DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

CHARACTERISTICS AND CHEMISTRY OF ODORS FROM SELECTED INDUSTRIAL FACILITIES IN İZMİR

by
Faruk DİNÇER

July, 2007
İZMİR

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We have read the thesis entitled "**CHARACTERISTICS AND CHEMISTRY OF ODORS FROM SELECTED INDUSTRIAL FACILITIES IN İZMİR**" completed by **FARUK DİNÇER** under supervision of **PROF.DR.AYSEN MÜEZZİNOĞLU** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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ABSTRACT

The relationship between odor concentrations (olfactometry) and chemical concentrations (gas chromatography-mass spectrometry) is studied for the odorous air compositions of a landfill, a wastewater treatment plant (WWTP), a rendering plant, and Aliağa town which has large petroleum and petrochemical industries in Izmir. Samples taken from the university campus located in a non-industrial and non-urban area are also studied for comparison. Ambient air samples were taken into special bags for sampling of odors. In the laboratory odorous chemicals in the samples were transferred into adsorbent tubes and analyzed using a combination of thermal desorption and GC-MS.

Several volatile organic compounds (VOCs) are identified and quantified at these facilities in three sampling campaigns. The compounds measured in the odorous gas composition are the aldehydes, ketones, esters, halogenated compounds, volatile fatty acids, aromatic compounds, esters as well as reduced sulfur compounds.

Statistical evaluations showed that a relationship exist between odor and chemical group concentrations at the studied facilities except rendering plant. The relationships of odor concentrations with the different groups of chemicals revealed that the concentrations of aldehydes and monoaromatics are the best estimators in odor concentrations.

Based on the odor contribution ratios of the studied compounds the results of the study revealed that propanal, toluene, and hydrogen sulfide were dominating in the odor emissions of the studied industrial facilities.

Keywords: odor concentration, olfactometry, VOC, GC-MS, landfill, wastewater treatment plant, rendering plant, odor contribution ratio

İZMİR'DE SEÇİLEN ENDÜSTRİYEL FAAYİLETLERDEN KAYNAKLANAN KOKULARIN NİTELİĞİ VE KİMYASI

ÖZ

İzmir'de bulunan deponi alanından, atıksu arıtma tesisi ünitelerinden, bir et entegre tesisinden ve Aliağa ilçesindeki petrokimya ve rafineri tesisinden kaynaklanan kokunun seviyeleri olfaktometri (koku konsantrasyonu) ve kokulu gazın kompozisyonu da gaz kromatografisi-kütle spektrometrisi (GC-MS) yöntemiyle bu tez kapsamında incelenmiştir. Ayrıca bir endüstri bölgesi veya yerleşim alanına uzak olan kampus alanından karşılaştırma yapmak için örnekler alınmıştır. Kokulu hava örnekleri özel torbalar kullanılarak alınmıştır. Bu örnekler laboratuvarda adsorban tüpler üzerine konsantre edilmiş ve termal desorber ilaveli gaz kromatografisi-kütle spektrometrisi kullanılarak analizlenmiştir.

Yapılan örnek alma ve analizler sonucunda kokulu gazın kompozisyonunda çok sayıda kokulu bileşik tespit edilmiştir. Kokulu gazların kompozisyonunda belirlenen maddeler çeşitli aldehit, keton, halojenli bileşik, aromatik bileşik, uçucu yağ asitleri ve indirgenmiş kükürt bileşiklerini içermektedir.

Yapılan istatistik analizler sonucunda koku konsantrasyonları ile kimyasal madde gruplarının konsantrasyonları arasında et entegre tesisi dışındaki tüm kaynaklarda bir ilişkinin olduğu bulunmuştur. Aldehit ve monoaromatik bileşiklerin koku konsantrasyonu en iyi ifade eden gruplar olduğu tespit edilmiştir.

Kokuya katkı oranlarına bağlı olarak yapılan değerlendirmede propanal, toluen ve hidrojen sülfürün örnek alınan kentsel ve endüstriyel koku kaynaklarında koku konsantrasyonları içinde en önemli yeri tuttuğu belirlenmiştir.

Anahtar sözcükler : koku konsantrasyonu, olfaktometri, uçucu oraganik bileşik, GC-MS, deponi, atıksu arıtma tesisi, et entegre tesisi, koku katkı oranı

CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 Introduction

Odor is a human sensory experience and smelling an odor is a sensation resulting from the reception of a stimulus by the olfactory sensing system, which consist of two separate systems: the olfactory epithelium and the trigeminal nerve. The chemicals that stimulate the olfactory sense are called odorants. Odor perception can be described as the response to odor active volatiles that enter from the respiratory system through nostrils (van Ruth, 2001).

