS, DMDS, dimethyl trisulphide (DMTS), acetic and butanoic acid, toluene, ethyl benzene, styrene, p-cresol, heptanal, alpha-pinene and limonene (I). Example chromatograms from sniffing analysis are shown in Appendix 2, Fig. 1, where the intensity rates of sniffed compounds are presented. In sniffing analysis benzene caused odour once in the sludge dewatering sample although its concentration did not reach the odour threshold concentration. In one sniffing case (not the example chromatograms) also odour of 3-carene was detected in bar screen sample and the odour of 1-methylthiopropane was detected in the bar screens and in the sludge dewatering. Allyl methyl sulphide was also detected by its odour in sludge dewatering and in bar screens (not the example sniffing chromatogram).

TABLE 6 The arithmetic average concentration of the most abundant and odorous VOCs at plant A (min-max values in parenthesis, *n* = 6. Where a single concentration is presented, that compound existed only once during measurements).

Compound	Concentration (µg/m^3)		
	Bar screen	Grit removal	Sludge dewatering
methane thiol	bdl	bdl	270
allylmethyl sulphide	1.9 (bdl-3.4)	bdl	9.1 (bdl-26.1)
1-(methylthio)propane	2.4	bdl	9.2 (bdl-19.7)
DMS	168 (22.1-305)	3.1 (0.9-5.0)	240 (19.6-360)
DMDS	28.3 (10.2-38.5)	3.6 (1.1-5.4)	95.3 (29.6-177)
DMTS	3.7 (bdl-6.6)	0.9	36.7 (9.5-75.8)
benzene	4.47 (1.7-8.1)	2.3 (1.7-2.8)	20.3 (3.8-49.8)
toluene	153 (108-181)	12.2 (6.6-17.5)	447 (288-710)
ethylbenzene	3.5 (bdl-7.5)	0.7 (bdl-1.1)	40.3 (12.9-37.5)
p/m-xylene	3.0 (bdl-4.9)	6.8 (bdl-18.2)	15.3 (8.0-19.2)
styrene	62.2 (18.1-89.9)	4.4 (2.6-5.9)	235 (177-328)
p-cresol	bdl	bdl	39.1
decane	bdl	bdl	30.1 (bdl-55.9)
undecane	1.02	6.2	85.1 (bdl-173)
heptanal	7.7 (bdl-15.1)	11.7 (5.6-21.6)	6.9
octanal	16.6 (bdl-26.4)	14.9	bdl
nonanal	14.9 (bdl-26.4)	41.4 (15.9-84.4)	bdl
chloroform	7.0 (bdl-19.0)	bdl	7.5
1,2-dichloroethane	517 (151-956)	154 (48.8-252)	405 (87.9-848)
tetrachloroethane	nd	0.80	62.7
alpha-pinene	8.8 (5.1-11.3)	1.7 (1.0-2.9)	17.6 (5.7-27.1)
3-carene	4.2 (bdl-9.7)	0.6 (bdl-3.1)	22.5 (bdl-61.8)
limonene	90.2 (56.0-113)	3.7 (3.1-4.6)	247 (69.8-564)
acetic acid	78.7	54.2	44.4
butanoic acid	1.5	1.8	6.1

bdl: below detection limit

4.1.2 WWTP B (I)

VOC results from the WWTP B are presented in Table 7. Odorous compounds are determined by comparing the concentrations to the odour thresholds presented in Appendix 1. The odour threshold exceeding VOCs from the municipal wastewater treatment plant B bar screens and in grit removal were hydrogen sulphide, dimethyl sulphide, dimethyl disulphide, acetic acid, butanoic acid, alpha-pinene, limonene, heptanal, octanal and nonanal. In sludge dewatering also toluene concentration exceeded the odour threshold concentration in addition to odorous compounds in bar screens and grit removal (I) (Table 7). In sniffing analysis, in addition to the mentioned compounds, the odorous compounds were determined the 3-carene beta-pinene and beta-myrcene (Appendix 2, Fig. 2).

TABLE 7 The arithmetic average concentrations of most abundant and odorous VOCs at plant B (min-max values in parenthesis, *n* = 6. Where a single concentration is presented, that compound existed only once during measurements).

Compound	Concentration (µg/m^3)		
	Bar screen	Grit removal	Sludge dewatering
methane thiol	bdl	bdl	bdl
DMS	9.0 (1.3-22.1)	4.8 (0.6-9.9)	51.8 (bdl-153)
DMDS	7.2 (3.8-14.0)	3.8 (1.6-5.1)	40.1 (2.1-112)
toluene	20.9 (5.7-42.0)	11.8 (6.5-15.2)	113 (5.6-324)
p-xylene	11.1 (6.4-24.6)	3.0 (bdl-7.5)	1.6 (bdl-3.7)
undecane	33.3	bdl	bdl
heptanal	6.0 (bdl-21.1)	14.1 (bdl-19.7)	8.3 (bdl-21.8)
octanal	21.1	18.5 (bdl-36.2)	12.0 (bdl-21.8)
nonanal	27.6 (bdl-53.6)	37.8 (bdl-90.3)	25.4 (bdl-54.1)
alpha-pinene	49.0 (2.9-114)	48.9 (1.1-128)	53.3 (bdl-159)
camphene	6.4	bdl	10.0
beta-pinene	24.4	28.5	40.0
3-carene	28.8 (5.8-70.9)	88.1	108
limonene	61.3 (4.9-109)	95.1 (9.6-266)	71.3 (1.4-212)
acetic acid	29.0	32.5	22.2
butanoic acid	3.0	0.6	4.8

bdl: below detection limit

4.1.3 WWTP C (II)

The VOCs measured at the plant C are presented in Table 8. The detailed odorous compounds in bar screens were DMS, DMDS, DMTS, heptanal, toluene (in one measurement time) and limonene. p-xylene and alpha-pinene caused odour perception in sniffing (Appendix 2, Fig. 3) although their odour thresholds were not exceeded.

In grit removal the odorous compounds according tto the odour thresholds were DMS, DMDS, DMTS, toluene, alpha-pinene and limonene. Odour of 3-carene and ethyl benzene were detected in sniffing analysis (Appendix 2, Fig. 3). In primary clarifier only DMS, DMDS and octanal exceeded their odour threshold concentrations. In sniffing analysis also toluene and hexanal caused odour although their threshols odour concentrations were not exceeded (Appendix 2, Fig. 3).

When considering sludge thickening unit, the odorous compounds exceeding odour thresholds were DMS, DMDS, DMTS (on one measurement time), heptanal, octanal, toluene, alpha-pinene and limonene. In sludge dewatering the odorous compounds were the same as in sludge thickening except to alpha-pinene, heptanal and octanal, that were not detected above the odour thresholds. Additionally, 3-carene, allyl methyl sulphide (not shown in the example chromatogram), diethyl ether, p-xylene, styrene and hexanal caused odour perceptions in sniffing analysis, although their odour thresholds were not exceeded according to the measurement results (Appendix 2, Fig. 4).

TABLE 8 Arithmetic average concentrations of the most abundant and odorous VOCs in plant C (n = 4 in grit removal, primary clarifier and sludge thickening, n = 5 in bar screens and sludge dewatering), min-max values in parenthesis.

Compound	Concentration (µg/m³)				
	Bar screens	Grit removal	Primary clarifier	Sludge thickening	Sludge dewatering
DMS	6.5 (1.4-11.0)	16.1 (8.7-24.9)	0.9 (bdl-2.9)	56.3 (51.6-69.0)	26.4 (3.9-104)
allylmethyl sulphide	nd	nd	nd	8.2 (bdl-22.7)	nd
DMDS	13.1 (6.9-22.6)	21.7 (11.3-45.2)	1.6 (bdl-3.6)	83.9 (34.5-162.0)	22.5 (5.0-32.5)
DMTS	6.3 (1.4-19.4)	32.9 (3.5-103)	nd	2.7 (bdl-10.8)	1.9 (bdl-9.6)
methyl chloride	1.5 (bdl-2.8)	8.5 (0.8-22.8)	nd	nd	nd
chloroform	2.8 (bdl-9.8)	nd	nd	nd	nd
tetrachloroethene	1.9 (5.0-4.6)	14.8 (bdl-37.4)	nd	nd	nd
acetone	12.5(bdl-29.9)	17.2 (bdl-40.0)	6.5 (bdl-14.0)	28.1 (bdl-73.6)	nd
2-butanone	2.0 (bdl-4.5)	nd	3.4 (1.2-5.6)	nd	13.7 (bdl-44.1)
pentanal	1.6 (bdl-8.0)	nd	nd	nd	nd
hexanal	3.5 (bdl-13.5)	nd	7.6 (3.9-15.9)	4.9 (bdl-8.6)	1.5 (bdl-4.4)
heptanal	6.7 (bdl-16.7)	3.8 (bdl-19.0)	3.2 (bdl-6.5)	6.7 (bdl-15.3)	1.5 (bdl-7.4)
octanal	nd	nd	16.5 (bdl-43.5)	16.1 (bdl-37.6)	nd
benzene	2.3 (0.3-5.3)	2.8 (bdl-4.5)	nd	nd	2.6 (bdl-6.7)
toluene	45.8 (18.0-107)	115 (54.9-231)	10.2 (5.7-16.7)	155 (11.7-451)	96.9 (17.9-219)
ethylbenzene	3.5 (bdl-11.8)	7.4 (2.3-17.9)	nd	nd	nd
p-xylene	9.2 (2.5-32.9)	17.0 (3.9-46.8)	2.1 (bdl-5.6)	7.9 (bdl-26.2)	6.0 (1.5-12.5)
o-xylene	1.0 (bdl-1.8)	nd	0.9 (bdl-3.6)	nd	nd
styrene	nd	nd	nd	22.8	nd
alpha-pinene	10.9 (5.3-18.5)	17.7 (8.1-28.6)	2.5 (0.8-4.7)	39.4 (3.6-109)	13.8 (1.0-13.7)
beta-pinene	1.1 (bdl-5.3)	nd	nd	nd	nd
3-carene	6.8 (bdl-13.7)	nd	nd	nd	28.44 (3.3-61.4)
limonene	55.3 (32.7-86.4)	133 (37.3-170)	4.0 (2.9-5.4)	41.2 (17.6-95.5)	59.8 (13.1-129)
undecane	32.0 (bdl-52.4)	90.5 (66.3-144.0)	1.3 (bdl-5)	nd	nd
dodecane	13.8 (bdl-33.4)	9.62 (bdl-48.1)	nd	nd	9.7 (bdl-33.4)
2-propanol	9.3 (bdl-29.2)	16.7 (bdl-52.2)	nd	nd	nd
diethyl ether	77.4 (32.8-142)	157 (65.4-246)	30.5 (bdl-111)	273 (66.4-537)	14.0 (0.6-19.4)

bdl: below detection limit, nd: not detected

4.1.4 Seasonal variation of compound groups in municipal WWTPs (I, II)

Municipal WWTPs are susceptible to seasonal variation because changes in temperature of influents are great. Distributions of compound groups are presented in Figures 6, 7 and 8.

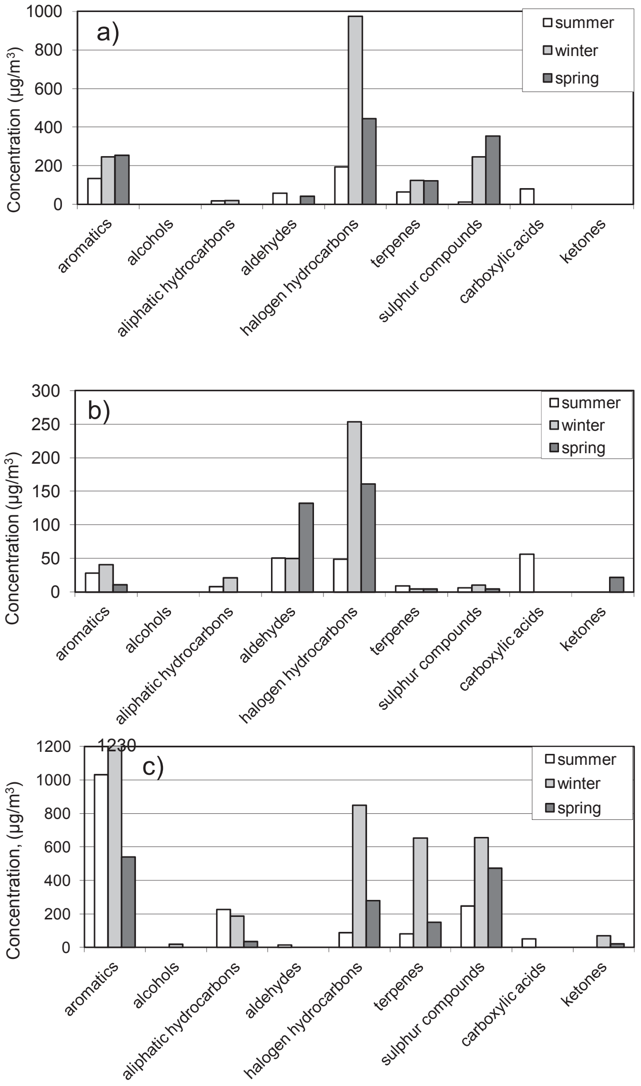


FIGURE 6 Distribution of compound groups in different seasons in plant A a) trash rakes, b) grit removal and c) sludge dewatering.

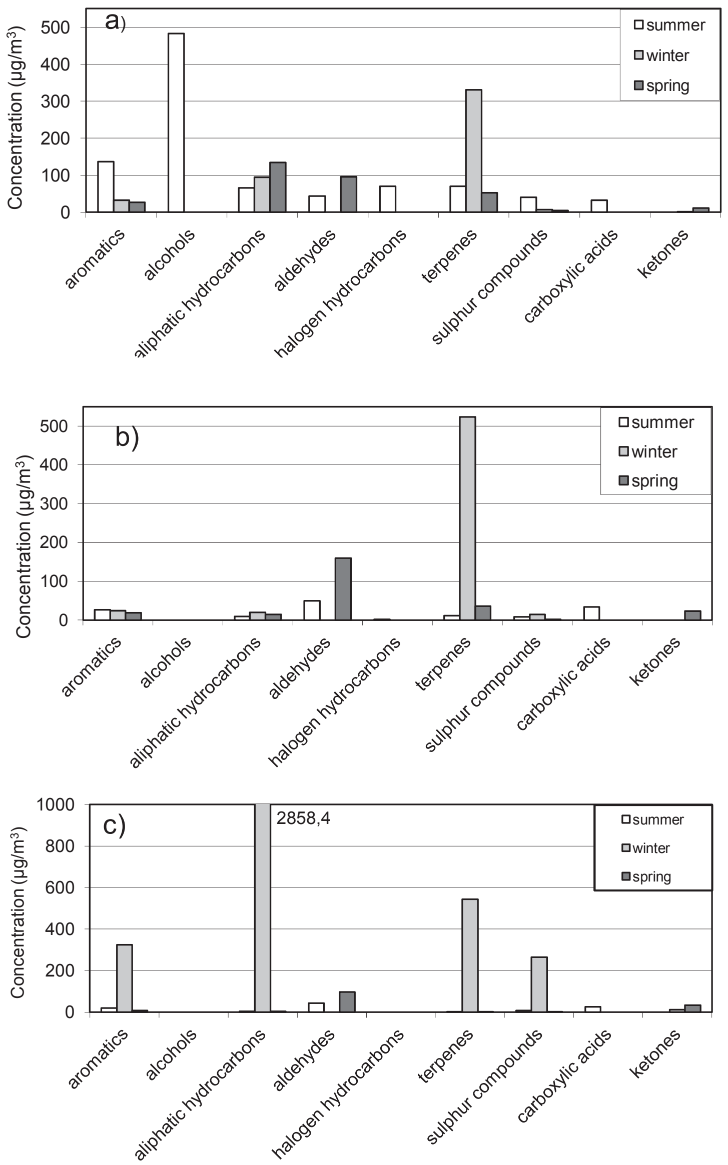


FIGURE 7 Distribution of compound groups in different seasons in plant B a) trash rakes, b) grit removal and c) sludge dewatering.

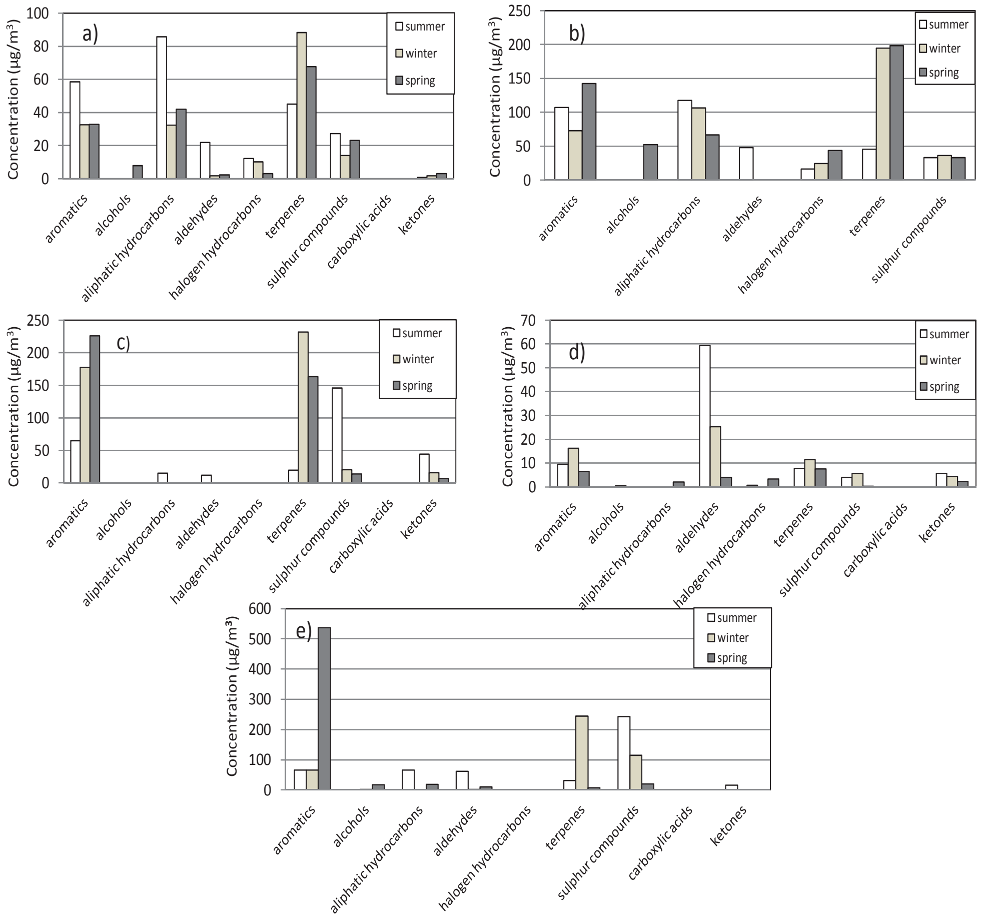


FIGURE 8 Distribution of organic compound groups in WWTP C in different seasons. a) trash rakes, b) grit removal, c) sludge thickening, d) primary clarifier, e) sludge dewatering.