Odor pollution is of growing concern in industrial and agricultural areas (Defoer et al., 2002) and odor complaints are common in urban communities where residential neighborhoods are located near industrialized areas (Sarkar et al., 2003). Odorous emissions result from many municipal, industrial, and agricultural activities, e.g., composting plants, wastewater treatment, livestock farming, food processing, petroleum refining, paint finishing, and chemical production (Both, 2001). Most of the pollution problems in air are recognized as ‘‘odor’’ by the public (Miedema et al., 2000; Dincer et al., 2004). Recently, many countries have reported an increase in complaints due to odorous emissions. One reason for these odor-related problems is the expanding residential development near traditionally agricultural and industrial areas (Mahin, 2001). So researches based on the comprehension, characterization and abatement of odors has been very active in recent years (van Harreveld, 2004; Both, 2001).

The World Health Organization (WHO) says: “Health is a state of complete physical, mental and social well-being and not merely the absence of disease and infirmity”. Odor damages health because of irritation and the nuisance it causes. Odor nuisance, especially near to places where they are emitted to the atmosphere, have been implicated as a cause of decreased quality of life with probably additional negative consequences on human health and welfare (Rabaud et al., 2003). The health symptoms most frequently attributed to odors include eye, nose, and throat irritation, headache, nausea, diarrhea, hoarseness, sore throat, cough, chest tightness, nasal congestion, palpitations, shortness of breath, stress, drowsiness, and alterations in mood (Steinheider et al., 1998; Wing and Wolf, 2000; Schiffman et al., 2001). These symptoms begin upon exposure to the odor and are lost as the odor is removed.

Public complaints to odor depend on the concentration of the odorous gas, its perception threshold, presence of other odorous compounds and the hedonic tone of the odor. Co-presence of several odorous gases in mixture may create different perceptions in human subjects compared to the perception due to each one of the specific components in pure form at the same concentration. Thus, each source may have a different odor character and the air quality created by the odorous emission might be different from one source to another.

Most of the researches on odor have been on determination of odor of active volatile components (aroma) in food industry and for identification and quantification of odorants in drinking water, wastewater and other related odor sources such as compost plants, landfills, rendering plants, etc. Similarly odor assessment based on the dispersion of odors has been a popular method in odor research. Limited studies are found in literature to explain the relationship between odor and the chemical composition of the odorous gases. Studies based on the odor abatement technologies also exist in the literature.

Odor measuring techniques are based on either chemical analysis using a variety of instruments or sensory analysis using human nose as a detector. Our nose is a highly sensitive organ which provides a lot of information on the odor nuisance. Many of the chemical detectors are not as sensitive as the human nose for many odor active compounds (van Ruth, 2001). The olfactory organ or epithelium located in our nose is capable of detecting and discriminating between several thousands of different odors even at very low concentrations.

Olfactometry is the most common method for measuring odor concentrations. It is the measurement of odor by presenting a sample of odorous air to an independent panel. A range of dilutions using neutral air is prepared and responses from the panelists on whether they can detect the odor are recorded. The measurement is made by using an olfactometer and the units are defined according to CEN terminology (CEN, 2003). Olfactometry is an effect-related measuring method which has two objectives (VDI, 1986);

a) To determine the power of the human sense of smell, with known odorant concentrations serving as defined stimulus intensities and thus as scale increments
b) To determine unknown odorants concentrations with the help of the human sense of smell as the detector

Odor emissions causing nuisance are usually mixtures of numerous odorous compounds. In many cases, most of the odorants are present at very low concentrations. For a complex mixture of odorants the use of gas chromatography (GC) in connection with various detectors has been applied to identify the chemical composition of odorous samples (Smet, 1999). The development of analytical techniques such as solid phase microextraction (SPME)-GC/MS (Kleeberg et al., 2005, Davoli et al., 2003) and the use of well known techniques such as Thermal Desorption (TD)-GC/MS (Rabaud et al., 2002) for the chemical characterization of odorous mixtures are examples of efforts for identification of the different compounds responsible for the odor.

1.2 Aim of Study

The main objective of this study is to find out the odor levels and chemical characterization of odor related to selected industrial and urban facilities that create odor annoyance and nuisance.

The specific objectives of the study are as follows;

1. To measure the odor concentrations of industrial odor sources by olfactometry.
2. To characterize the odorous emissions of the odor sources by using analytical methods.
3. To evaluate the relationship between odor and chemical concentrations by using statistical methods.
4. To evaluate the obtained odor and chemical data based on odorous component contribution analyses[1].

First objective of the study is a part of an EU project named “Odorous Emissions and Immissions Management Policy in Turkey” that aimed to device a regulatory mechanism for odor control in Turkey (LIFE Project, Final Report, 2005).

1.3 Scope of Study

This study is carried out in the city of Izmir, Turkey which is a metropolitan city with major industrial, touristic and agricultural activities. The concentrations and composition of odors emitted from some specific sources in relation to the odor complaints by the public is investigated in the scope of this thesis.

The studied odor sources were: (1) landfill gases at the domestic and industrial sanitary landfill (Harmandalı–İzmir), (2) ambient air around the petroleum and petrochemical industries (Aliağa– İzmir), (3) odors that are emitted from wastewater treatment plant of Izmir (Çiğli-İzmir), (4) odorous stack gases and ambient air around a rendering plant (Buca–İzmir), and (5) university campus located in a non-industrial and non-urban area (Buca–İzmir). University campus was sampled at three different hours of one day.

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[1] These analyses were done by using a unitless number which is the ratio of the concentration of an odorous compound to its odor threshold concentration.

Odor concentrations were determined by olfactometric measurements and 72 organic gases in the odorous air composition were analyzed. The studied organic gases were found to belong to 7 different chemical groups: (1) aldehydes, (2) esters, (3) halogenated compounds, (4) ketones, (5) monoaromatics, (6) volatile fatty acids (VFAs), and (7) reduced sulfur compounds (RSCs). Names, odor characteristics and odor threshold concentrations of these 72 compounds are given in Appendix-A with respect to chemical classification above.

1.4 Thesis Outline

The thesis is organized in five chapters. Following an introduction in Chapter One, Chapter Two presents the information on the terms and definitions about odor, odor sources, olfactometric evaluations and the instrumental analysis of previous studies. Also in this chapter some regulatory information together with some information about odor abatement techniques are submitted. Chapter Three describes the materials and methods used for determination and characterization of odors. Methods for the data evaluation are also given in Chapter 3. Results of olfactometric and analytical measurements and evaluation of these results are given in Chapter Four. Chapter Five summarizes the key findings of the research, explains the relationship between olfactometric and analytical measurements with respect to studied facilities.

CHAPTER TWO
LITERATURE REVIEW

This chapter presents information on the basic concepts, terms and definitions about odor, odor sources, olfactometric evaluations of some of these sources and results of instrumental analyses according to previously made research. Regulatory work based on similar research and some odor control processes are also presented in this chapter.

2.1 Terms and Definitions

The terminology used in literature for odor has unique elements. For example in an odor complaint, odor annoyance and nuisance should be defined and considered together. Annoyance is the name of complex human reactions that occurs as a result of an immediate exposure to an ambient stressor (odor) that, once perceived, causes negative cognitive appraisal. Nuisance is the cumulative effect on man, caused by repeated events of annoyance over an extended period of time that leads to modified or altered behaviour (van Harraveld, 2001).

Several dimensions of human responses to odor sensation can be scientifically characterized; thresholds, intensity, character and hedonic tone (Cha, 1998).

Threshold refers to theoretical minimum concentration of odorant that is necessary for perception in specified percentage (usually 50%) of the population. Generally two types of threshold can be evaluated. These are detection and recognition thresholds. Detection threshold is the lowest concentration of an odorant that will elicit a sensory response in the olfactory receptors of 50 percent of population that are being tested. Recognition threshold is defined as the minimum concentration recognized as having a characteristic odor quality by a specified percentage population (50%). Recognition threshold differs from detection threshold as it is the point that a specific odor character description can be attributed to sensory response.

Over the years many terms have been used in the literature to express odor concentration. One of them is odor unit (OU). OU used to describe odor concentration of the odorous sample. Odor unit is that quantity (number of molecules) of odorants which just induces an odor sensation when dispersed in 1 m^3 of neutral air. Then odor concentration of an odorous sample is odor unit divided by volume unit (m^3), thus OU m^{-3}.

The odor concentration is defined as the dilution factor at which 50% of the panel could detect the odor. Only those panel members who passed screening tests with n-butanol (certified reference gas, CAS 72-36-3) and who adhered to the code of behavior were selected as panelists for olfactometry measurements (CEN, 2003). The odor concentration is calculated according to the response of the panel members and is displayed in OU m^{-3}, and refers to the physiological response from the panel equivalent to that elicited by 40 ppbv n-butanol evaporated in 1 m^3 of neutral gas as described in protocols of European standard EN 13725 (CEN, 2003).

The second dimension is **intensity** and refers to the perceived strengths of the odor sensation. Intensity increases as a function of concentration. The relationship between intensity and concentration may be described as a theoretically derived logarithmic function according to Fechner's Law (VDI, 1986; CEN, 2003):

$$S = k_w * \log (I / I_0) \tag{1}$$

where;

S: perceived intensity of sensation (theoretically determined)
I: physical intensity (odor concentration)
I_0: threshold concentration and
k_w: Weber-Fechner constant

Alternatively the relationship can be described as a power function according to Stevens (1961):

$$S = k\, I^n \tag{2}$$

where
S: perceived intensity of sensation (empirically determined)
I: physical intensity (odor concentration)
n: Stevens exponent
k: constant

Category scales were developed to measure odor intensity. One of the most widely used scales was developed for a 1930 study of odor used as gas alarms. The scale has six simple categories (Table 2.1).

Table 2.1 Odor Classification Scale

Category Scale	**Odor annoyance**
0 (No odor)	No detectable odors
1 (very faint)	An odor that would not be noticed by an average person ordinarily, but could be detected by an experienced inspector or a very sensitive individual
2 (faint)	An odor that is so weak that the average person might detect it if attention were called to it, but that could not otherwise attract her or his attention
3 (easily noticable)	An odor of moderate intensity that would be readily detected and might be regarded with disfavor (a possible nuisance in inhabited areas)
4 (strong)	An odor that would force itself upon the attention and one might make the air very unpleasant (a probable nuisance, if found in inhabited areas)
5 (very strong)	An odor of such intensity that the air would be absolutely unfit to breathe (term to be used only in extreme cases)

The other dimension of odor is its **character or quality**, or what the odor smells like. ASTM publication DS 61 (Dravnieks, 1985) presents character profiles for 160 chemicals and mixtures. This dimension is useful in air pollution control to describe the odor source and process because different odor characters are associated with various processes and industries. Table 2.2 shows a short list of industrial odor character descriptions.