When considering the seasonal variation, carboxylic acids were found at plants A and B and they were detected only on summer measurements. Terpenes were in highest concentrations in winter and in spring in plant C thrash rakes, grit removal and sludge thickening and in wintertime at plant B in all measurement sites. Seasonal variation of halogen compounds was determined in plant A where the halogen compounds were at highest in winter. Seasonal variation in sulphur compound concentrations was determined only in sludge dewatering and sludge thickening units in plant C where the concentrations of sulphur compounds were highest in summer measurements. Also aromatics were predominant in the plant C in summer.

4.2 Odorous VOCs in the biofilter (II)

The VOCs were analysed in biofilter of the WWTP C incoming and outflowing gas (Table 9). Odour threshold exceeding compounds were DMS, DMDS, DMTS, toluene, ethylbenzene, hexanal, heptanal, octanal, alpha-pinene and limonene (Appendix 2, Fig. 5). When reviewing the compound groups, the best reduction in concentration was gained in aldehyde, aromatic and sulphur compound groups and the lowest reduction in chlorinated compound group. The highest reduction regarding single compounds was achieved in cases of 2-butanone, allyl methyl sulphide, ethyl benzene and hexanal. Poorly reduced compounds were limonene, methylene chloride and chloroform. The total reduction percentage of relevant compound groups considering odours in average was 58.2% (Table 9). However, TVOC concentration was reduced only by 25.4%. Odour and compound removal efficiency of biofilter in percentage was calculated as follows:

$$RE = (C_{gi} - C_{go}) / C_{gi} \times 100 \qquad (1)$$

where RE is the removal efficiency, C_{gi} is the concentration of compound or odour in the inlet and C_{go} is the compound or odour concentration in the outlet gas flow (Datta & Allen 2005).

4.3 Olfactometric results in WWTP C (II)

In the WWTP C the odour concentration was measured by olfactometry (Table 10). The highest odour concentration values were measured at the biofilter incoming gas, as expected because it is a combination of air from the bar screen room and grit removal room. Biofilter reduction potential for odour concentration (OU/m^3) was 63.6 % in average.

TABLE 9 VOC concentrations (arithmetic average, *n* = 4) and the average biofilter removal efficiency at the biofilter unit, min-max values in parenthesis.

Compound	VOC concentration (μg/m³)		Biofilter removal efficiency (%)	Compound group reduction (%)
	Incoming wastegas to biofilter	Outgoing gas from biofilter		
sulphur compounds				62.9
DMS	43.4 (6.3-116.7)	17.8 (8.3-27.4)	59.0	
DMDS	69.6 (4.1-215.5)	32.1 (6.2-67.2)	53.9	
allylmethyl sulphide	5.1 (bdl-18.7)	nd	100.0	
DMTS	16.1 (bdl-33.1)	9.9 (2.9-25.5)	38.5	
chlorinated comp.				–7.2
methylene chloride	3.3 (bdl-10.6)	4.0 (bdl-8.9)	–30.0	
chloroform	23.1 (bdl-92.5)	19.5 (bdl-76.0)	15.6	
aromatic compounds				64.7
toluene	375.4 (64.1-879.2)	132.7 (47.4-303.2)	64.7	
ethylbenzene	11.7 (bdl-42.5)	2.7 (bdl-6.1)	92.2	
p-xylene	38.5 (bdl-130.5)	6.0 (4.5-8.7)	48.7	
o-xylene	12.7 (bdl-50.7)	12.8 (9.0-18.0)	66.8	
aldehydes				76.7
hexanal	36.3 (bdl-141.5)	2.8 (bdl-11.1)	78.7	
heptanal	12.6 (bdl-50.2)	4.9 (bdl-11.3)	61.1	
octanal	25.6 (bdl-102.3)	8.8 (bdl-35.2)	65.6	
terpenes				21.3
alfa-pinene	37.2 (21.0-59.4)	22.5 (5.6-38.7)	39.5	
limonene	93.4 (13.1-194.4)	90.6 (20.8-149.3)	3.0	
others				71.8
diethyl ether	272.3 (47.3-648.3)	153.5 (20.5-268.2)	43.6	
2-butanone	11.4 (4.1-26.9)	nd	100.0	
TVOC	2480 (1430-4310)	1850 (938-2790)	25.4	

bdl: below detection limit, nd:not detected

TABLE 10 Odour concentration at different sites in the wastewater treatment plant, results as an arithmetic average and min-max values in parenthesis (*n*=4).

Site	Odour concentration (OU/m³)
Bar screens	7900 (3800-12000)
Grit removal	8100 (3200-13000)
Primary clarifier*	157 (57-380)*
Sludge thickening	4330 (1100-7100)
Sludge dewatering	3530 (1500-7600)
Biofilter, incoming gas	11630 (1400-30000)
Biofilter, outflow	4230 (1300-8000)

*OU/m³/m²

4.4 VOCs in pulp mill wastewater (III)

Table 11 shows the concentrations of the most abundant and/or odorous volatile organic compounds in the air of pulp mill waste water treatment plant aeration pond, pulp mill primary clarifier, the fibre line control room and in office building. The airborne odorous compounds at the pulp mill WWTP according to their odour threshold concentrations were DMS, DMDS, alpha-pinene, limonene and p-cymene and they exceeded their odour thresholds multiple times (Table 11). Toluene exceeded its threshold concentration only in aeration pond, nonanal was present in the odour threshold exceeding concentrations in fibre line control room and in office. When considering the sniffing analysis, the odour was caused also by beta-pinene, beta-myrcene, 3-carene, borneol, camphene and camphor in aeration pond, and by hexanal, camphene, 3-carene, p-cymene and borneol in pulp mill primary clarifier (Appendix 2, Fig. 6). The sniffing analysis revealed camphene and 3-carene as the odorous compounds in the pulp mill office and fibre line control room (Appendix 2, Fig. 7). In addition, the distribution of compound groups in different seasons was studied (Fig. 9).

Table 12 presents the compounds that caused distinctive or strong odour perceptions in combined instrumental and sensory analysis of liquid samples and are therefore considered as the odour causes of liquids in the WWTP Odorous VOCs determined by sniffing are presented in Appendix 2, Fig. 8 & 9. The strongest odours in sniffing analysis of liquids were observed from Effluent fraction (Ef) 3 (Appendix 2, Fig. 9) as well as the concentrations in that sample were the highest. Because of the limited data of odour thresholds in water for these compounds, the odorous compounds are evaluated by sniffing analysis only.

Changes in compound group distribution were studied in different seasons (winter and summer) in order to see the effect of ambient temperature in different groups and their concentrations. Percentage results in air in different sampling sites at the pulp mill wastewater plant are presented in Fig. 9 and percentage results in liquid fractions are shown in Fig. 10.

TABLE 11 The average airborne concentrations of the most odorous VOCs in the area of effluent ponds and indoors of pulp mill (min-max values in parenthesis, *n* = 3 in aeration pond and primary clarifier, *n* = 2 in fibre line control room and office building).

Compound	Concentration (µg/m³)			
	Aeration pond	Pulp mill primary clarifier	Fibre line control room	Office building
2-methyl-1,3-butadiene	20.0 (2.9-31.0)	nd	nd	0.3
2-methyl-2-propenal	4.0	1.0	nd	nd
heptanal	17.6 (2.5-30.0)	9.5 (9.2-9.8)	5.7	4.3
octanal	nd	44.4	nd	21.1
H_2S	710	420	nd	nd
DMS	160 (8.3-439)	20.1 (4.1-27.0)	51.0 (24-83)	3.2 (0.4-8.3)
thiophene	9.1 (1.4-19.0)	0.8 (0.6-1.0)	2.0 (0.7-3)	nd
2-methylthiophene	10.2 (3.0-28.1)	1.0	nd	nd
allyl methyl sulphide	15.2	nd	nd	nd
DMDS	7.1 (0.9-20.6)	60.1 (40.0-80.1)	170 (54-286)	5.0 (0.8-14)
benzene	35.0	nd	1.9	3.2
toluene	120 (17.5-103)	10.2 (4.7-20.0)	10.1 (9.3-17.1)	8.1 (2.2-14.3)
ethylbenzene	10 (4.2-24.0)	nd	2.1 (1.0-2.2)	0.3
p-xylene	50.0 (31.2-90.0)	1.1 (1.1-1.9)	4.1 (2.1-5.1)	5.1 (0.5-2)
styrene	10.0 (8.1-25.0)	nd	2.0	8.2
p-cymene	140 (80.1-389)	110 (38.7-173)	60.1 (29.1-97.2)	14.1 (0.9-34.1)
alpha-pinene	580 (257-1790)	740 (641-836)	701 (535-866)	180 (31.0-437)
camphene	40.0 (16.0-46.0)	70.1 (38.0-109)	50.6 (16.1-78.2)	10.1 (1.0-24.0)
beta-pinene	34.5	100 (78.2-129)	120 (57.1-179)	30.0 (3.2-71.3)
3-carene	390 (160-970)	481 (352-615)	410 (217-596)	80.1 (9.2-221)
4-carene	30.1 (26.1-272)	nd	7.1 (4.3-9.3)	nd
limonene	380 (188-932)	310 (171-445)	240 (144-342)	40.1 (4.0-107)
camphor	100 (0.5-160)	27.0	9.0 (5.0-13.3)	3.0
borneol	43.7	58.8	14.1 (4.4-23.7)	2.7 (0.6-4.8)
chloroform	90.1 (20.0-191)	170 (132-200)	10.1 (4.2-18.1)	0.6
nonanal	nd	nd	13.7	14.9 (13.1-16.6)
total amount of sesquiterpenes	200 (30.0-4830)	280	50.1 (19.1-82.2)	236

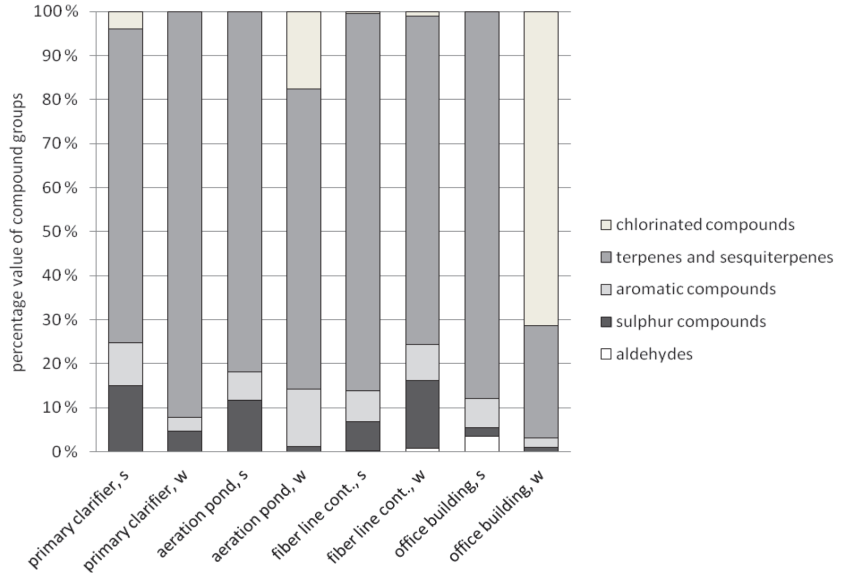


FIGURE 9 Percentage distribution of airborne VOC groups in different seasons in pulp mill area s) summer, w) winter.

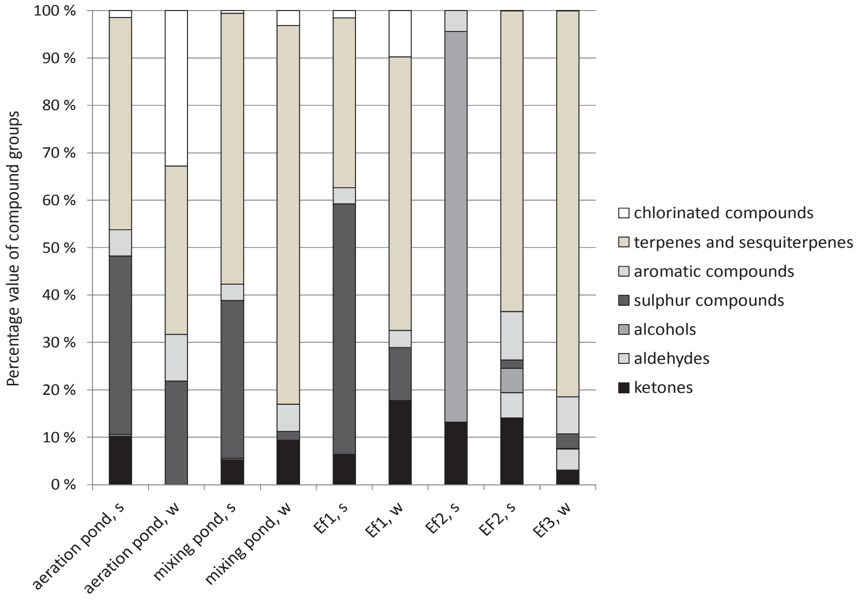


FIGURE 10 Percentage distribution of VOC groups in liquid samples in different seasons in pulp mill effluent fractions s) summer, w) winter.

TABLE 12 Average VOC concentrations of liquid samples from different effluent fractions in kraft pulp mill (min-max values in parenthesis, *n*=2).

Compound	Concentration (µg/l)				
	Aeration pond	Mixing pond	Ef1	Ef2	Ef3
2-methylpropanal	nd	nd	nd	nd	3190 (3030-3350)
3-methylbutanal	nq	nd	nq	nd	8540 (8510-8570)
hexanal	nq	nd	nq	nq	8890 (7140-10640)
heptanal	nq	nq	nq	nq	1970 (1320-2610)
2-butanol	5.0	41.0	nd	14300	150
3-methyl-1-butanol	nd	nd	nd	nd	781
1-hexanol	nq	nq	nd	nd	1330 (632-2020)
1-heptanol	nd	nd	nd	nd	18010
toluene	7.0	20.2 (10.1-33.1)	9.2	6.0	1240 (1030-1440)
styrene	3.0	8.0 (6.2-11.0)	nd	761	350 (270-421)
p-cymene	30.1 (9.1-40.2)	200 (110-290)	7.0 (21.1-12.1)	nd	16740 (12470-21000)
bentsaldehyde	6.2	nq	nq	nq	2580 (1910-3250)
buthylbenzene	nd	20.1(4.2-30.1)	nd	nq	1480 (1040-1910)
methyl-methylethenylbenzene (ni)	20.2	70.2 (61.0-80.1)	70.1 (20.2-121)	nq	6410 (3720-9090)
2-methoxyphenol (guaiacol)	nd	nd	nq	nd	7930 (6070-9780)
4-ethoxy-2-methylphenol	nd	nd	nd	nd	4790 (4130-5440)
acetone	120	311 (150-471)	251 (140-351)	530	10860 (9510-12200)
2-butanone	20.1	140 (112-161)	70.1 (41.0-100)	1430	650 (151-1150)
3-methylcyclopentanone	nd	nd	nd	321	nq
2-heptanone	nd	50.1 (21.0-80.3)	20.1	nd	4960 (1350-8570)
3-octanone	nd	nd	nd	nd	6400
methanethiol	nd	20.2	21.0	nd	60.1 (9.1-110)
DMS	180 (1.1-350)	450 (10.3-892)	321 (20.1-610.3)	nd	361 (201-521)
thiophene	nq	3.2 (1.2-4.3)	3.0 (0.1-5.4)	nd	140 (41-241)
DMDS	161	1450 (52.1-2840)	1370 (101-2640)	nd	4940 (4570-5300)

Table 12 continues.

Table 12 continued.

Compound	Concentration (µg/l)				
	Aeration pond	Mixing pond	Ef1	Ef2	Ef3
2-methylthiophene	nq	2.0 (1.1-3.0)	nd	nd	272 (210-331)
3-methylthiophene	nq	nq	nd	nd	202
DMTS	7.1	411	290 (6.1-580)	nd	nq
methyl-methylethyl disulphide	nd	6.0	nd	nd	430 (310-550)
alpha-pinene	31.0 (1.1-50.1)	870 (271-1470)	790 (231-1340)	nd	15500 (10000-21000)
camphene	3.0 (2.1-4.0)	50.1(20.1-80.2)	0.03 (10.0-51.0)	nd	3040 (1920-4160)
beta-pinene	695	100 (23.6-176.6)	141	nd	1920 (556-3280)
alpha-fellandrene	nq	40.2 (20.0-51.0)	10.0	nd	3130 (2010-4240)
3-carene	21.0 (1.0-30.1)	571 (170-972)	380 (110-651)	nd	13700 (7560-19900)
4-carene	10.2	51.1	10.1	nd	3870 (3180-4560)
limonene	20.0 (10.-30.3)	601 (262-931)	170 (61.0-281)	nd	28400 (25600-31300)
terpenoid (22,20)^{ni}	51.1	240	nd	nd	3850(2410-5280)
camphor	70.0 (0.1-131)	142(112-162)	20.2 (10.2-30.2)	nd	2440 (410-4460)
borneol	nq	210 (20-391)	61.1 (32.0-90.3)	nd	18500 (17500-19600)
terpenoid (23,34)^{ni}	nq	nq	nq	nd	14600 (13200-16100)
alpha-terpineol	nq	432	50.1	nd	44000 (40800-47200)
sesquiterpenes, sum	160.0(0.3-310)	2170 (1940-2400)	156 (110-202)	nd	198000 (112000-277000)
chloroform	25.0(20.1-30.0)	90(71.1-110)	110	nd	220 (200-231)
2-acetyl-5-methylfurane	nd	nd	nd	nd	6960 (3900-13500)

nd: not detected, nq: not quantified, ni: not identified

4.5 VOCs in municipal waste treatment

4.5.1 Composting (IV)

The drum composting hall and the control room of the Oulu drum composting facility are the locations where plant employees work most of the day. The measured concentrations of the most abundant and odorous volatile organic compounds in the drum composting hall and in the control room are presented in Table 13. The odour threshold exceeding compounds in the hall were acetic acid, butanoic acid, 2,3-butanedione, 2-butanol, ethyl acetate, DMS, DMDS, alpha-pinene and limonene. In the control room the odour threshold exceeding compounds were the same excluding the DMS that was not detected in the control room above detection limit concentrations. According to the sniffing analysis of the samples from the composting hall, the odorous compounds were also 3-hydroxy-2-butanone, beta-myrcene, nonanal, 3-methyl-1-butanol, 2-methyl-1-butanol and 3-carene (Appendix 2, Fig. 10). In the control room the odorous compounds were 3-hydroxy-2-butanone, p-xylene and beta-myrcene (Appendix 2, Fig. 10).

TABLE 13 Average concentrations of the most abundant and odorous VOCs in the composting hall. *n*=6 in the hall and *n*=2 in the control room, min-max values in parenthesis.

Compound	Concentration (µg/m^3)	
	Composting hall	Control room
acetic acid	322 (nm-1020)	160
butanoic acid	31.9 (nm-140)	20.2
2,3-butanedione (diacetyl)	339 (bql-8200)	390 (8.2-770)
2-butanone	250 (2.0-560)	180 (30.1-320)
3-hydroxy-2-butanone	1740 (bql-8200)	400 (41.0-751)
2-butanol	250 (bdl-690)	60.1 (31.3-80.3)
3-methyl-1-butanol	50.0 (bql-130)	50.4 (3.0-102)
3-methylbutanal	9.3 (bql-30.0)	0.3
methyl acetate	44.3 (3.0-110)	31.0 (2.0-60.2)
ethyl acetate	188 (20.0-490)	230 (30.0-430)
ethyl hexanoate	26.8 (bql-70.0)	20.0 (1.0-40.2)
DMS	3.0	nd
DMDS	1.7 (1.0-4.0)	5.1
alfa-pinene	51.7 (2.0-120)	90.0 (3.0-171)
beta-pinene	13.3 (bql-40.0)	30.1
beta-myrcene	36.7 (bql-110)	14.0 (8.0-20.2)
3-carene	11.2 (bdl-30.0)	15.5 (1.0-31.0)
limonene	692 (20.0-1400)	360 (50.1-671)

bdl: below detection limit, bql: below quantification limit

4.5.2 Optical sorting of municipal waste (V)

The most odorous VOCs and other odorous compounds were measured in the waste sorting plant and the results are presented in Table 14. Highest concentrations were determined in process hall. Odour threshold exceeding compounds in the process hall were acetic acid, 2,3-butanedione, ethyl acetate, ethylbenzene, p-cymene, alpha-pinene and limonene. In sniffing analysis also 3-hydroxy-2-butanone was labeled as odorous compound (Appendix 2, Fig. 11). Odour threshold exceeding compounds in the control room were only 2,3-butanedione, acetic acid, ethyl acetate and limonene.

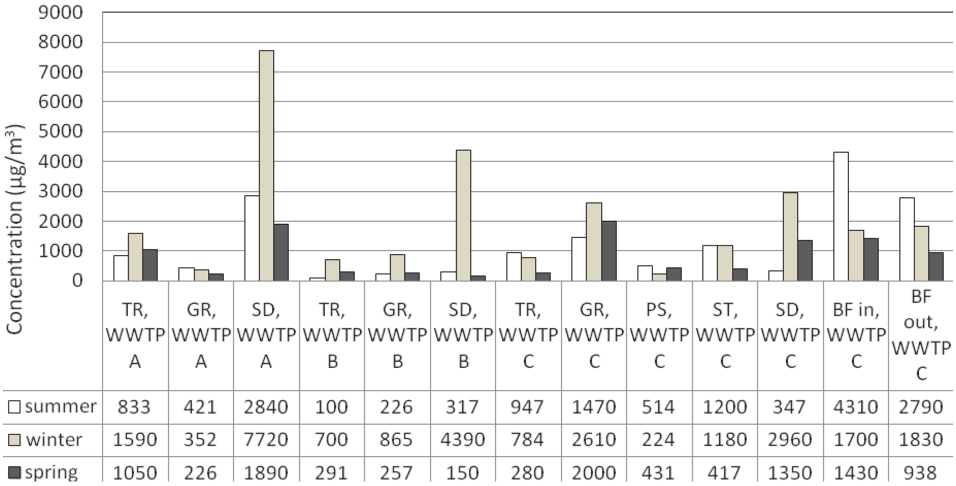
TABLE 14 Average concentrations of VOCs in optic sorting plant, *n* = 4 in process hall and *n* = 2 in control room, min-max values are in parenthesis.

Compound	Concentration (μg/m^3)	
	Process hall	Control room
ethanol	248 (130-400)	81.0*
2-propanol	90.1 (bdl-220)	26.1*
2,3-butanedione (diacetyl)	87.5 (21.4-282)	7.0 (0.7-14.1)
3-hydroxy-2-butanone	133 (42.0-441)	nd
acetic acid	45.3 (bql-173)	41.0*
ethyl acetate	108 (31.1-340)	20.2*
benzene	12.3 (10.3-14.3)	2.3
toluene	29.7 (19.5-50.8)	3.30 (2.3-4.3)
ethylbenzene	41.0 (11.0-102)	2.0 (0.8-4.0)
p-xylene	87.4 (41.1-192)	7.1 (3.2-11.0)
p-cymene	111 (40.2-211)	3.1 (2.0-4.3)
propylbenzene	34.8 (32.0-9.0)	nd
C3-alkylbenzene	115 (bql-340)	nd
alpha-pinene	42.5 (21.0-71.2)	4.2 (3.0-5.3)
limonene	1200 (651-2230)	45.1 (31.0-60.2)
nonane	62.5 (bql-181)	3.7 (2.1-5.2)
4-methylnonane	67.5 (11.0-205)	2.3 (0.5-4.1)
2-methylnonane	57.5 (22.1-151)	nd
3-methylnonane	42.5 (11.1-120)	nd
decane	85.0 (bql-262)	nd
undecane	320 (41.3-950)	3.0 (2.0-4.0)
trichloroethene	170*	3.1*
tetrachloroethene	290*	nd

*detected only once, nd: not detected, bdl: below detection limit, bql: below quantification limit

4.6 TVOC concentrations in the studied plants

TVOC (total volatile organic compounds) calculations were made from the samples taken from waste and wastewater treatment plants and from the biofilter of WWTP C. Variation between measurement days were great as can be seen from Figures 11, 12 and 13.



	TR, WWTP A	GR, WWTP A	SD, WWTP A	TR, WWTP B	GR, WWTP B	SD, WWTP B	TR, WWTP C	GR, WWTP C	PS, WWTP C	ST, WWTP C	SD, WWTP C	BF in, WWTP C	BF out, WWTP C
□ summer	833	421	2840	100	226	317	947	1470	514	1200	347	4310	2790
▨ winter	1590	352	7720	700	865	4390	784	2610	224	1180	2960	1700	1830
■ spring	1050	226	1890	291	257	150	280	2000	431	417	1350	1430	938

FIGURE 11 TVOC concentrations in WWTPs in different seasons (TR: trash rakes, GR: grit removal, SD:sludge dewatering, ST: sludge thickening, PS: primary clarifier, BF: biofilter).

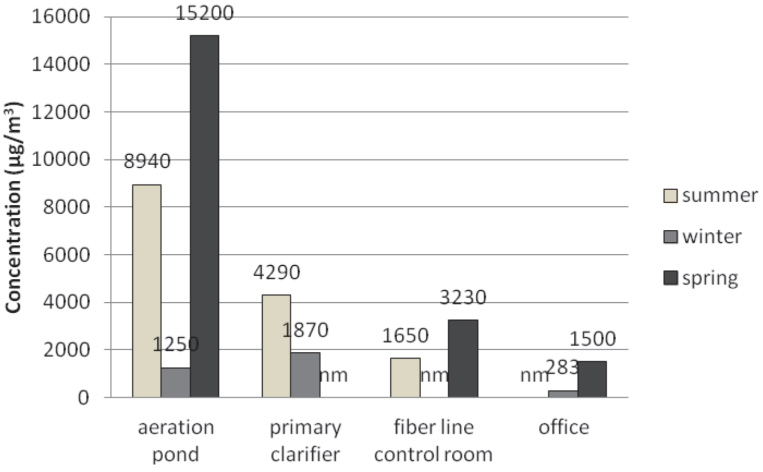


FIGURE 12 TVOC concentrations in pulp mill effluent sites in different seasons. nm=not measured.

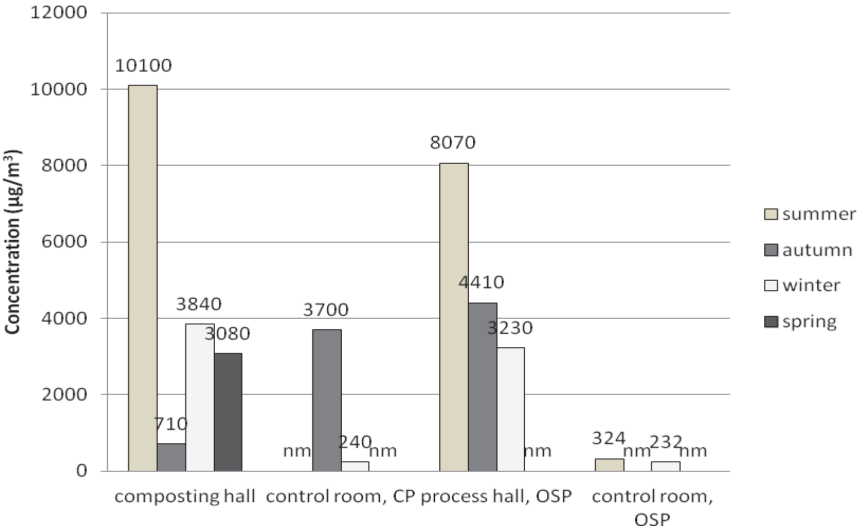


FIGURE 13 TVOC concentrations in studied biowaste composting plant (CP) and waste optic sorting plant (OSP) in different seasons. nm=not measured.

4.7 H_2S and NH_3 in studied plants

The concentrations of H_2S and NH_3 were determined from all the measurement sites (Table 15). H_2S was abundant in WWTP B exceeding the concentrations of 12.7 mg/m^3 at highest. H_2S was present in the incoming gas to the biofilter at plant C. Also H_2S was detected in the pulp mill WWTP. In other plants H_2S did not exceed high concentrations and in most of the cases the concentrations were below detection limit (0.15 mg/m^3). NH_3 was detected only in WWTP A sludge dewatering (Table 15).

TABLE 15 Hydrogen sulphide and ammonia concentrations in studied plants.

Plant	Sites	Concentration (mg/m^3)	
		H_2S	NH_3
WWTP A	trash rakes	bdl	bdl
	grit removal	bdl	bdl
	sludge dewatering	bdl	1.76–4.23
WWTP B	trash rakes	4.23–12.7	bdl
	grit removal	1.40	bdl
	sludge dewatering	0.67	bdl
WWTP C	trash rakes	bdl	bdl
	grit removal	bdl	bdl
	primary clarifier	bdl	bdl
	sludge thickening	bdl	bdl
	sludge dewatering	bdl	bdl
WWTP C Biofilter	incoming gas	0.75	bdl
	outflowing gas	bdl	bdl
Pulp mill WWTP	primary clarifier	0.42	bdl
	aeration pond	0.71	bdl
	fiber line control room	bdl	bdl
	office	bdl	bdl
Oulu composting	composting hall	bdl	bdl
	control room	bdl	bdl
Hämeenlinna optic sorting plant	process hall	bdl	bdl
	control room	bdl	bdl

bdl: below detection limit

5 DISCUSSION

5.1 Main findings of the thesis

5.1.1 Odorous VOCs in municipal WWTPs

Odour threshold exceeding compounds in plant A bar screen were sulphur compounds (DMS, DMDS) toluene, heptanal, octanal, nonanal, limonene, acetic acid and butanoic acid. In grit removal the odour threshold exceeding compounds were DMS, DMDS, heptanal, octanal, nonanal, acetic acid and butanoic acid. In plant A sludge dewatering site the odour threshold exceeding compounds were methane thiol, DMS, DMDS, DMTS, toluene, ethyl benzene, styrene, heptanal, alpha pinene, limonene, acetic acid and butanoic acid. Allyl methyl sulphide, 3-carene and methylthiopropane are very likely also the odour compounds according to the sniffing analysis, but because of the lack of threshold reference for them, it is not possible to estimate whether they have exceeded the odour threshold (I).

In plant B the odour threshold exceeding compounds were also sulphur compounds: DMS, DMDS and H_2S in some extent in the first part of process. Furthermore, in all measurement sites odour threshold was exceeded by three aldehydes: heptanal, octanal and nonanal and from the terpene group alpha-pinene and limonene were contributing to the overall odour. As in the plant A, the carboxylic acids (acetic acid and butanoic acid) were determined also in plant B in odour threshold exceeding concentrations (I). Toluene concentration exceeded odour threshold concentration in sludge dewatering site. Other odorous compounds were 3-carene beta-pinene and beta-myrcene according to the sniffing analysis.

Odour threshold exceeding compounds at the plant C bar screen were DMS, DMDS, DMTS, heptanal and limonene. In grit removal odour causing compounds due to their odour thresholds were DMS, DMDS, DMTS, toluene, alpha-pinene and limonene. In Primary clarifier the odorous compounds were

DMS, DMTS and octanal. Odour in sludge thickening was due to the DMS, DMDS, heptanal, octanal, toluene, alpha-pinene and limonene. In sludge dewatering the odorous compounds were the same as in the sludge thickening site excluding alpha-pinene, heptanal and octanal. Hydrogen sulphide was detected as an odorous compound only in the incoming gas to the biofilter (II). Additionally, in this study, 3-carene in bar screens and sludge dewatering, allyl methyl sulphide in sludge dewatering, diethyl ether in all sites and hexanal in bar screens, primary clarifier, sludge thickening and sludge dewatering caused odour perceptions in sniffing analysis. Variation in the thresholds presented in literature can be great depending on the determining methods and the subjective nature of odour perception, and therefore these results achieved from the sniffing analyses can´t be ignored.

The origin of organic sulphur compounds, H_2S and aldehydes like heptanal and octanal, is most likely the result of the anaerobic degradation of organic matter; alpha-pinene and limonene are possibly originated from household discharges, because they are very common odorants in cosmetics and cleaning agents (Vincent 2001).

In general, the concentrations of key odorant VOCs in different plants are in very same range. The highest concentrations of sulphur compounds were found in plant A. Also p-cresol that is a key odorant in manure and feces was found only on plant A. Differences between plants were found in toluene and styrene concentrations as well as in terpene concentrations. Toluene and styrene were abundant in plant A and terpenes were generally found in higher concentrations at plant B. These compounds originated from industrial wastewater sources and it is suggested, that the quality of incoming wastewater has an effect on the quality of indoor air and thus on the composition of VOCs and odour analysed in wastewater treatment samples.

The highest concentrations of single VOCs in general were found in the sludge dewatering or thickening unit samples. This was probably due to the centrifugal dewatering system used in the thickening unit that releases compounds adsorbed to the sludge material. The results achieved in this study agree with the results that are found in recent studies made by Zarra et al. (2008, 2009) in Germany. They have mentioned the most odorous compounds to be DMDS found in the highest concentrations in a sludge thickener unit. In our study exceptions to this were the concentrations of limonene in plant B and dimethyl trisulphide (DMTS) in plant C which were highest in grit removal. Concentrations in the grit removal of plant C were also higher than in the bar screens, although since the raw waste water and solids are present in the bar screens, it would have been presumable that the bar screens would also be the most odorous sites. The higher concentrations in grit removal were most likely due to the high velocity and turbulence in the grit removal ponds of plant C and thus the stripping of VOCs from the liquid phase to the air.

The total number of VOCs was reduced when moving towards the end of wastewater processing, but the concentrations of odorous compounds such as DMS, DMDS, except the hydrogen sulphide, were increased due to the sludge processing, and allylmethyl sulphide at plants A and C was present in sludge thickening adding a garlic like malodour in the air. These compounds were typical for sludge and sludge that are decomposing either aerobically or anaerobically (Lomans et al. 2002).

5.1.2 Seasonal variation of compound groups in municipal WWTPs

When considering the seasonal variation, carboxylic acids were found at plants A and B and they were detected only on summer measurements as shown in Figures 6 and 7 (Chapter 4.1.4). Carboxylic acids are known to be formed during the fermentation of organic matter especially in anaerobic environment (Hvitved-Jacobsen & Vollertsen 2001). It is possible that warm effluents and higher ambient air temperature in summertime has enhanced the microbial activity and the decaying of organic matter by anaerobic heterotrophic microbes in the sewer system and the conditions at the treatment plant has not been aerobic enough to degrade the produced carboxylic acids.

Furthermore, in plant A the seasonal variation is shown best so that majority of all compound groups were at highest concentrations in winter samples especially in sludge dewatering unit probably due to the decreased ventilation. However, this trend is not perceptible in plants B and C (Fig. 7 and 8, Chapter 4.1.4). The results of seasonal variation in plant B show that influent consisted of terpenes in winter sampling days and the variation of influent composition is shown in Figure 7. In plant C the terpenes were also in highest concentrations in winter in all other sites than the grit removal. Sulphur compound concentrations were highest in summer measurements in plant C sludge dewatering and sludge thickening units (Fig. 8). This is probably due to the warmer effluents that allow the microbes function more efficiently in the sewers than in the wintertime, when effluents are cold (<10 ºC). However, this trend was not shown in plants A and B. Other compound groups did not show any uniform behavior in concentrations between different seasons and between different plants. It seems that the distribution of groups in the indoor air of WWTPs process sites is dependent on the constitution of incoming effluents and the ventilation situation rather than the temperature variations.

5.1.3 Appearance of toluene in WWTPs

One interesting feature found in the analysis is toluene, which is present in all of the plants studied in quite high concentrations especially in sludge thickening in plant A and B, in grit removal in plant C and in the incoming gas to the biofilter in plant C. Toluene has an odour threshold concentration of 80 μg/m^3 (Appendix 1) that is relatively low and therefore toluene is considered as one of the odour causing components. The origin of toluene can be industrial processes and household chemicals. The variation in concentration could be due to the aeration of grit removal ponds and the temperature rise in sludge thickening. According to toluene’s physical-chemical properties (Appendix 1), it has poor water solubility and it is easily released to the atmosphere especially if aeration is in use. Furthermore, it may also adsorb onto the solid material in the wastewater and then be released, if conditions like temperature or pressure is changed. Another explanation is toluene formation as a result of microbial degradation of proteins in anoxic conditions, which has happened, for example, in anoxic freshwater sediments according to research results reported by Juttner (1991). This theory is supported also by results achieved in this study, as the concentrations of toluene increase towards the end of wastewater processing chain, where the organic material has degraded more. Likewise, this phenomenon and quite high toluene concentrations were also found in the measurements of biogas produced by anaerobic digestion of sewage sludge (Marczak et al. 2006, Rasi et al. 2007).

5.1.4 VOC and odour reduction in WWTP C biofilter

When investigating the results acieved from the plant C´s biofilter incoming and outflowing gas, it is shown that the highest reduction regarding single compounds was achieved in cases of 2-butanone, allyl methyl sulphide, ethyl benzene and hexanal. Poorly reduced compounds were limonene, methylene chloride and chloroform (II). This is due to the chemical nature of these compounds and the capacity of microorganisms to use different substances as nutritional substrates. The metabolic pathway and the enzymatic systems in the biodegradation processes depend on the molecular structure of pollutant: aliphatic compounds are most easily degraded or transformed, then the aromatics, chlorinated compounds and after that the cyclic hydrocarbons (Le Cloirec et al. 2005). This order of degradation/transformation efficiency was shown in our study also according to the single VOC results presented in Table 9 (Chapter 4.2) where the aliphatic compounds (in this case aldehydes, ketones and ether) are degraded or transformed more easily than the aromatic compounds or cyclic hydrocarbons that are in this case terpenes. Chlorinated compounds were not degraded/transformed at all. In the case of limonene and other terpenes it is possible that they are also released to the exhaust gas from the woodchips in the biofilter material that was mixed with sludge compost. For single compounds the total reduction percentage in average was 58.2 % (Table 9). Biofilter reduction potential for odour concentration (OU/m^3) was 63.6 % in average.