Table 2.2 A Short List of Industrial Odor Descriptors

Odor Character Descriptor	Potential Sources
Nail polish	Painting, varnishing, coating
Fishy	Fish operation, rendering, tanning
Asphalt	Asphalt plant
Plastic	Plastic plant
Damp earth	Sewerage
Garbage	Landfill, resource recovery facility
Weed killer	Pesticide, chemical manufacturer
Gasoline, sulfur	Refinery
Airplane glue	Chemical manufacturer
Household gas	Gas leak
Rotten egg	Sewerage, refinery
Rotten cabbage	Pulp mill, sewerage sludge
Cat urine	Vegetation

The last dimension of odor is **hedonic tone.** This is a category judgment of the relative pleasantness or unpleasantness of the odor. The hedonic tone is influenced by both odor quality and intensity as well as the concentration. The perceived pleasantness or unpleasantness of odors have been shown to affect memory (Ehrlichman and Halpern, 1998), task performance (Baron, 1990), anxiety (Reed et al., 1994), mood and emotions (Marchand and Arsenault, 2002; Alaoui-Ismaili et al., 1997) in human beings.

2.2 Odor Sources

Odor problems exist in various types of industries. Odor emission sources can be characterized in quantity and in quality for example from the following sources: composting plants, municipal solid waste (MSW) landfills, rendering plants, chemical plants, refineries, food processing plants, slaughterhouses, wastewater treatment plants, livestock facilities, piggeries and poultries, dairies, pulp and paper industry, fish processing facilities, and etc..

On the other hand, the type of the odor source is important not only to get representative and reproducible results but also necessary to adapt the appropriate sampling technique. According to VDI 3790 (2000), the types of odor source can be divided into four categories as follows:

- point sources,
- line sources,
- area sources,
- mobile sources.

Examples for point sources are stacks or open gas collectors. Line sources are characterized through their elongated sizes, e.g., long cracks in the restoration layer of a landfill. Substances from area sources are emitted over relatively large areas. Examples of the area sources are open; single-level biofilters for cleaning exhaust gases or landfill sites. Mobile sources change their position, e.g., delivery vehicles.

Furthermore, the types of sources can be divided into active or passive. ‘‘Active’’ indicates that there is an outward airflow, for example, point sources like stacks are active sources. Another example of active sources is composting piles with forced aeration. Landfills are the examples of passive area sources.

2.3 Previous Studies

Most of the research on odor have been on determination of odor active volatile (aroma) components of food industry (i.e. dairy products) and for identification and quantification of odorants in drinking water, wastewater and other related odor sources such as compost plants, landfills, rendering plants, livestock facilities, etc. and odor assessment based on the dispersion of odors. Studies concerning odor control technologies are also presented in literature.

2.3.1 Studies on food production facilities

Odor perception is one of the foremost criteria used by the consumers to assess the quality of a food product. Odors enable the evaluation not only of acceptance but also of preference of food. Food odors are composed of a large number of volatile compounds and one of the most important purposes in food research is to identify the volatile compounds that are responsible for these odors (Hallier et al., 2004).

Volatile (aroma) components of various dairy products have received a great deal of attention (Cruoni & Bosset, 2002). Maarse & Visscher (1989) identified more than 600 volatile compounds in cheese. However, there is a general agreement that only a small fraction of these compounds are really responsible for cheese flavor. In many cases, the most abundant volatiles may have little, if any, odor significance in dairy products.

Rabaud et al. (2003) reported that industrial dairies emit a wide variety of volatile organic compounds at significant concentrations. Volatile organic compounds emitted from an industrial dairy were identified and quantified while simultaneously correlating them to odor. Sampling was performed using sorbent tubes that were then analyzed using thermal-desorption GC/MS with concurrent olfactometry. A total of 35 compounds were identified and quantified, and varied in concentration from 0.08 to 747.76 µg m^{-3}. In another study, Sunesson et al. (2001) identified 70 VOCs in eight dairy farms in northern Sweden where 2-butanone and ethyl acetate were found at the highest levels.

Compounds that are attributed to dairy farms included acids, esters, alcohols, aldehydes, ketones, halogenated, amines and hydrocarbons (Rabaud et al., 2003; Rabaud et al., 2002; Sunesson et al., 2001). Few compounds exhibited offensive odors, and those that did were present at low concentrations.

Gas chromatography–olfactometry (GC-O) has been widely used technique that enables identification of odor active compounds from complex mixtures of volatiles present in food product extracts (van Ruth & Connor, 2001). GC–O, proposed by Fuller et al. (1964) consists of sniffing the gas chromatographic effluent of an odor extract of food. In this method the GC effluent is sniffed and when an odor was perceived a description is given. Therefore, the division of identified volatile compounds into odor active and non-odor active volatile compounds is guaranteed by the use of the human nose as a detector (Arnaud et al., 2004).

2.3.2 Studies on water and wastewater

Wastewater has the potential for causing odor nuisance complaints in the surrounding community. These complaints may arise from the community because of gas leaks from the manholes of the sewer systems, emissions from wastewater treatment plant units and sludge area (WWTPs). In recent years public concern over odors originating from wastewater collection, transfer and treatment operations is increasing (Stuetz et al., 1999; Gostelow and Parsons, 2000). During the transfer of wastewater to treatment facilities significant amounts of malodorous gases may be emitted from manholes and terminals, especially if the wastewater develops anoxic conditions.

Odorous compounds that are released into the atmosphere from wastewater collection and treatment facilities include both inorganic and organic gases and vapors. Many of the odorous gases result from anaerobic decomposition of organic matter containing sulfur and nitrogen (ASCE, 1995). Sewer gases contain H_2S, NH_3, CO_2 and CH_4 mainly, and the first two are strongly malodorous. H_2S is the predominant odorant associated with wastewater Devai and DeLaune, 1999; Cheremisinoff, 1988; Hobson, 1997). Sewer gas includes other highly malodorous compounds such as mercaptans and other reduced organic sulfur compounds (Müezzinoğlu, 2003; Cheng et al, 2005) and amines such as indole and skatole (Harkness, 1980; Young, 1984) in lower concentrations. Organic acids, aldehydes and ketones might be present in the composition of sewer gas mostly due to the presence of industrial wastewater discharges (Bonnin et al., 1990; ASCE, 1995). Odors that cause nuisances in wastewater collection and treatment facilities have been described as “sulfury” or “like rotten eggs” (Devai and DeLaune, 1999) or in some cases “canned corn” (Cheng et al., 2005) depending on the type of malodorous sulfur compound present.

Koe (1985) correlated H_2S with overall odor concentration determined by olfactometry and found that a reasonable fit could be obtained using a modified Steven's law relationship as shown in the following:

$$C_{OU} = k \; . \; C^{n}_{H2S} \qquad (3)$$

where

C_{OU} is the odor concentration expressed as OU m^{-3} and C_{H2S} is the H_2S concentration (ppm). Gostelow and Parsons (2000) showed “k” to be between approximately 30,000 and 53,000 and values of “n” to be between 0.38 and 0.62.

Reported thresholds for H_2S range between approximately 0.0001 and 0.02 ppm (Bonnin et al., 1990), although a value of 0.0005 ppm is often used. This would suggest that the relationship between odor and H_2S concentration, where H_2S is the only odorant, is

$$Cou = 2000 \; . \; C_{H2S} \qquad (4)$$

Hydrogen sulfide and sulfur containing organic compounds levels were measured in the air at the deltas of the polluted creeks in the city of Izmir, Turkey and it was found that these malodorous compounds have high concentrations in the air samples. Within the scope of the study organic sulfur compounds such as methane thiol, ethane thiol, 2-propane thiol, 2-butane thiol, dimethylsulfide, dimethyldisulfide, thiophene, diphenylsulfide and hydrogen sulfide were studied in the air at selected urban sites where odor nuisance was recognized. Flux measurements from polluted surfaces were preferred rather than direct ambient air measurements. Organic sulfur emission fluxes from the creek surfaces were found above the values reported in the literature (Müezzinoğlu, 2003).

Odors in drinking water is a matter of concern for water suppliers, and a frequent source of complaint by consumers, who mostly associate the presence of unpleasant odors due to the possible health risks (Diaz et al., 2005). The European Council

Directive 98/83 (EEC) recommended that water intended for human consumption should include odor parameter and thus water suppliers have to carry out qualitative and/or quantitative determinations.

Earthy and musty odors are the descriptions of odors most frequently cited by consumers. The major causes of earthy-musty odors are associated with algae metabolites such as geosmin and 2-methyl-*iso*-borneol (MIB), with odor thresholds in water of the 1–10 µg m^{-3} (McGuire et al., 1981; Pirzabari et al., 1992). Recently, much interest is shown in chlorinated anisoles that can create a musty odor to water at low concentrations. Odor threshold values for 2,3,6-trichloroanisole has been reported in a wide range (0.0007 µg m^{-3} to 7 µg m^{-3} (Diaz et al., 2005) whereas for 2,4,6-trichloroanisole threshold values ranged from 0.03 µg m^{-3} (Diaz et al., 2005) to 4 µg m^{-3} (Benanou et al., 2004). These compounds are probably formed by biomethylation of halogenated phenols or formed in water treatment processes, during transport through the distribution system or by microorganisms living in low chlorine disinfection areas of the water distribution system (Benanou et al., 2004).