5.1.5 Odorous VOCs in pulp mill effluent plant

The odorous compounds in pulp mill effluent plant according to the threshold odour concentrations GC-MS analysis were DMS, DMDS, alpha-pinene, limonene, toluene (only in aeration pond), nonanal (in fibre line control room and in office) and p-cymene and they exceeded their odour thresholds multiple times (Table 11). When considering the sniffing analysis, the odour was caused also by beta-pinene, beta-myrcene, 3-carene, borneol, camphene and camphor in aeration pond, by hexanal, camphene, 3-carene, p-cymene and borneol in pulp mill primary clarifier (Appendix 2, Fig. 6). The sniffing analysis revealed hexanal, camphene and 3-carene as the odorous compounds in the pulp mill office and fibre line control room (Tables 11 and 12, Chapter 4.4). Findings of the present study are also supported by earlier studies. Many researchers have defined the reduced sulphur emissions like hydrogen sulphide, DMS, DMDS and methane thiol (MeSH) to be responsible for pulp mill odours from the primary sources like end of pipe emissions (Brownlee et al. 1995, Bordado & Gomes 2001, 2002, Ojala et al. 2005) and also being abundant in effluent (Lange & Christensen 2004). Another group of odorous VOCs that are very common in pulping, are terpenes (Strömvall & Pettersson 1993, Lange & Christiansen 2004). In addition to these expected odorants, aromatic compounds, especially toluene and p-cymene, caused quite strong odour perceptions in sniffing analysis done simultaneously with the GC-MS analysis and also exceeded their odour threshold concentrations causing solvent or glue like and woody odour as well.

Sesquiterpenes were present also in many samples and it is assumed here that they are contributing to the overall odour, but precise analysis of sesquiterpenes as odour causes was not possible because of the lack of odour threshold data for them. Furthermore, another reason that they were not possible to identify precisely from the chromatogram was due to overlapping and also due to the lack of model compounds. The odour descriptions for several sesquiterpenes are floral, earthy, and they are used widely in flavour and fragrance chemistry.

Differences in VOC composition between sampling sites were determined (Fig. 9, Table 11, Chapter 4.4). Sulphur compounds were at highest at the aeration pond, especially DMS, but interestingly the highest concentration of DMDS was detected in the fiber line control room. Concentrations of sulphur compounds at the office building were quite low but still above the odour threshold in cases of DMS and DMDS. Most of the terpenes were at highest at the aeration pond, as expected. Interesting is that on one measurement, terpene concentrations were surprisingly high at the office building compared to the normal level of indoor concentrations of terpenes. Elevated single VOC concentrations were detected in terpene groups, for example alpha-pinene occurring in 866 $\mu g/m^3$ at highest in the fiber line control room. Also sesquiterpenes were found out in quite high concentration once in office building. In fact, concentration of sesquiterpenes was higher in office building than in the fiber line control room.

When considering liquid samples from effluent fractions, high concentrations of sesquiterpenes were abundant in Ef3 (Table 12, Chapter 4.4) and therefore also in the wastewater processing, from where they are possibly drifted to the indoors of office building. Sum of all terpenes and sesquiterpenes was 579 $\mu g/m^3$ in office and 1590 $\mu g/m^3$ in fiber line control room.

Terpenes have very characteristic odours and their threshold odour concentrations (TOCs) can be quite low (Appendix 1). Terpenes are very insoluble into the water and their emission potential from the pond surface is very high. Therefore they are easily released to the ambient air from the open effluent pond surface.

5.1.6 Seasonal variation of compound groups in pulp mill effluent plant

Highest concentrations of VOCs in the gaseous samples were observed at the aeration pond in the summertime (Fig. 12, Chapter 4.6). This is probably due to higher ambient temperature that fortifies the volatilisation of VOCs from the liquid surface. 55.7% of all VOCs were terpenes and sesquiterpenes in the summer time and 65.2% in the winter time (Fig. 9, Chapter 4.4).

Terpenes and sesquiterpenes were the major odorant group in every effluent fraction in liquid samples excluding the effluent fraction Ef2 (Fig. 10, Chapter 4.4). Highest percentage amount of terpenes were found in winter at the mixing pond and in the effluent fraction Ef3. Overall, the terpene fractions have been larger in liquid in winter probably due to low ambient temperature inducing lesser volatilisation of compounds. In the summertime, higher amounts of sulphur compounds are present in the effluents especially in primary clarifier and mixing pond. Reason for this would be simply that effluent originating from pulping contained more sulphurous compounds, or that on a warm summer day, degradation of organics would happen faster and if the conditions were partly anaerobic like it could be at the primary clarifier pond, reduced sulphur compounds were formed. There are no great changes of aromatic compounds between winter and summer.

5.1.7 Odorous VOCs in composting plant

The odour threshold exceeding compounds in the hall were acetic acid, butanoic acid, 2,3-butanedione, 2-butanol, ethyl acetate, DMS, DMDS, alpha-pinene and limonene. In the control room the odour threshold exceeding compounds were the same excluding the DMS that was not detected in the control room above detection limit concentrations. According to the sniffing analysis of the samples from the composting hall, the odorous compounds were also 3-hydroxy-2-butanone, beta-myrcene, nonanal, 3-methyl-1-butanol, 2-methyl-1-butanol and 3-carene (Appendix 2, Figure 10). In the control room the odorous compounds were 3-hydroxy-2-butanone, p-xylene and beta-myrcene. Especially 2,3-butanedione and 3-hydroxy-2-butanone are products of fermentation and are found in several food products like milk, butter etc. (Bassit et al. 1993). Very similar pattern of odorous compounds in different sites of a composting plant were found in recent study made by Gallego et al. (2012) excluding the ketones 2,3-butanedione and 3-hydroxy-2-butanone. In that study the most odorous compounds were also different carboxylic acids, DMS and DMDS, different alcohols and terpenes.

Disagreeable, sweet, alcohol-like odour in the drum composting hall was among others due to 2-butanol. A similar situation in regard to odour-causing VOCs was observed in the Hyvinkää drum composting plant (Hänninen et al. 2002). The highest concentrations of single VOCs in the composting hall of Oulu composting plant were observed in summer 2002 but some high VOC concentrations were detected also in winter 2003 (Fig. 13, Chapter 4.6).

The results of VOCs in the control room show a great variation in concentrations. Concentrations were generally lower in the control room than the composting hall except one measurement time in autumn 2002. The main compounds responsible for the sweet, pungent odour in the control room were 2,3-butanedione, ethyl acetate, acetic acid and limonene and the TVOC concentration was quite high (3700 µg/m^3). Concentrations of the odour-causing compounds were much lower in winter 2003 and the overall odour in the control room was then very mild and barely detectable. The VOCs detected were typical of composting plants: carboxylic acids and their esters, some alcohols, ketones, aldehydes and terpenes (Wilber & Murray 1990, Wilkins 1994, Tolvanen et al. 1998, Hänninen et al. 2002). The overall odour was sour, sweet, a bit rancid and biowaste-like at both sampling sites.

5.1.8 Odorous VOCs in optic sorting plant

Overall odour in the optic sorting process hall in Hämeenlinna was sweet, rotten. The main compounds due to the odour in the optic sorting process hall in Hämeenlinna according to GC/MS/sniff- analysis were ethanol, 2,3-butanedione, 3-hydroxy-2-butanone, acetic acid, ethyl acetate, p-cymene, alpha-pinene and limonene in the optic separation process hall (V) (Table 14, Chapter 4.5.2). These compounds also exceeded their odour threshold concentrations. They are very typical odorous compounds in biowaste composting and management facilities (Wilber & Murray 1990, Wilkins 1994, Fischer et al. 1999) indicating the presence of food wastes also in solid waste treatment. Especially limonene was found out in relatively high concentrations; even 34% of the TVOC value consisted of limonene in the waste receiving hall. Limonene has been detected in excess also in other solid waste related VOC researches (Davoli et al. 2003, Imppola et al. 2003, Staley et al. 2006). Possible origins of limonene are household discharges, because it is very common odorant and ingredient in cosmetics and cleaning agents (Vincent 2001).

Hydrocarbons (aromatic and aliphatic) were found abundant in process hall (Table 14). However, aliphatic hydrocarbons were not considered as the odorous compounds because their odour threshold concentrations are relatively high and were not exceeded in these measurements. Hänninen et al. (2002) found out the similar situation concerning hydrocarbons in another Finnish dry waste treatment plant when mixed waste was handled. In addition, fairly large concentrations of aromatic and aliphatic hydrocarbons are found also by Pierucci et al. (2005) in studies considering the aerobic biological processing of municipal solid waste and by Statheropoulos et al. (2005) who stated the benzene, toluene, ethylbenzene and naphtalene to be the priority pollutants in mixed waste. The origin of such compounds is suggested to be the mixed waste itself and also the packaging material printing ink solvent residuals, glues etc. Furthermore, these BTEX (i.e. benzene, toluene, ethylbenzene, xylenes) have been stated as the most abundant compounds near municipal solid waste treatment plants (Chiriac et al. 2007, Vilavert et al. 2012) and in the indoor air of municipal solid waste treatment plants (Gallego et al. 2012). Concentrations of ethylbenzene and xylene presented here are in the same range as presented in other comparable study by Chiriac et al. (2007).

It is possible that these hydrocarbons originate from the mixed waste or from vehicle exhaust gases, oils etc. Alkanes, alkenes ketones and aromatics are also reported to originate from emissions of plastic packaging (Hodgson et al. 2000).

Late summer measurement results indicate that biowaste has already started to decay and the decomposition of organic matter occurs already in the collection bins as suggested also in the studies by Persoons et al. (2010), because concentrations of 2,3-butanedione and acetic acid, both indicators of biowaste early stage decomposition (Eitzer 1995), were much higher than in the winter measurements when biowaste has presumably been frozen in the collection bins. In winter 2004 all concentrations found out to be much lower except the dominant compound group, terpenes, especially limonene. In cold weather biowaste may have been frozen in the collection bins. In winter 2004 concentrations of all VOCs were much lower except the dominant compound group, terpenes, especially limonene Interesting is that organic sulphur compounds like dimethyl sulphide or dimethyl disulphide, which are known to be very odorous and mentioned to be abundant at waste management and in the decaying of food wastes (Komilis et al. 2004) were not detected above the detection limits (0.1 µg/m^3) at any of the measurement sites.

5.1.9 TVOC concentrations in studied plants

The highest TVOC concentrations in municipal WWTPs were detected in the sludge dewatering room of plant A: during the winter, the concentration was measured at an all-year high of 7720 µg/m^3 (Fig. 11, Chapter 4.6). Also in WWTP B the TVOC concentrations were highest in winter. However, the same trend was not as obvious in WWTP C. The decrease in ventilation during the cold winter could be one explanatory factor for this result. Also the sludge age has been higher in winter being 12–14 days instead of the sludge age in summer for example in plant A that has been around 7-9 days. The sludge age may have had an impact on the higher concentrations of VOCs. In comparison, the low TVOC concentration being 150 µg/m^3 detected at the plant B sludge dewatering room was probably due to the modern closed-system dewatering machine, which had been constructed and introduced prior to this measurement period. Lower TVOC and compound group concentrations were measured in spring and summer (Fig 11). Comparing these achieved Finnish results to similar study made in Portuguese WWTPs (Teixeira et al. 2012) it seems that in Finland the TVOC values are higher. In the Portuguese study the TVOC results varied from 36–1727 µg/m^3, when in Finnish WWTPs the range has been from 150–7720 µg/m^3.

In pulp mill WWTP the highest TVOC concentrations were observed in spring measurements being highest in the aeration pond (15.2 mg/m^3). 56.8 % of analysed VOCs were terpenes and sesquiterpenes. Another dominant compound group was alkyl benzenes, 12.4 % of all VOCs. Pulp mill effluent had also terpenes as the dominant group, 55.7 % of all VOCs were terpenes and sesquiterpenes in the summer time and 65.2 % in the winter time. Lowest TVOC concentrations were determined in office in wintertime (Fig. 12, Chapter 4.6).

When considering the studied waste management plants, the TVOC concentrations in the composting hall and optic sorting process hall were highest in summer measurements (Fig. 13, chapter 4.6). This may be due to the higher ambient temperature and thus the biowaste has started to decompose earlier and easier than in winter or spring, when the biowaste has been even frozen in the collection bins. TVOCs of composting plant control room show a great variation. In general the concentrations in control rooms were 6-7 % of the TVOC concentration in the processing halls of composting plant or the optic sorting plant. In optic waste sorting plant TVOC concentrations are lower than in some other studies made in the waste management plants by for example Scaglia et al. (2011) but comparing to the results presented by Navas-Rodriquez et al. (2012) the TVOCs are in the same concentration range.

5.1.10 H_2S and NH_3 in studied plants

In studies considering wastewater treatment and odours, hydrogen sulphide (H_2S) is mentioned to be one of the major odorants (Stuetz et al. 1999, Hvitved-Jacobsen & Vollertsen 2001, Hobson & Yang 2001). However, in this case the studied municipal wastewater treatment plants did not have high H_2S concentrations except the plant B on one measurement time. In fact, H_2S was found only once in detection limit exceeding concentration in grit removal and two times in biofilter incoming gas at the plant C and once in the trash rakes and grit removal at the plant B. In addition, in the pulp mill WWTP H_2S was detected in quite low concentrations being 420–710µg/m^3 (Table 15, Chapter 4.7). The detection limit for H_2S was 150 µg/m^3. The problem with H_2S is, indeed, the fact that it can be adding the malodour, but it is not detectable with instruments that have even moderately low detection limits, since the odour threshold concentration for H_2S is very low; 0.7 µg/m^3. It seems that in WWTPs the H_2S control by precipitation by ferrosulphate ($FeSO_4$) and by the pH control has shown to be effective. Ammonia was detected only in plant A´s sludge dewatering samples in this study. In waste management H_2S or NH_3 was not detected in detection limit exceeding concentrations.

5.2 Possible health risks of analysed VOCs in terms of occupational exposure limit concentrations and indoor guideline thresholds

5.2.1 Occupational exposure limit concentrations and guidelines

Occupational exposure limit concentrations (OEL concentrations) for a selection of individual volatile organic compounds occurring in diverse working environments are set by the Finnish Ministry of Social Affairs and Health. These values can be used as a guideline in assessing the risk of occupational exposure to particular compounds. Concentrations of the OELs are multiple times, often decades, higher than the odour thresholds for certain compounds. In addition, World Health Organizations Air quality guidelines for Europe are used as a reference in this thesis. OEL values and recommendation concentrations are presented in Table 16. In this thesis the presumption of occupational exposure is set to consider the whole 8 hour workday and it is assumed that employees work in the worst areas for 8 hours. It is also assumed that the measured VOC concentration in the process halls and process sites remains the same for the whole workday. This way the comparing of achieved results to the 8 hour OEL values is the most straightforward. Usually the situation in plants is better and employees do not work in the worst areas for the 8 hour but shorter periods of time and thus they are less exposed to VOCs.

Multiple exposure analysis and calculations for VOCs could be made by following equation for compounds that have a similar effect on health (2) (Finnish Ministry of Social Affairs and Health 2012):

$$C_1/OEL_1+C_2/OEL_2+C_3/OEL_3+\ldots C_i/OEL_i \geq 1, \qquad (2)$$

where the C_i is the concentration of measured compound and OEL_i is the occupational exposure limit for measured compound. If the calculated sum of all concentration/OEL ratios exceeds 1, multiple exposure exist in the working area.

However, these calculations were not able to be performed in this thesis because of the lack of OEL data for the majority of the VOCs found in the sites studied here. In addition, the concentrations of available OELs are tens or hundreds of times higher than the concentrations measured in this study.

Finnish Ministry of Social Affairs and Health has also set indoor air regulations considering TVOC values and in this regulation the TVOC concentration limit for poor indoor air quality is 600 $\mu g/m^3$ according the Indoor air classification (Finnish Ministry of Social Affairs and Health 2003). This limit is for households, schools, daycares, offices etc. so it has to be applied with caution in cases of waste management. However, it gives a certain guideline for workplaces in industry.

TABLE 16 Occupational exposure limits (OELs) and WHO guideline values found in scientific literature for certain compounds found in the study (Finnish Ministry of Social Affairs and Health 2012, WHO 2000).

Compound	OEL (8 hour) (µg/m^3)	WHO Guideline values for exposure (24 h) (µg/m^3)
toluene	190 000	260
ethylbenzene	220 000	-
p-/m-xylene	220 000	-
styrene	86 000	260
p-cresol	22 000	-
decane	-	-
undecane	-	-
heptanal	-	-
octanal	-	-
nonanal	-	-
chloroform	10 000	9 780
1,2-dichloroethane	4 000	700
alpha-pinene	560 000	-
limonene	140 000	-
methane thiol	1 000	-
DMS	-	-
DMDS	-	-
DMTS	-	-
acetic acid	-	-
butanoic acid	25 000	-
2,3-butanedione	710*	
3-hydroxy-2-butanone	-	-
2-butanone	-	-
2-butanol	300 000	-
ethyl acetate	150 000	-
diethyl ether	1 100 000	-
ammonia (NH_3)	14 000	-
hydrogen sulphide (H_2S)	12 700	150

*from (NIOSH)

5.2.2 Wastewater treatment

The concentration of any single determined organic compound did not exceed OEL concentrations at any of the measurement sites of studied wastewater treatment plants in this study. The obvious problem at wastewater treatment plant B was the occasional presence of hydrogen sulphide in the trash rake room at levels that exceeded the Finnish OEL. As shown in Table 15 (Chapter 4.7), the hydrogen sulphide concentration was 12.7 mg/m^3 which is also the concentration of Finnish OEL (8 hour) for hydrogen sulphide. The highest level of ammonia, 4.2 mg/m^3, was detected in the sludge dewatering room at plant A. In plants B and C, ammonia was not detected in any measurement times.

The interest considering health risks in wastewater treatment was focused on plant A, where 1,2-dichloroethane and styrene, considered to be quite harmful compounds for human health, occurred. 1,2-dichloroethane effects the central nervous system, and it is also been demonstrated to be mutagenic during in vitro tests using mammalian cells (WHO Air quality Guidelines for Europe 2000). On average, the rural background concentration of 1,2-dichloroethane is estimated to be 0.4-1.0 µg/m³ in Western Europe. In the WHO guidelines, the recommended maximum value for continuous exposure to 1,2-dichloroethane (24 h) is 700 µg/m³. Furthermore, styrene is found to be genotoxic and it has neurological effects. The WHO guideline concentration (24 h) for styrene in air is 260 µg/m³ (WHO Air quality Guidelines for Europe 2000). As shown in Table 6 (chapter 4.1.1) the concentration of 1,2-dichloroethane was at its highest (960 µg/m³) in the plant A trash rake area, and the concentration of styrene was at its highest (330 µg/m³) in the sludge dewatering area. Of course the workers do not work for 24 hours and thus the exposure is lower. When using the equation (3) that is modified from the calculation of 8 hour average formula of OEL values (Finnish ministry of social affairs and health 2012) for shorter exposure time, the exposure concentration of workers becomes lower than the recommended value by WHO as follows:

$$C_{24h} = (T_{ew} \times C_m + T_b \times C_b) / 24 \tag{3}$$

where the T_{ew} is time of exposure, C_m is the measured concentration T_b is the time spent in background and C_b the background concentration.

When applying this equation with the time of exposure T_{ef} of 8 hours/day, the results are 320µg/m³ for 1,2-dichloroethane for 24 hour and 110 µg/m³ for styrene for 24 hour. The background concentration for styrene is assumed to be zero.

TVOCs of studied WWTPs varied from 260-4150 µg/m³ being at highest (7719 µg/m³) in plant A in winter (Fig. 11, Chapter 4.6). According to studies of Mölhave et al. (1991) of TVOC concentrations causing health effects it is possible that some health effects exist in these concentrations.