2.3.3 Studies on landfills and compost plants

Municipal solid waste (MSW) landfills are potential sources of offensive odors creating annoyance in urban areas (Sironi et al., 2005; Sarkar et al., 2003). Odor pollution has become a growing concern during the last decades for urban communities located near or downwind the MSW landfills. The annoying odors released to the atmosphere from landfills may cause decreased quality of life and possibly more negative consequences on human health and welfare (ATDSR, 2006).

The relationship between odor and chemical concentrations was investigated by Defoer et al. (2002) for vegetable, fruit and garden (VFG) composting plants and for the emissions of an animal rendering plant treated by bio-filtration. These studies compared the profiles of odor concentrations and chemical concentrations of compounds in different chemical classes. For the VFG composting plants, the study revealed a good linear relationship of the odor concentration with the total volatile organic compounds (VOC) concentration. Terpenes (65% of total VOC concentration), followed by ketones (8%), hydrocarbons (8%), alcohols (7%), esters (5%), aldehydes (3%) and sulfur compounds (3%) are the important groups for VFG composting emissions. And the odor concentrations of the biofilter effluent vary between 390 - 13050 OU m^{-3}. For biofilter emissions of the animal rendering plant, the total VOC concentration was a poor estimator for odor concentration. However, for this type of odor, concentrations of organic sulfur containing compounds correlated well with odor concentrations. The most important groups are the sulfur containing compounds (44% of total VOC concentrations), followed by hydrocarbons (28), and chlorinated compounds (15%), ketones (16%), aldehydes (7%) and alcohols (2%). And the odor concentrations vary between 1740 to 83540 OU m^{-3}. The results of the study also showed that the relationship between chemical and odor concentrations is specific for each type of odor.

Zou et al. (2003) conducted a study to characterize the ambient VOC levels in different seasons in a landfill in South China. Some of these compounds such as benzene, toluene and chlorinated species are toxic and hazardous to human health. Benzene and alkylbenzenes are the dominant species in the detectable compounds ranging from 4.3 to 1667 $\mu g\ m^{-3}$ in summer and 0.1 to 23 $\mu g\ m^{-3}$ in winter. They reported high levels of benzene, toluene and chlorinated VOCs. However, their study did not cover odor concentrations.

The chemical characterization of odorous samples taken from a sanitary landfill was studied (Dincer et al., 2006) in İzmir, Turkey. The relationship between odor and chemical concentrations was also investigated. The study compared the profiles of odor concentrations and chemical concentrations of compounds in different chemical classes.

Davoli et al. (2003) reported an analytical approach for characterization of odorous VOCs by solid phase microextraction (SPME) followed by GC-MS in landfills for a wide range of compounds (i.e., from highly polar volatile fatty acids to non-polar hydrocarbons).

Somewhat different from other studies, Sironi et al. (2005) conducted a study in order to calculate an odor emission factor at the landfills in Italy. In the study, the results of odor concentration measurements sampled from the principal odor sources of seven different and dimensionally representative Italian Municipal Solid Waste (MSW) landfills are presented. Experimental data are then used to estimate an Odor Emission Factor (OEF). The average OEF is calculated to be 5.5±3.4 OU_E $s^{-1}m^{-2}$. This value is consistent with the OEFs that can be calculated based on existing literature data, such as surface flux rates relevant to the Landfill Gas (LFG) emissions through the landfill surface. USEPA (1997) and VDI 3790 (2000) reported OEFs were 5.7 and 4.0 OU_E $s^{-1}m^{-2}$, respectively.

Noble et al. (2001) found a close correlation ($r^2=0.90$, $P<0.001$) between odor concentration and the combined H_2S and DMS concentration in mushroom [Agaricus bisporus (Lange) Imbach] compost production. Odorants that exceeded their published olfactory detection thresholds by the greatest order of magnitude, in decreasing order, were: H_2S, dimethyl sulfide (DMS), butanoic acid, methanethiol, and trimethylamine. Prediction of the odor concentrations will enable rapid and low-cost identification of odor sources on mushroom composting sites.

Van Durme et al. (1992) reported DMS, DMDS (dimethyl disulfide), limonene and α-pinene to be the main odorants that are present for wastewater sludge composting facility.

Biasioli et al (2005) studied the possibility of monitoring with proton transfer reaction-mass spectrometry (PTR-MS) odors emitted in various situations related to composting plants of municipal solid waste (MSW), i.e., waste storage, waste management, and biofilters. Comparison of PTR-MS volatile profiles of the gaseous mixtures entering and exiting a biofilter suggests the possibility of fast and reliable monitoring biofilter efficiency. The authors also investigated the relationships between the olfactometric assessment of odor concentration and PTR-MS spectral line intensity finding a positive correlation between the former and several masses and their overall intensity (r^2=0.80). The main objective of the study is to show that its rapid and sensitive response and the possibility of accurate calibration with olfactometry makes PTR-MS a powerful and innovative tool for monitoring composting plants and, in general, a useful reference for studies in odor control.

2.3.4 Studies on other odor related facilities

Livestock and poultry industries are becoming concerned about the odors that are generated from their operations (Schiffman et al., 2001). Public concerns regarding related air, water and soil pollution have increased with the growth of these industries.