5.2.3 Pulp mill effluent

The highest concentrations were detected in terpene groups at the pulp mill wastewater plant. The odour of some terpenes, terpenoids and sesquiterpenes can be strong and sharp, and when existing in higher concentrations, terpenes are considered as a health risk because they irritate for example eyes and the mucous membranes of nose (Kasanen et al. 1998, Mölhave et al. 2000). In studies of Cometto-Muniz et al. (1998) it was discovered that 3-carene evokes eye irritation existing in concentrations above 15 mg/m³. No additional effect of several terpenes existing together was studied. Compared to the results of this study, the concentrations achieved here do not exceed the possible irritation effect concentrations mentioned in the scientific literature, so it remains undetermined whether the terpenes and sesquiterpenes are the sources of eye and mucosa irritation.

TVOC in office building was 1500 µg/m^3 and in fibre line control room 3230µg/m^3 at highest (Fig. 12, Chapter 4.6), which were fairly high in comparison to regular indoor VOC concentrations occurring normally under 600µg/m^3 (households, offices, schools, daycares etc.) (Finnish Ministry of Social Affairs and Health 2003). Indoors the concentrations and composition of VOCs can be effected by emissions from furniture, construction materials and possible cleaning agents or fragrances and it cannot be uniformly determined that all terpenes and aromatic compounds are directly emitted from the effluent ponds. However, concentrations of mentioned compound groups are high if compared to typical office building indoor concentrations without the load from the adjacent effluent processing facility. Therefore it is assumed that the major portion of aromatics and terpenes in indoors are originated from effluent ponds.

5.2.4 Composting plant

In the drum composting plant in Oulu measured VOCs did not exceed the 8 hour OEL concentrations. However, VOC concentrations in the process hall were quite high, especially of acetic acid and ketones: acetic acid, 2,3-butanedione, 2-butanone and 3-hydroxy-2-butanone occurred in levels of 250-2090 µg/m^3 (Table 13, chapter 4.5.1). In addition, concentrations of airborne microbes may rise to levels that are hazardous to health according to Tolvanen et al. (2005). Therefore the receiving hall for biowaste can be considered as the problematic area for occupational hygiene.

Furthermore, in recent international scientific publications the possibility of 2,3-butanedione as a cause of lung disease, bronchiolitis obliterans, “pop corn lung” has been discussed and a proposal of suitable OEL for that has been given being 710 µg/m^3 (Egilman et al. 2011). In proposal given by National Institute of Occupational Safety and Health USA (NIOSH 2011) the exposure limit for 2,3-butanedione were 18 µg/m^3 for 8 hours and 90 µg/m^3 for 15 minutes. Interestingly, in recent scientific literature 2,3-butanedione is very rarely referred to be present in VOC studies considering waste treatment and odours or occupational health issues. There are only few articles that mention 2,3-butanedione determined in VOC analysis made in waste management (Tolvanen et al. 1998, Louhelainen et al. 2001, Gallego et al. 2012). In our studies the levels of 2,3-butanedione have been in the range of 8-1150 µg/m^3 in the process hall and the control room and thus the exposure in harmful concentration is possible especially if the worker stays on the process hall area for the whole workday. In Finland no limits considering the 2,3-butanedione are available for the present. Also the compound produced by fermentation with 2,3-butanedione, 3-hydroxy-2-butanone, was found in quite high concentrations but no limiting concentrations or data considering health effects are available for it at present.

Another health concerning compound according to Rosenfeld et al. (2007) is benzene that has been found in composting probably as a contaminant. It was suggested that it should be measured. However, in this study benzene was not found in composting facility.

The situation considering VOC results is typical for composting facilities; the concentration of the single volatile organic compound is far below the OELs but above its threshold odour concentration. Similar conclusion was made also in studies by Rosenfeld et al. (2007). Workers are also exposed to several VOCs simultaneously and the synergy of several VOCs is not very well known. Even though the Finnish OELs considering volatile organic compounds were not exceeded in this study and also none of the primary health effects associated with VOCs was not to be expected, unpleasant odour may cause secondary symptoms such as nausea and hypersensitivity reactions. Also the synergetic reactions of several VOCs and the effect of this synergism on health are not known very well. Bioaerosols such as the fungal spores and bacteria found at the waste handling sites also increase the risk of health problems. In composting and waste management in general, the bioaerosols concentrations may be abundant as determined in studies by Tolvanen (2001) and Tolvanen & Hänninen (2007) and be causing the health effects (Bunger et al. 2002, Heldal et al. 2003).

5.2.5 Optic sorting plant

Situation in the control room of the optic sorting plant was quite good regarding to TVOC concentration range 232-324µg/m^3 (Fig. 13, chapter 4.6). Determined TVOC concentrations are not very high related to the Finnish indoor air quality assessment levels. The recommended maximum TVOC concentration in the indoor air is 600 µg/m^3 according to Finnish indoor air quality classification 2002.

However, TVOC concentrations in the process hall were quite high, varying between 2300 µg/m^3 and 8070 µg/m^3. When comparing to other studies, TVOC concentrations are lower than in studies made in the waste management plants by for example Scaglia et al. (2011) but comparing to the results presented by Navas-Rodriquez et al. (2012) the TVOCs are in the same concentration range. In some studies it is noted that TVOC concentrations at 300-3000 µg /m^3 may be irritating and concentrations between 3000-25000µg/m^3 is reported to be acutely discomfortable (Hunter & Oyama 2000). It is very feasible that exposure to this amount of VOCs does not cause primary health effects, but it is possible though, that secondary effects like nausea and hypersensitivity reactions may appear, especially when exposed to several VOCs simultaneously. Furthermore, process hall air in the optic sorting plant contained 280 µg/m^3 of 2,3-butanedione which is above the recommended 8 hour concentration limits given by NIOSH.

5.3 Odour concentrations in wastewater treatment and their correlation to analysed VOCs

The correlation of measured odorous VOC concentrations with olfactometric results was studied by examining the linearity of concentrations and Pearson's correlation coefficients of 22 different measurements (II). The curves achieved from linearity analysis are presented in Figures 14 and 15. The compounds chosen for the correlation examination were DMS, DMDS, toluene and limonene because of their contribution to the overall odour in the wastewater treatment according to the TD-GC-MS-sniff analysis. Diethyl ether was not considered as an odorant compound analysed in TD-GC-MS-sniff analysis because of its´ quite high odour threshold concentration, but it was taken into the correlation examination, because it was detected at every measurement site in relatively high concentrations. Thus, it was necessary to explore the possible enhancing or additive effect of diethyl ether on the overall odour.

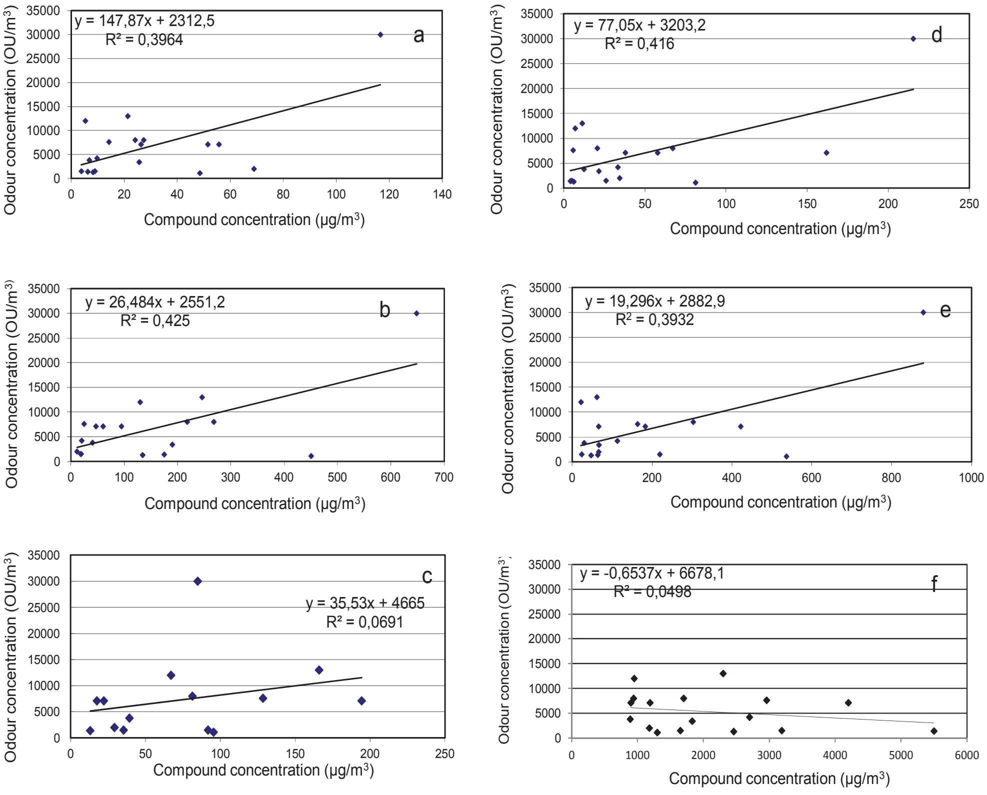


FIGURE 14 Correlation of concentration of determined single odorous VOCs [DMS (a), diethyl ether (b), limonene (c), DMDS (d), toluene (e)] and TVOC (f) with measured Odour Unit results (OU/m^3).

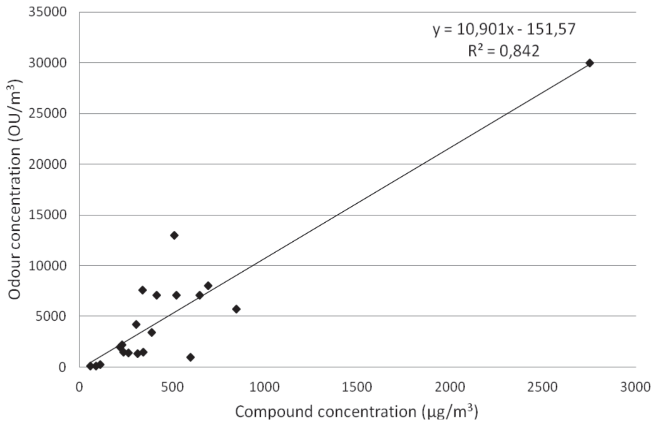


FIGURE 15 Correlation of the sum of concentrations of determined odorous VOCs and measured Odour Units (OU/m^3).

According to the linearity analysis of curves presented in Fig. 14, single odorous compounds did not show a direct correlation with the overall odour described as the Odour Units/m^3. In addition, diethyl ether did not show a direct correlation to the overall odour concentration either. Pearson's correlation coefficients for single odorants were between 0.07 and 0.43 (Fig. 14). In the case of TVOC concentration, any correlation in comparison with the overall odour expressed as odour units was not detected. The Pearson's correlation coefficient was in fact 0.05. This is probably due to the relatively high concentrations of hydrocarbons like undecane or dodecane that are not odorous compounds because of the high odour thresholds, but they are calculated to the sum of VOCs described as TVOC. Contribution of different hydrocarbons to the odour is minor and this causes the disproportion between TVOC and odour concentrations.

However, a rather good correlation between odour concentration (OU/m^3) and VOCs was found out in calculations where all the odorous VOCs such as DMS, DMDS, DMTS, alpha-pinene, limonene, toluene and in some occasions 3-carene, nonanal and heptanal and hydrogen sulphide concentrations that exceeded the odour threshold concentrations were added together and compared with Odour units/m^3 (Fig. 15). Pearson's correlation coefficient for the sum of odorous VOCs and hydrogen sulphide was 0.842. Similar conclusions of the correlation of odour concentration with the sum of odorous compounds were also drawn in studies made by Kim & Park (2008).

Uncertainty to the correlation calculations was caused by the fact that all possible odorous compounds (organic or inorganic) may not have been determined by available methods. Of course, in some cases the GC-MS-sniff technique does not represent the complete screening of all possible odorous compounds, and, for example, some small molecule amines that may be the odorants too, were not detected by this method. Moreover, larger molecules, the so called semi volatile organic compounds (SVOCs, boiling points 250-380 °C) could not be measured by GC-MS-sniff focused to measure only VOCs (boiling points 6-250°C). The problematic analysis of H_2S also brought uncertainty to the results, because H_2S probably have been an odorous compound, although it was not possible to analyse it instrumentally due to the relatively high detection limit of analysis equipment. The results presented in the study made by Gostelow & Parsons (2000) showed that if hydrogen sulphide exists in high concentrations, meaning several milligrams per cubic meter, the correlation between odour concentration and solely the hydrogen sulphide is good and it can be determined as the major odour component. Nevertheless, the results of our study showed that odour concentration can be roughly estimated in the base of sum of odour threshold exceeding compounds in places where H_2S content is very low without taking into consideration the additive or antagonistic effects of compounds.

5.4 Advantages and limitations of the method TD-GC-MS-Sniff in analysing the environmental odours

GC-MS has been widely used in air quality analysis. Concentrations of airborne odorous compounds are not necessarily very high and normal direct injection system analysis methods are not able to detect all the odorous compounds in ambient air or even in process air from for example the compost drum or wastewater treatment plants ventilation ducts. In these cases the TD-GC-MS method has an advantage in concentrating the sample so that the compounds are detectable by GC-MS.

Another advantage of the method presented here is sniffing by which it is possible to trace the key odorous compounds from all compounds in GC-MS that can be dozens or hundreds in one sample. The limits of traditional instrumental techniques have directed the attention to odour measurement procedures that relies on the use of human nose as a detector (Brattoli et al. 2011). This has been the case also in development of sniffing-technique or GC-MS-O methods. Furthermore, the threshold odour concentrations presented in literature vary depending on the method and people analyzing them, it is not always directly only the threshold exceeding compounds that are causing the odour. Therefore it is important to evaluate also the compounds that cause odour perception in sniffing analysis as possible odorants and contributors to the overall odour.

The method used in our study proved to be rather reliable and the repeatability of analyses has been quite good. The RSD% of repeated standard analyses for 26 compounds has been lower than 10% for all other compounds than 2,3-butanedione being 18.4% and for heptanal being 19.3%. It seems that the carbonyl compounds as polar compounds are more vulnerable to the moisture effects in analysis and also to the interaction with the column material.

In addition, linearity of all the standard compounds was tested and all other compounds had their correlation coefficient being 0.995 and higher as recommended except 2-hexanone (0.9872) and benzaldehyde (0.9869).

The main limit of GC-MS procedure is in the complexity of odour and therefore all possible odorous compounds (organic or inorganic) may not have been determined by available methods. The perceived odour is a mixture of dosens even hundreds of compounds, that can be also inorganic, like H_2S and NH_3. Furthermore, other concentrations of some odorous compounds may be lower than the instrumental detection limit. Of course, in some cases the GC-MS-sniff technique does not represent the complete screening of all possible odorous compounds, and, for example, some small molecule amines that may be the odorants too, were not detected by this method. Moreover, larger molecules, the so called semi volatile organic compounds (SVOCs, boiling points 250-380 ºC) could not be measured by GC-MS-sniff focused to measure only VOCs (boiling points 6-250ºC). In the future it would be important to test and develop for example multisorbent methods also for analyzing the compounds in a broad volatility range. Also technique presented here does not allow the evaluation of the additive/synergic effect of single odorants in the true odour mixture. The overall odour intensity is best to measure with the dynamic olfactometry.

The methodological problems can arise from the subjective nature of odour assessment, decreasing alertness of assessors or from the non-random sequence in which the compounds elute. Decreasing alertness will be important factor if there is only a few compounds to perceive or they show only low odour intensity, when the stimulus is brief or the session is long and if the assessor is not motivated.

6 CONCLUSIONS

Odorous compounds vary naturally according to the source of the emission and it was shown in this study that the odour composition is plant specific. Therefore, in the cases of assessing the best odour abatement method in plants the detailed odour component assessment shown in this study is very useful. The knowledge about the composition of odour and the contributing factors help to decide the most effective odour abatement method for certain plant.

When considering the wastewater treatment, the odorous compounds are mainly the organic sulphur compounds and hydrogen sulphide in some extent as well as limonene and toluene and some aldehydes like heptanal and octanal. In most cases the incoming wastewaters especially from industry already have an important role in defining the intensity and character of wastewater odour as well as in the safety of indoor air in the WWTP working areas. Furthermore, sulphur compounds dominate the odour from latter parts of wastewater processing, especially the sludge management stages. This is due to the degradation of organic material. In Pulp mill wastewater treatment, the odour compounds are naturally the terpenes like alpha-pinene and limonene, and sesquiterpenes in some extent. Other odorous compounds are sulphur compounds like dimethyl sulphide and dimethyl disulphide and also some aromatic compounds like toluene and p-cymene which were analysed as the odour compounds according to the sniffing analysis.

In organic waste management as in the composting, the odour causing components are different carboxylic acids, usually acetic acid and butanoic acid, ketones like 2,3-butanedione, 3-hydroxy-2-butanone, esters like ethyl acetate and terpenes, especially limonene that are released as metabolic products in decaying of food or other goods. In some cases also alcohols like 2-butanol as the odorous compound were detected in the composting hall. With the municipal solid waste, the odorous compounds are also ketones like 2,3-butanedione and 3-hydroxy-2-butanone, esters like ethyl acetate, and aromatic compounds like ethyl benzene and p-cymene. As a difference from composting, aromatic and aliphatic hydrocarbons are abundantly present in solid waste sites. However, these compounds, especially the aliphatic hydrocarbons, are not considered as the major odour causes.

Concentrations of VOCs in waste and wastewater treatment were not remarkably high. When comparing them to the occupational exposure limits given by the authorities in Finland, the concentrations did not exceed the limits. Still some remarks were noticed; for example 1,2-dichloroethane and styrene were determined in one WWTP (Plant A) at quite high concentrations according to the WHO classification and regulations given for the indoor air. In cases of WWTPs the industrial based solvent discharges seemed to influence to the potential health hazard of indoor air in the plants. In waste management and especially in composting, the concentrations of 2,3-butanedione, that is a possible cause of bronchiolitis obliterans, exceeded the limits or limit proposals given by US NIOSH.

In wastewater management TVOC concentrations varied a lot depending on the site at the plant. The highest TVOC concentration was in sludge dewatering units where the TVOC concentration was 7720 μg/m^3 at one measurement time. In waste management (composting and sorting stations of waste) TVOC concentrations were in the range of 232–2300 μg/m^3 and considering the scientific studies made of health effects of several VOCs simultaneously, the possibility of health risk exists. At present there is very limited data available of the health effects of occupational limit concentrations of several VOCs and TVOC combinations presented in this study. In addition, with other exposure factors like microbes and dust present in these plants, it is important to continue the analysis of simultaneous exposure to these factors and their possible health effects.

Total sum of odorous compounds seemed to correlate with measured odour concentration. The rather good correlation was achieved by calculating the sum of concentrations of single VOCs exceeding odour thresholds and VOCs that were intense odour causes in sniffing analysis. Thus these compounds altogether can be considered as some kind of indicators of possible odour annoyance. When reviewing the single compound concentration correlations to the overall odour concentration, no correlation between them was observed. Thus it was not possible to demonstrate that a single compound has a strong effect on overall odour and they are not possible to use as a target compounds alone. When comparing the TVOC concentration with OU/m^3 results, no correlation between them were determined. This was due to aliphatic hydrocarbons that existed in samples but are not contributing to the overall odour in measured concentrations.

Sniffing analysis revealed several compounds that caused odour in simultaneous sniffing of samples but do not have the determined odour threshold concentration. In future it is important to continue determining thresholds for these compounds so that the evaluation of their contribution to the overall odour is possible.

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YHTEENVETO (RÉSUMÉ IN FINNISH)

Hajua aiheuttavat haihtuvat orgaaniset yhdisteet (VOC) jätteen- ja jäteveden käsittelyssä

Tässä väitöstyössä tutkittiin erilaisten jätevesien ja jätteiden käsittelyn yhteydessä syntyviä haju- ja VOC-päästöjä. Tutkimukset suoritettiin yhdyskuntien jätevedenkäsittelylaitoksilla, paperi- ja sellutehtaan jätevedenkäsittelylaitoksella, kompostointilaitoksella, jossa menetelmänä oli rumpukompostointi sisätiloissa, sekä sekajätteen optisella erottelulaitoksella, jossa erotteluprosessi tapahtuu sisätiloissa. Tutkimusmenetelmänä käytettiin kaasugromatografi-massaspektrometriä, johon on yhdistetty samanaikainen haistelu. Kokonaishajupitoisuudet mitattiin olfaktometrillä.

Haihtuvien orgaanisten yhdisteiden (VOC) lähteitä jätteenkäsittelyssä ovat kaatopaikat, jätteiden poltto, kompostointi, jäteveden käsittely sekä jätevesilietteiden tai kompostin levitys maaperään. Suuri osa haihtuvista orgaanisista yhdisteistä on myös hajua aiheuttavia yhdisteitä. Erityisesti jätteenkäsittelystä tai jätevedenkäsittelylaitoksilta tuleva hajupäästö koetaan epämiellyttävänä ja elämänlaatua heikentävänä tekijänä. Epämiellyttävä haju voi aiheuttaa väestössä huolta myös hajupäästön sisältämien yhdisteiden mahdollisista terveyshaitoista. Tämän työn tarkoituksena oli selvittää yksityiskohtaisesti yhdyskuntien ja teollisuuden jätevesien käsittelyn yhteydessä esiintyvät haihtuvat orgaaniset yhdisteet sekä samoin yhdyskuntien kuivajätteiden että biojätteen kompostoinnin yhteydessä muodostuvat ja esiintyvät haihtuvat orgaaniset yhdisteet.

Yhdyskuntien jäteveden hajuun vaikuttaa luonnollisesti tulevien jätevesien laatu. Tämä todettiin erityisesti jätevedenkäsittelylaitoksella B, jonka tuloksissa oli havaittavissa paljon terpeenejä, jotka eivät ole tavanomaiselle yhdyskuntien jätevedelle tyypillisiä. Samoin laitoksella A havaittiin styreeniä ja 1,2-dikloorietaania, jotka ovat todennäköisimmin peräisin teollisuuden jätevesistä. Jätevedenkäsittelyssä tavanomaisia hajua aiheuttavia yhdisteitä olivat pääsääntöisesti orgaaniset rikkiyhdisteet, erityisesti dimetyylisulfidi, dimetyylidisulfidi, metaanitioli sekä dimetyylitrisulfidi. Muita kokonaishajuun vaikuttavia yhdisteitä olivat heptanaali ja oktanaali, joiden hajukynnysarvot ovat verrattain matalat. Aromaattisista yhdisteistä hajukynnyksen ylitti jokaisella laitoksella tolueeni. Terpeeneistä alfa-pineeni sekä limoneeni ylittivät hajukynnysarvon. Laitoksilla A ja B havaittiin lisäksi etikkahappoa sekä butaanihappoa. Todennäköisiä hajunaihauttajia olivat myös 3-kareeni ja allyylimetyylisulfidi, jotka analyysin yhteydessä suoritetussa haistelussa havaittiin selvinä tai voimakkaina hajukokemuksina. Näille yhdisteille ei ole toistaiseksi kirjallisuudessa esitetty hajukynnysarvoja, jolloin arvio siitä, ovatko ko. yhdisteet hajunaiheuttajina, perustuu haistelijan subjektiiviseen arvioon hajun laadusta ja voimakkuudesta. Pelkistyneitä rikkiyhdisteitä havaittiin jätevedenpuhdistamoilla erityisesti lietteenkäsittelyvaiheissa ja jätevedenkäsittelyprosessin loppuvaiheissa.

Sellu- ja paperintuotannon yhteydessä muodostuvan jäteveden hajuhaitat ovat pääosin peräisin jätevedessä olevista pelkistyneistä rikkiyhdisteistä, terpeeneistä ja seskviterpeeneistä sekä aromaattisista yhdisteistä, joita tässä tutkimuksessa havaittiin. Rikkiyhdisteiden ja terpeenien määrä oli suurin esiselkeytysaltaalla. Terpeenien ja seskviterpeenien osuus analysoiduista VOC:eista oli enimmillään 65,2 %. Nämä yhdisteet ovat pääosin peräisin sellunkeittoprosessista sekä sen sivutuotteiden valmistuksesta. Ne ovat ominaisuuksiltaan hyvin hydrofobisia sekä tiheydeltään vettä kevyempiä, joten ne pääsevät haihtumaan altaiden pinnalta erittäin helposti. Yhdisteitä tavattiin myös tehtaan toimistorakennuksesta kohtalaisen suurina pitoisuuksina.

Kiinteiden jätteiden käsittelyssä ja kompostoinnissa hajua aiheuttavia yhdisteitä olivat erilaiset karboksyylihapot, esterit, ketonit sekä terpeenit. Nämä yhdisteet ovat tyypillisiä orgaanisen materiaalin metabolian välituotteita. Lisäksi kuivajätteen käsittelyn päästöissä oli huomattava määrä alifaattisia sekä aromaattisia hiilivetyjä. Nämä yhdisteet eivät kuitenkaan ole hajun aiheuttajia, sillä niiden hajukynnysarvot ovat verrattain korkeat.

Väitöstyössä tutkittiin myös eri hajuyhdisteiden pitoisuuksien korrelaatiota kokonaishajun voimakkuuteen. Verrattaessa mitattuja VOC-pitoisuuksia analysoituihin kokonaishajupitoisuuksiin havaittiin, että yksittäisten hajua aiheuttavien yhdisteiden pitoisuudet sekä TVOC pitoisuudet eivät korreloi kokonaishajun voimakkuuteen. Kuitenkin verrattaessa kokonaishajua hajua aiheuttavien yhdisteiden pitoisuuksien summaan, saatiin kohtalainen korrelaatio (0,842) hajunaiheuttajien sekä kokonaishajun välille.

Tässä työssä mitattuja VOC pitoisuuksia verrattiin olemassa oleviin terveydellisiin raja-arvoihin, joita olivat suomalaiset HTP-arvot (haitalliseksi tunnetut pitoisuudet) sekä WHO:n vuonna 2000 antamat suositukset VOC:eille sisä- tai ulkoilmassa. Lisäksi joitakin yhdisteitä verrattiin Yhdysvaltalaisen NIOSH (National Institute of Occupational Health and Safety) laitoksen antamiin suosituksiin. Tutkimuksessa havaittiin, että tutkimuksissa mukana olevilla laitoksilla yksittäisten VOC:ien pitoisuudet eivät ylittäneet Suomessa annettuja haitalliseksi tunnettujen pitoisuuksien raja-arvoja. Kuitenkin jätevedenkäsittelyssä laitoksella A havaittiin styreeniä ja 1,2-dikloorietaania WHO:n suositusarvoja lähellä olevina pitoisuuksina. 1,2-dikloorietaanin pitoisuus oli korkeimmillaan 960 µg/m^3 ja altistumisaika huomioon ottaen laskettu altistuminen 24 tunnin aikana 320 µg/m^3. WHO:n suositusarvo jatkuvalle altistumiselle on 700 µg/m^3 (24 h). Styreenille WHO:n antama suositusarvo on 260 µg/m^3. Styreenin pitoisuus oli jätevedenkäsittelylaitoksella A korkeimmillaan 330 µg/m^3 ja altistumisaika huomioon ottaen laskettu altistuminen 24 tunnin aikana oli 110 µg/m^3. Kompostoinnissa sekä sekajätteiden käsittelyssä ja lajittelussa esiintyi 2,3-butaanidionia, joka nykytutkimuksissa on epäilty olevan ”bronchiolitis obliterans” keuhkosairauden aiheuttaja. NIOSH on määrittänyt 2,3-butaanidionille elintarviketeollisuuteen altistusrajat, jotka ovat 90 µg/m^3 (15 min) ja 18 µg/m^3 (8 h). Tutkimuksessa havaitut pitoisuudet vaihtelivat välillä 8 - 1150 µg/m^3, joten mahdollisuus altistumiseen on olemassa. Suomessa ja muualla

Euroopassa tälle yhdisteelle ei kuitenkaan ole asetettu käyttörajoituksia tai altistumisen raja-arvoja. Myös monille muille tutkimuksessa havaituille VOC:eille ei ole olemassa riittävää toksikologista dataa erityisesti hengitysteitse altistumisen arviointia varten.

Tutkimuksessa määritettiin laitosten työskentelytiloissa TVOC eli kokonais-VOC-pitoisuudet. TVOC-pitoisuudelle on Suomessa määritelty suositusarvoja, jotka koskevat sisäilmaa ja erityisesti asuntojen, koulujen, virastojen yms. sisäilman laatua. Laitosten TVOC-arvoja verrattiin sosiaali- ja terveysministeriön antamiin suositusarvoihin, joissa 600 µg/m^3 on arvo, jonka ylittävissä pitoisuuksissa sisäilman laatu voidaan luokitella heikoksi / välttäväksi orgaanisten yhdisteiden osalta. Jätevedenkäsittelylaitoksen tilojen TVOC-arvot vaihtelivat välillä 260 – 4150 µg/m^3. Korkeimmat arvot mitattiin lietteen kuivauksen yhteydessä sekä välppätiloissa. Sellutehtaan TVOC-pitoisuudet toimistossa ja kuitulinjan valvomossa olivat muutamina kertoina verrattain korkeat vaihdellen alueella 145 – 3230 µg/m^3. Suurimpina pitoisuuksina esiintyivät tällöin terpeenit ja aromaattiset yhdisteet. On todennäköistä, että toimiston sisäilmassa olevat yhdisteet ovat peräisin jätevedenkäsittelylaitoksesta tai läheisestä kuitulinjarakennuksesta. Kuitulinjan valvomon yhdisteet ovat luonnollisesti peräisin kuitulinjaprosessin yhteydessä vapautuvista päästöistä. Kompostointihallissa sekä optisella lajittelulaitoksella TVOC-arvot olivat myös osassa mittauksia verrattain korkeat. Kompostointihallissa vaihteluväli oli 710 – 10 100 µg/m^3 ja valvomossa 240 - 3700 µg/m^3. Optisen lajittelulaitoksen hallissa TVOC-pitoisuudet olivat alueella 2270 – 8070 µg/m^3 ja laitoksen valvomossa 232 – 324 µg/m^3. Pitoisuudet voivat toisinaan kohota tasolle, jossa ilmanlaatu VOC:ien osalta on välttävä/huono verrattuna annettuihin suositusarvoihin ja VOC:ien aiheuttamaa oireilua voi esiintyä.

Arvioitaessa työssä käytetyn analyysimenetelmän etuja ja rajoituksia hajuanalytiikassa, havaittiin käytetyn menetelmän toistotarkkuus ja lineaarisuus hyväksi analysoiduille VOC-yhdisteille. Menetelmällä on mahdollisuus havaita jopa ihan pienissä pitoisuuksissa hajua aiheuttavia yhdisteitä. Menetelmän rajoituksena on, että se tunnistaa yhdisteet, joiden kiehumispiste on välillä 0 – 260 °C ja on hyvin todennäköistä, että ns. puolihaituvissa orgaanisissa yhdisteissä (SVOC, kp 240 – 400 °C) on paljon yhdisteitä, jotka vaikuttavat kokonaishajuun. Toisaalta työssä havaittiin, että on edelleen suuri joukko yhdisteitä, joiden hajukynnyksiä ei ole määritelty missään tieteellisessä kirjallisuudessa. Samoin terveysperusteisia ohjearvoja tai yhdisteiden toksikologista tietoa oli hyvin niukasti saatavilla. Näihin asioihin tulisikin tulevaisuudessa panostaa tutkimusta ja menetelmien kehittämistä.

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APPENDICES

APPENDIX 1 Properties of compounds found in the study

Table 1 shows the odour threshold concentrations, odour descriptions and physical-chemical properties of odorous compounds found in this study.

TABLE 1 Odour threshold concentrations, odour descriptions (O´Neill & Phillips 1992, Ruth 1986) and some physical-chemical properties (CRC 1993, NIST2012) for odorous compounds found in this study.

Compound	Odour threshold concentration in air (µg/m^3)	Odour threshold concentration in water (mg/ml)	Odour description	Solubility in water (in 20 °C)	Boiling point (°C)
DMS	0.1	0.3	decayed cabbage	26.6	109
DMDS	0.3	0.16	decayed cabbage	27.4	37.0
DMTS	6.2	0.05	garlic, metallic*, sewer*	slightly soluble	165
H_2S	0.7	-	rotten eggs	117.6 (gas, pH 7)	-60.2
methanethiol	0.0003	-	decayed cabbge, sulphurous	2.3	5.95
thiophene	2.6	-	garlic	-	84.1
allylmethyl sulphide	-	-	garlic*, unpleasant	-	91.0
2-methylthiophene	-	-	sulphurous	miscible	93.0
acetone	940	-	sweet, solvent	3750	113
2-butanone	740	50 000	sweet, acetone-like	200	56.5
2,3-butanedione	0.07	-	toffee*, sweet, butter	100	79.6
3-hydroxy-2-butanone	-	-	sour milk*, butter	4.3	88.0
2-heptanone	94	-	sweet, banana	0.9	145
2-octanone	1.3	-	mild, fruity	miscible	173
2-propanol	2500	-	alcohol	miscible	82.3
2-butanol	400	500	sweet, alcohol	54	99.0
3-methyl-1-butanol	80	-	sweet, musty	5.9	131
1-hexanol	10	2500	green		156
1-heptanol	-	3	sweet, resin	69	176
diethyl ether	900-28 000	-	ether	931.0	34.5
methane chloride	-	-	sweet, chlorine	153.1	39.8
chloroform	-	-	chloroform	67.1	61.2

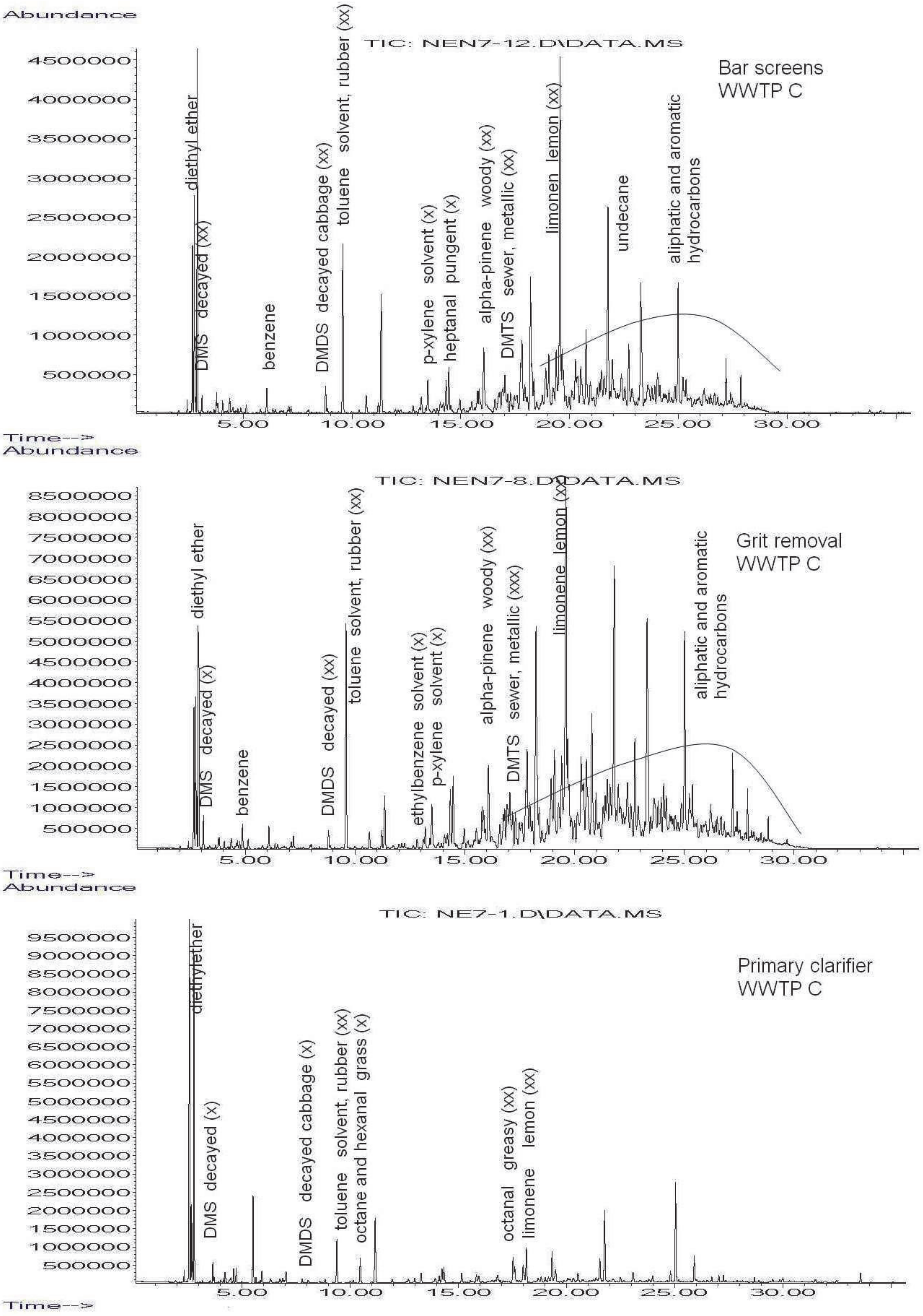

FIGURE 3 Example chromatograms with determined odorous compounds and sniffing results (odour descriptions with intensity markings by x:s) from the WWTP C sampling sites.

Table 1. continued.

tetrachloroethene	-	-	sweet, chorine	0.9	121
benzene	1500	-	solvent	23.0	81.9
toluene	80	-	paint, solvent	5.2	110
p-xylene	350	-	sweet, solvent	1.5	138
o-xylene	350	-	sweet, solvent	1.5	144
ethyl benzene	13	-	aromatic, sweet	1.4	136
styrene	73	730	rubber*, solvent	0.3	145
p-cymene	4	-	woody, musty	0.6	177
benzaldehyde	0.8	350	bitter almond	17 (15 °C)	179
2-methoxyphenol	-	21	spicy, vanilla	20	205
p-cresol	0.005	-	manure*, horse, creosote	2.4	201.8
3-methylbutanal	16	-	malt	14	90
pentanal	2.5	-	sharp	163.0	102
hexanal	28	4.5	green ,grass*	48.0	130
heptanal	6.0	3	greasy*, pungent	slightly soluble	153
octanal	7.8	-	greasy	slightly soluble	171
nonanal	0.3	-	greasy, burnt*	insoluble	195
alfa-pinene	16	6	woody, coniferous	0.037	155
beta-pinene	-	-	woody, coniferous	0.081	64.0
3-carene	-	-	lemon	insoluble	166
limonene	10	10	lemon	0.15	176
camphor	-	-	camphor	0.12	209
borneol	10	-	camphorous, spicy	insoluble	212
alpha-terpineol	-	330	woody, floral	0.4	217
undecane	-	-	alkane	-	196
dodecane	-	-	alkane	-	216
ethyl acetate	19.6	-	sweet, fruity	83	77.0
acetic acid	25	-	acetic, vinegar*	soluble	118
butanoic acid	0.4	-	rancid butter	soluble	164
ammonia	3600	-	ammonia	530 (gaseous)	-33.3

*analysers own description.