Fakhoury et al. (2000) conducted several olfactometric and analytical measurements from the ventilated headspaces of 39 laboratory reactors containing swine manure. In the study, ammonia and hydrogen sulfide were monitored continuously. A sensory panel evaluated odor concentrations that were collected in Tedlar bags using dynamic olfactometry. Gas chromatography was used to analyze trace gases collected on adsorption tubes. Results showed that odor concentrations ranged from 71 to 1426 OU m^{-3} (average 313 OU m^{-3}). Mean hydrogen sulfide and ammonia concentrations were found 475 ppb and 93 ppm, respectively. Hydrogen sulfide, p-cresol and butyric acid had the highest correlation with odor concentration.

Heber et al. (2000) measured odor and gas emissions from commercial swine lagoons by using a buoyant convective flux chamber (BCFC) with a surface air speed of 1 m s^{-1}. Odor concentration, intensity and hedonic tone were evaluated by panelists. Ammonia (NH_3), hydrogen sulfide (H_2S), carbon dioxide (CO_2), and sulfur dioxide (SO_2) concentrations were measured from the odor samples collected in 50-L Tedlar® bags. The geometric mean odor concentrations of the BCFC inlet and outlet and of samples taken at the downwind berm of the lagoons were 99, 155 and 67 OU m^{-3}, respectively. The overall arithmetic mean odor emission flux was found 4.6 OU s^{-1} m^{-2}. Overall mean gas emission fluxes were 101 µg s^{-1} m^{-2}, 5.7 µg s^{-1} m^{-2}, 852 µg s^{-1} m^{-2} and 0.5 µg s^{-1} m^{-2} for NH_3, H_2S, CO_2 and SO_2, respectively.

Schiffman et al. (2001) conducted a study for identification and quantification of odorous compounds from swine facilities in North Carolina. A total of 331 compound were identified and identified compounds were diverse, and included many acids, alcohols, aldehydes, amides, amines, aromatics, esters, ethers, halogenated hydrocarbons, hydrocarbons, ketones, nitrogen-containing compounds, phenols, sulfur-containing compounds and steroids.

A study was undertaken to identify the odor causing VOCs in packaging materials by using GC-MS. Results showed that twenty-five compounds were identified including carbonyl compounds (such as 3-methyl-butanal, 3-heptanone or octanal), carboxylic acids (such as pentanoic acid or hexanoic acid) known as odor causing compounds and hydrocarbons (such as decane, undecane or dodecane) (Ezquerro et al., 2002).

Bordado and Gomes (2003) reported that, hydrogen sulfide, methyl mercaptan, dimethyl mercaptan and dimethyl-disulfide are the malodorous gases that are responsible for Kraft pulp mills characteristic odor.

Another study was done to investigate geosmin and 2-methylisoborneol (MIB) levels from pulp mill effluent of treatment ponds. Odor threshold concentrations (OTCs) for geosmin and MIB have been reported to range from 4 to 10 and 9 to 42 $\mu g\ m^{-3}$, respectively (Krasner et al., 1983; Young et al., 1996). Samples taken from the bioreactor it was found that the geosmin levels were very high (1600 to 128000 $\mu g\ m^{-3}$) more then the OTC. For 2-methylisoborneol (MIB), concentrations were lower but they were still much higher then OTC. The study showed that geosmin and 2-methylisoborneol (MIB) contribute significantly to airborne odors (Watson et al., 2003).

In fat and oil processing, a number of procedures which may lead to exhaust gas pollution are used, including water-degumming, acid refining, bleaching, and deodorization. During the deodorization process, numerous odorous substances (e.g.,aldehydes, ketones, alcohols, hydrocarbons, furans, terpenes, and esters) are generated. A solid-phase micro-extraction (SPME) method has been developed for the extraction of odorous compounds from waste gas of a fat refinery. The odorous compounds were characterized by gas chromatography–mass spectrometry (GC–MS) and gas chromatography followed by simultaneous flame ionization detection and olfactometry (GC–FID/O). The method was successfully used to characterize an odorous waste gas from the refinery prior to and after waste gas treatment in order to describe the treatment efficiency of the used laboratory scale plant which consisted of a bioscrubber/biofilter combination and an activated carbon adsorber. The developed method is a valuable approach to provide detailed information of waste gas composition and complements existing methods for the determination of odors (Kleeberg et al., 2005).

Kim et al. (2006) found the odor intensities of reduced sulfur compounds (RSCs) in a large industrial complex. H_2S was found the highest RSC (average concentration 450 $\mu g\ m^{-3}$) in this study followed by CS_2. Also significant concentrations of DMS, and DMDS were found in the study.

Dincer and Muezzinoğlu (2006) conducted several olfactometric and analytical measurements from the ambient air around a refinery and a petrochemical complex. Odor concentrations were determined that were collected in Nalophan$^{®}$ bags using dynamic olfactometry. Gas chromatography was used to analyze the composition of odorous gas samples.