APPENDIX 2 Example chromatograms from different plants

Example chromatograms from different measurement sites are given in this Appendix (see Fig. 1-11). The odorous compounds with their odour descriptions and the odour intensity (x:s) are marked on the chromatograms.

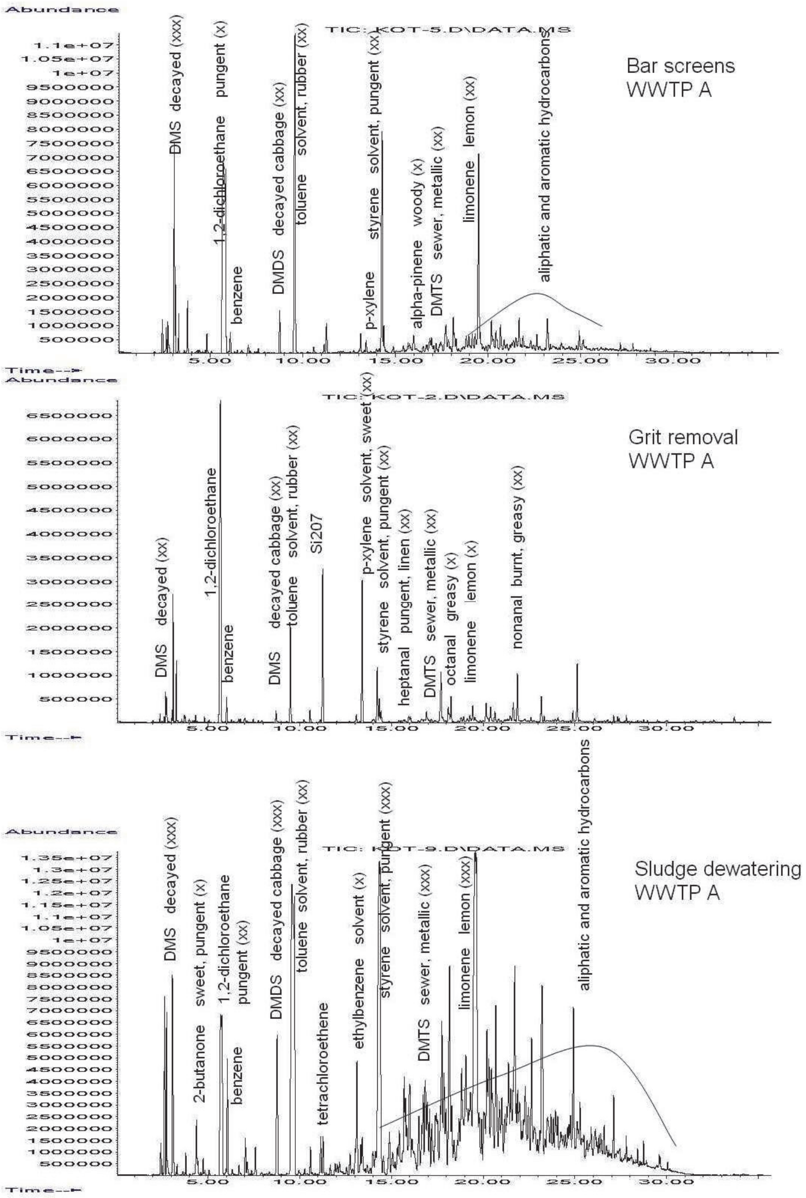

FIGURE 1 Example chromatograms with determined odorous compounds and sniffing results (odour descriptions with intensity markings by x:s) from the WWTP A sampling sites.

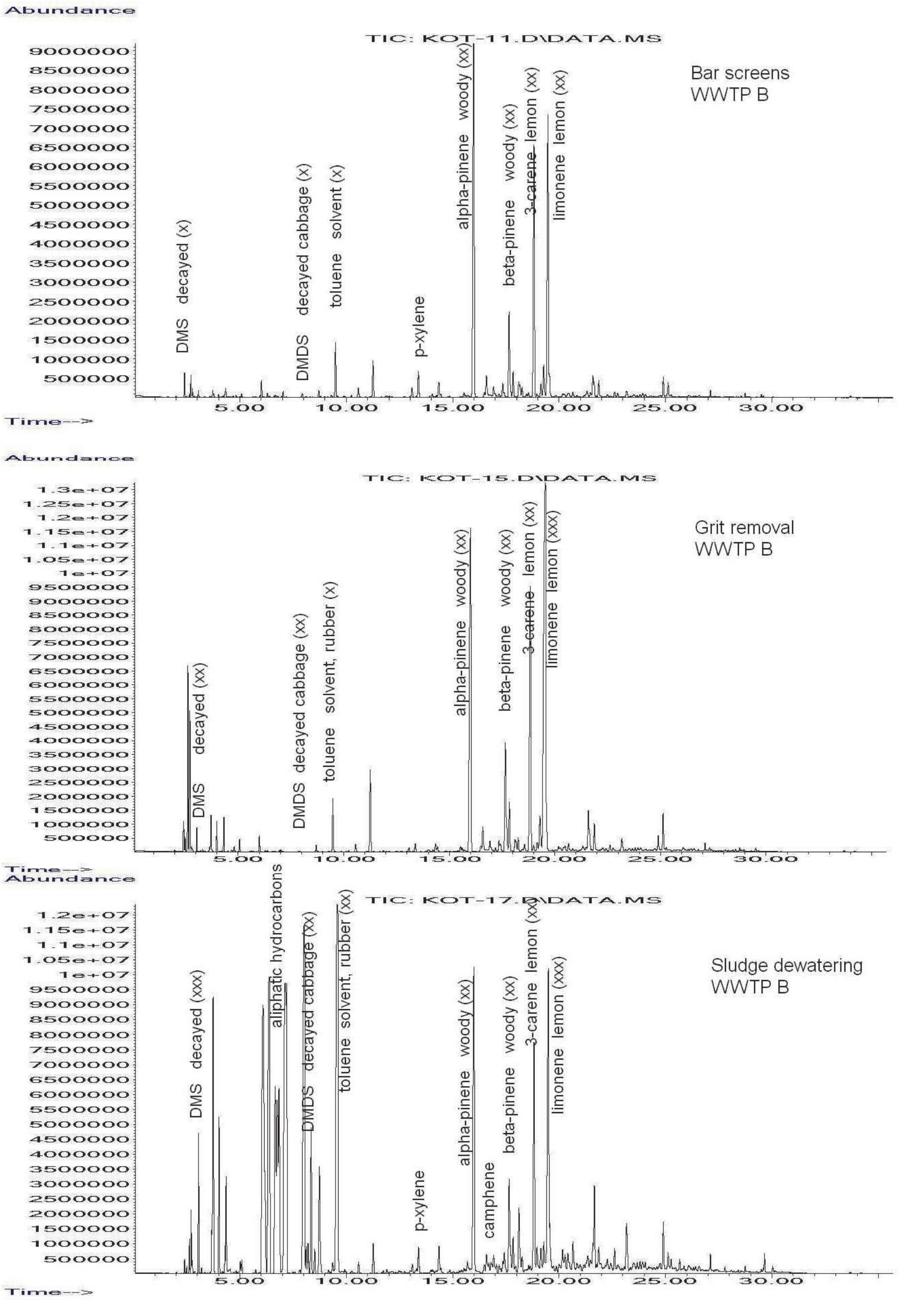

FIGURE 2 Example chromatograms with determined odorous compounds andsniffing results (odour descriptions with intensity markings by x:s) from the WWTP B sampling sites.

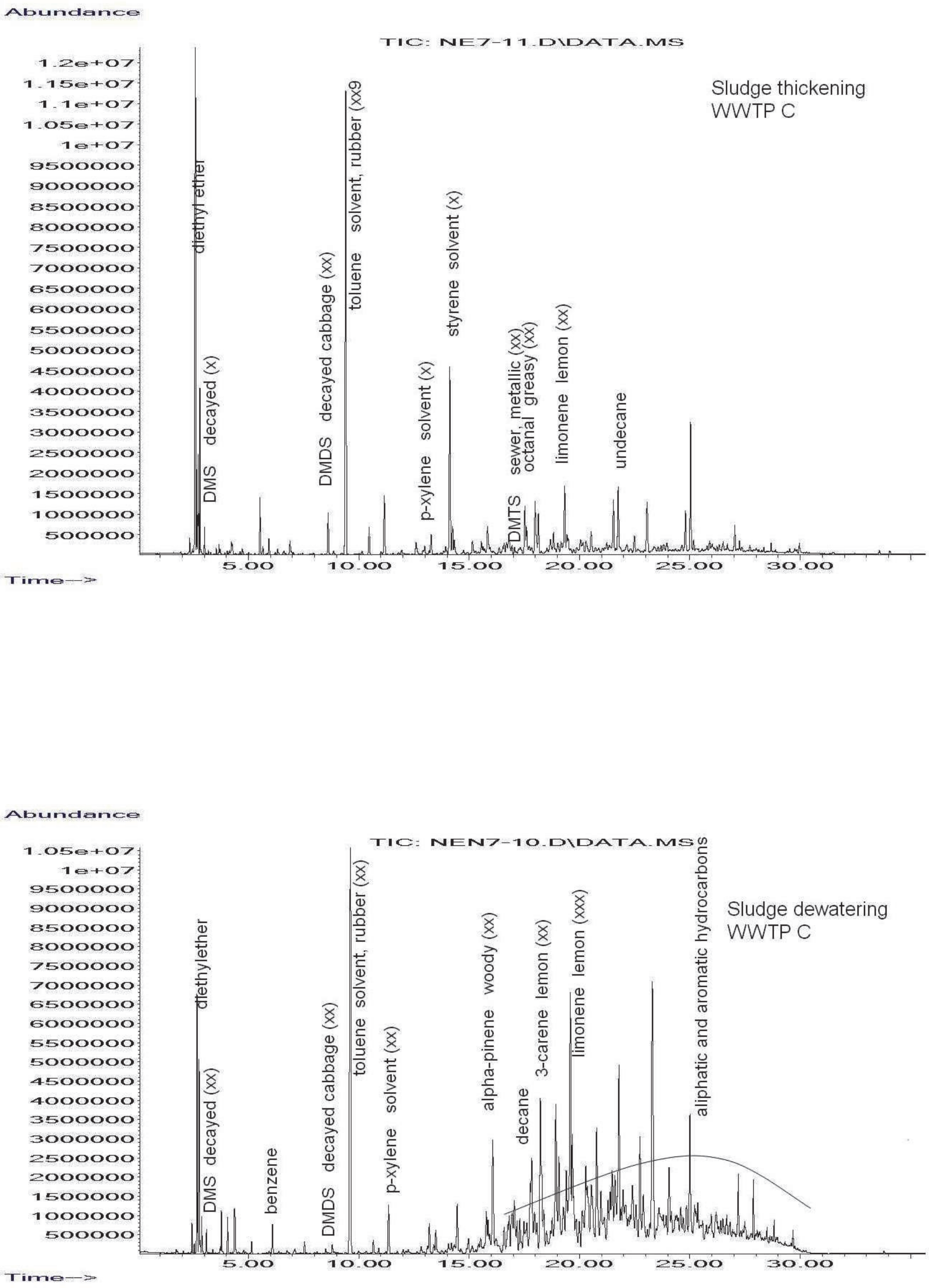

FIGURE 4 Example chromatograms with determined odorous compounds and sniffing results (odour descriptions with intensity markings by x:s) from the WWTP C sampling sites.

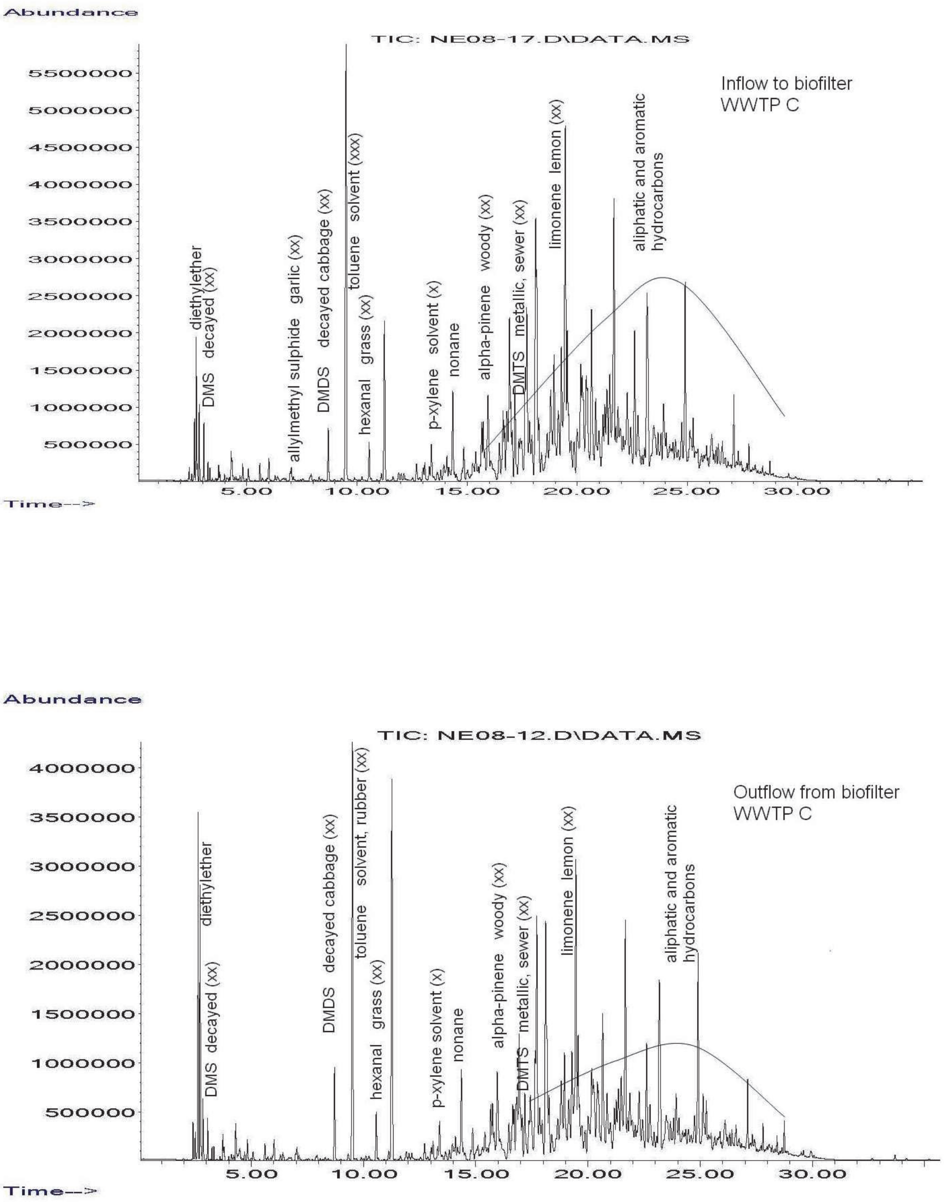

FIGURE 5 Example chromatograms with determined odorous compounds and sniffing results (odour descriptions with intensity markings by x:s) from the WWTP C biofilter sampling sites.

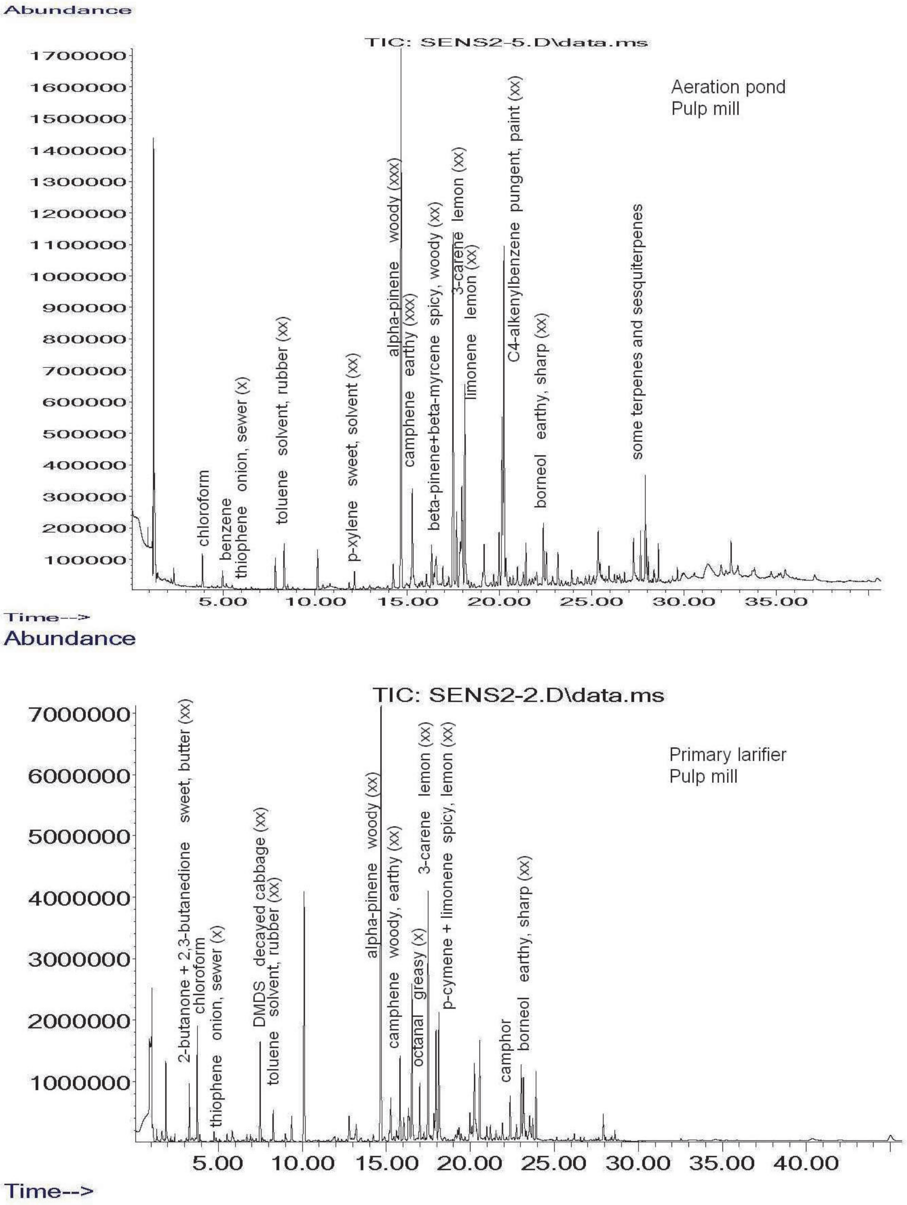

FIGURE 6 Example chromatograms with determined odorous compounds and sniffing results (odour descriptions with intensity markings by x:s) from the pulp mill WWTP air sampling sites.

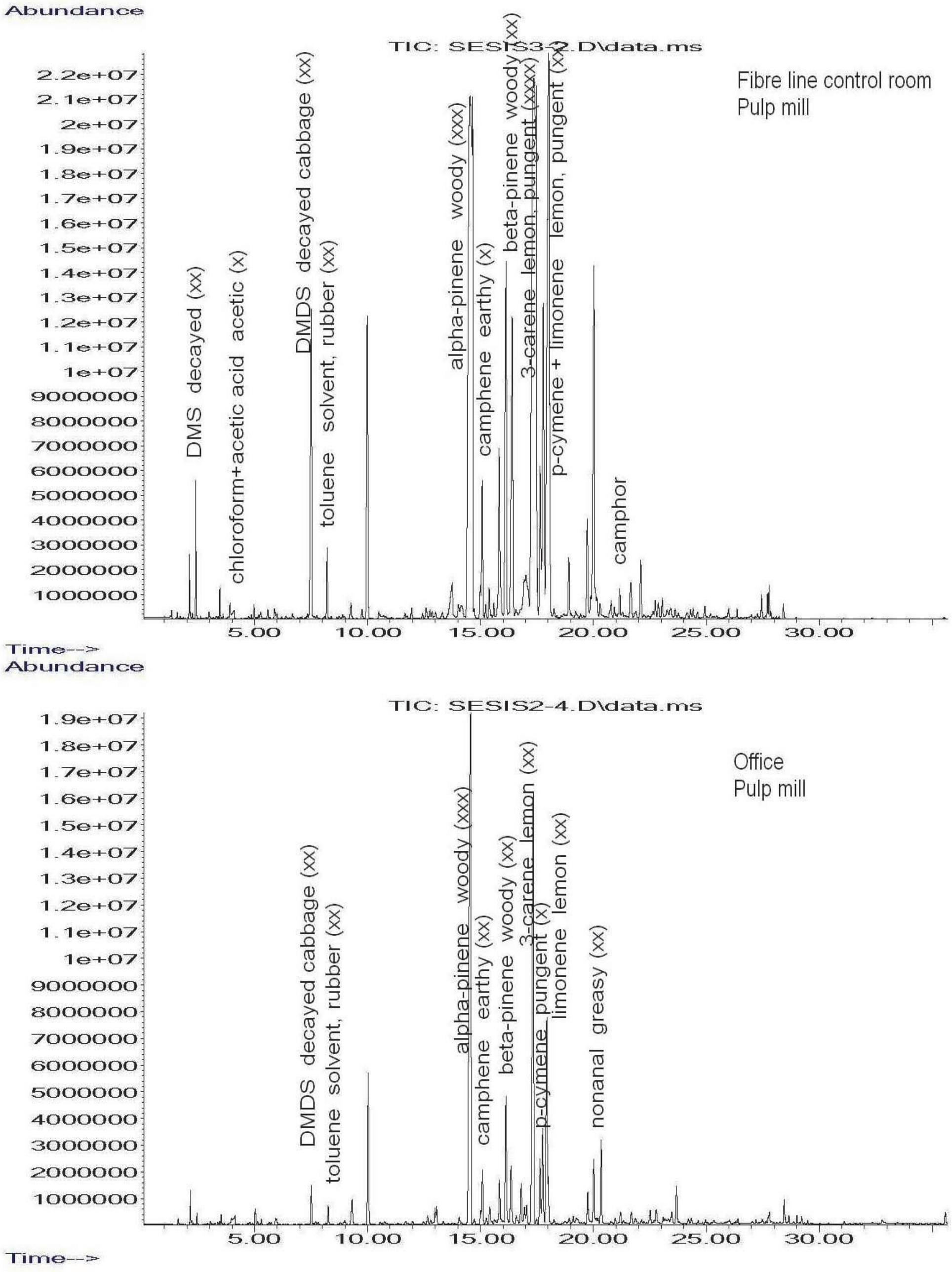

FIGURE 7 Example chromatograms with determined odorous compounds and sniffing results (odour descriptions with intensity markings by x:s) from the pulp mill WWTP air sampling sites.

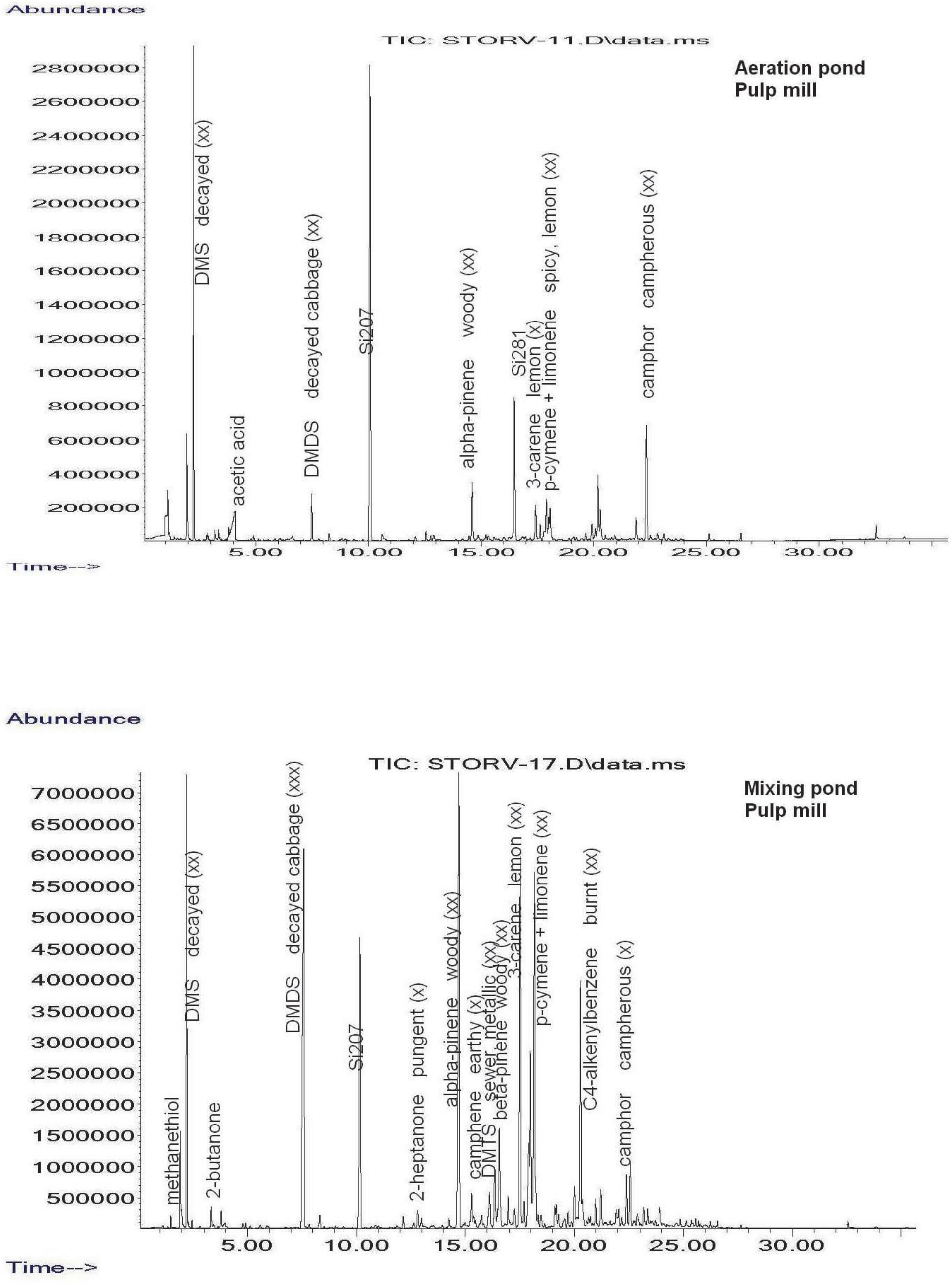

FIGURE 8 Example chromatograms with determined odorous compounds and sniffing results (odour descriptions with intensity markings by x:s) from the pulp mill WWTP liquid sampling sites.

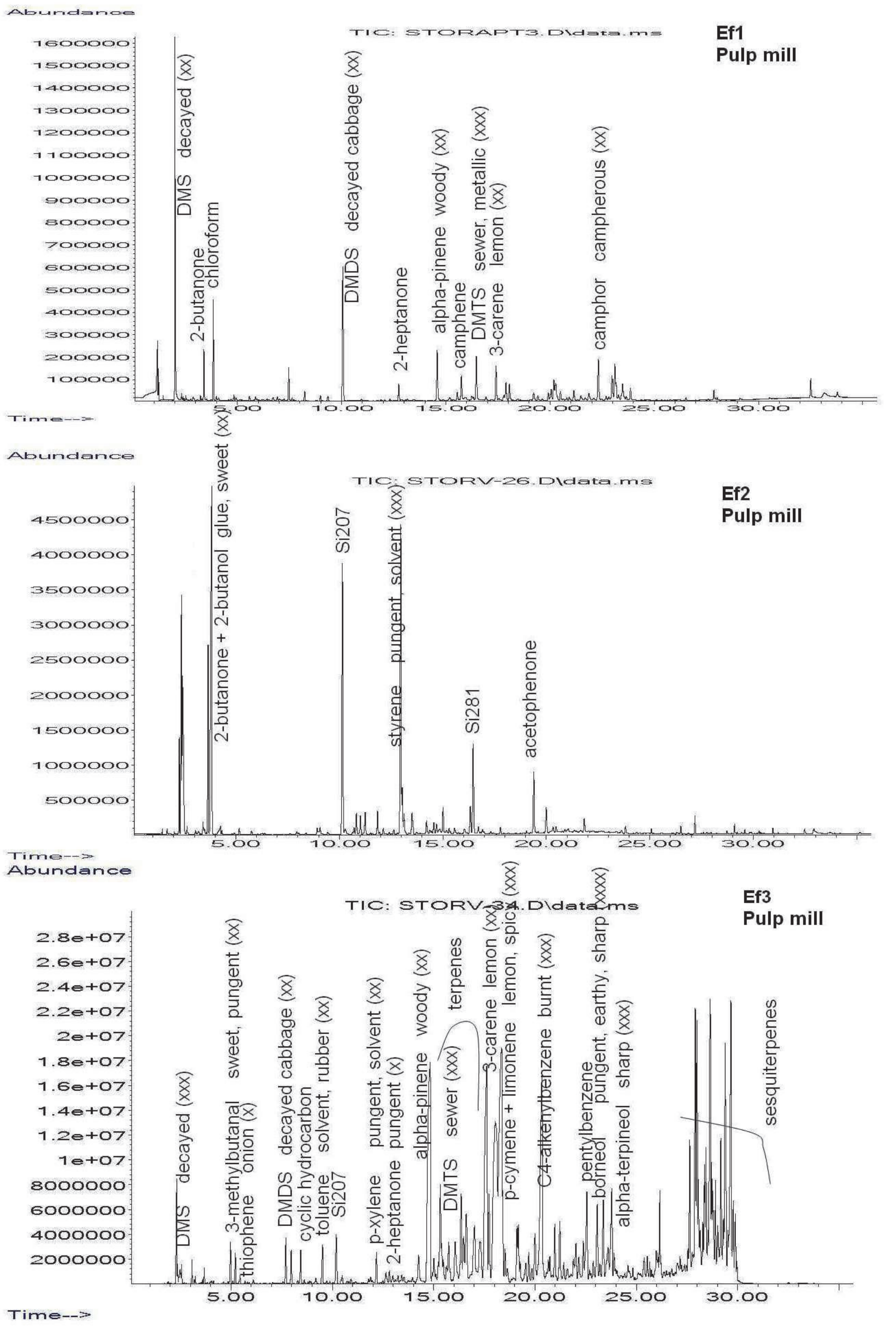

FIGURE 9 Example chromatograms with determined odorous compounds and sniffing results (odour descriptions with intensity markings by x:s) from the pulp mill WWTP incoming effluent fractions Ef1, Ef2 and Ef3.

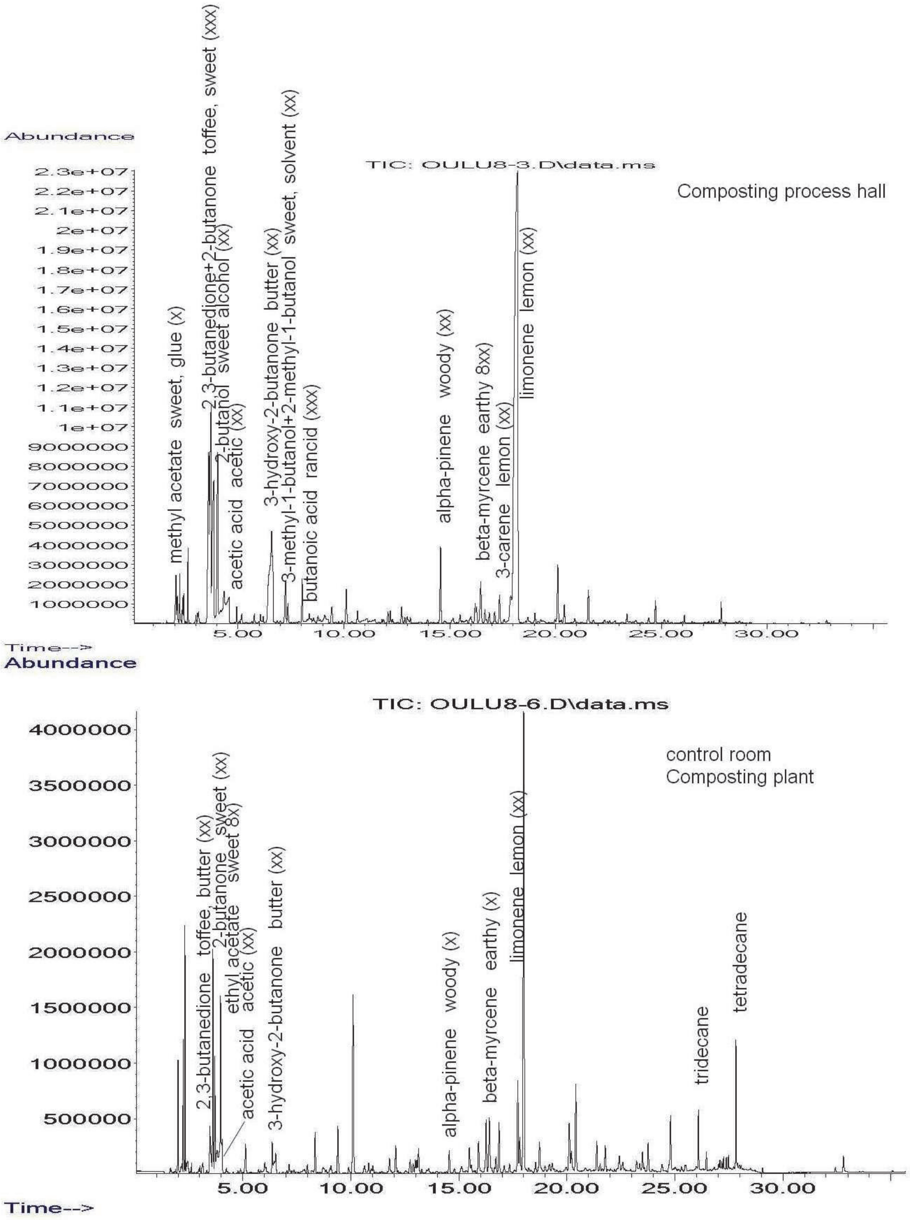

FIGURE 10 Example chromatograms with determined odorous compounds and sniffing results (odour descriptions with intensity markings by x:s) from the composting plant sampling sites.

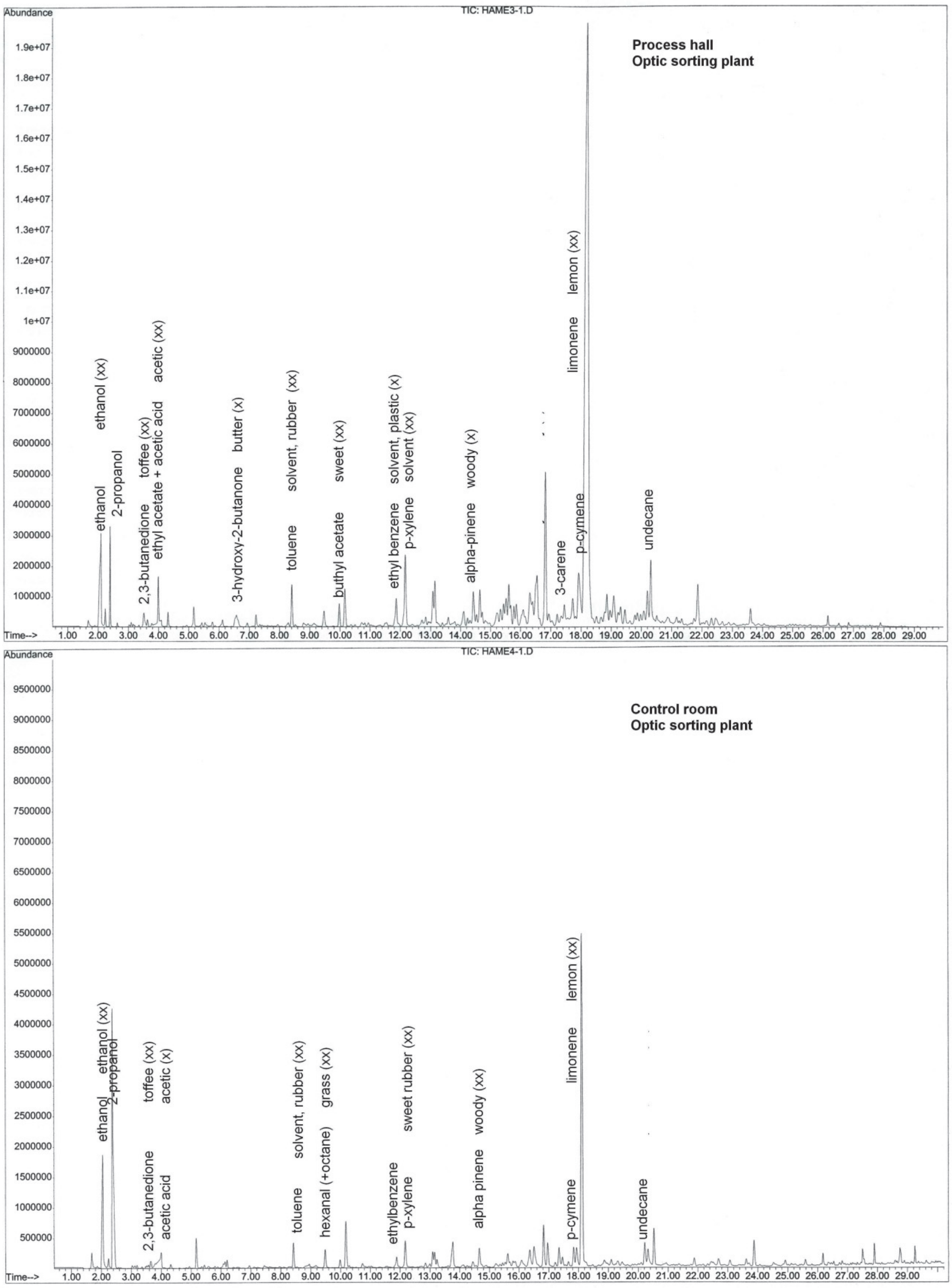

FIGURE 11 Example chromatograms with determined odorous compounds and sniffing results (odour descriptions with intensity markings by x:s) from optic sorting plant process hall and control room.

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