2.3.5 Studies based on the odor dispersion modeling

Direct relationship between odor-causing substance(s) and odor complaints are not easy to find. This is due to the fact that odor complaints from the public are associated with odor concentrations and psychophysical laws (Sarkar and Hobbs, 2002). Odor dispersion model is a tool that makes the numerical connection between odor emitting sources and their downwind receptors. Given necessary parameters for odor (source emission rates, stack height, exit temperature, exit velocity, etc.) and meteorological conditions (i.e. ambient temperature, wind speed and direction, etc.) odor concentrations at downwind locations can be predicted.

Like in other air pollution work, the relationship between the source odors and ambient levels can be established by using suitable atmospheric dispersion models. Then, by assuming that the quantity of odorous components in the flue gas is dispersing in the same manner as the perceived odors, the measured source odor concentration in OU m^{-3} units and the volumetric flow rate of the emitted gases were multiplied in order to find the emission strength.

This method of finding the odor emission strength is based on the information that odors or odorous compounds behave similar to other pollutants during dispersion, i.e. they are distributed according to Gaussian plume dispersion models at crosswind dimensions (Smith, 1995). Some of these models relate odor complaints by ambient odor levels originating from the odorous emissions according to the source characteristics and prevailing atmospheric conditions. In some cases dispersion models were used to estimate the emission flux rates from the measured ambient levels of odorants (Smith, 1995; Sarkar et al., 2003; Sarkar and Hobbs, 2003). And in some others odor emissions from industrial sources were dispersed in order to find allowable separation distances to the residential areas (Schauberger et al., 2001; Piringer and Schauberger, 1999; Schauberger et al., 2000).

The most widely used dispersion model for odor is the US EPA regulatory Industrial Source Complex Short-Term Model (ISCST3). Other dispersion models that are utilized in odor dispersion include the fluctuating plume model, PUFF model (i.e. CALPUFF) and etc.

Examples of odor dispersion modeling work based on the ISCST model are numerous. Nicell (1995) utilized ISCST model in order to predict odor impacts and potential odor complaints on the surrounding community from an industrial facility in Ontario, Canada. Ausplume model which is a Gaussian model based on ISCST has been applied to determine acceptable odor levels, in the community of a WWTP, for planning purpose (MacKenzie, 1995). McFarland (1995) utilized this model to predict odor concentrations from a livestock facility. Hess and Thota (1995) identified and ranked odor sources at WWTPs. Engel et al. (1997) modeled odor impacts from a composting facility utilizing ISCST model.

Elbir et al. (2007) utilized CALPUFF dispersion model for predicting the ambient odor concentrations around a meat packaging and rendering plant. Predicted odor concentrations were compared with the odor measurements carried out on the samples. The measured and predicted results correlated well, with a good agreement between the two series.

The emission fluxes from segments of the polluted stream surfaces in the city of Izmir were investigated during the summer of 2001 (Müezzinoğlu, 2003). These streams were acting like open sewers collecting industrial and domestic wastewaters until the problem was overcome in August 2001. Following these determinations, levels of H_2S in the city were mapped using the predictions made by the CALPUFF dispersion model with input data from the national meteorological station with hourly resolution (Müezzinoğlu and Elbir, 2003). Measured emission fluxes of H_2S from the surfaces of the odorous segments of the creeks were used as emission strength in the model.

Mussio et al. (2001) developed a fluctuating plume dispersion model to facilitate the prediction of odor-impact frequencies in the communities that are surrounded by elevated point sources. This model was used to predict not only the frequencies of occurrence of odors of various magnitudes for 1 h periods but also the maximum odor level. The model was tested with the data collected in the residential areas surrounding the paint shop of an automotive assembly plant. Most of the perceived odors in the vicinity of the 64, 46m high stacks ranged between 2 and 7 odor units and generally persisted for less than 30 s. Ninety-eight different field determinations of odor impact frequencies within 1 km of the plant were conducted during this study.

2.3.6 Odor control technologies

This section provides the descriptions and principles of some odor control processes.

As odor problems are very complex and finding the appropriate odor control technique is complicated, a general odor management approach must be available. This approach should include complete odor management including all emission sources with records, characterizations, and evaluations (Schlegelmilch et al., 2005a).

Odor concentration, and the odor load derived from this parameter by multiplying it with the volumetric flow rate, is the main criterion for the evaluation of an emission source for solution of the odor problem. The higher the odor load, the higher its impact on the environment. The organic carbon content of the waste gas is another important parameter, and is a criterion for testing the suitability of several waste gas treatment methods. By analyzing the chemical composition of the waste gas, the most relevant odorous substances can be identified and based on this knowledge, together with results from some pre-tests, a suitable treatment method can be chosen.

Table 2.3 gives information about some of the more commonly used odor treatment processes. Thermal treatment systems might be suggested for non-biodegradable compounds, biological systems may be the methods of choice for biodegradable substances.

Once all odorous emissions are detected and characterized, they need to be captured before an adequate treatment method can be applied to the waste gas. Collected waste gases should be treated according to their chemical composition, their physical condition, organic load, and volumetric flow rate. Very high efficiencies are required for the treatment of odorous emissions as humans are sensitive to very low concentrations of odorous substances. The applicability of the different treatment processes mainly depends on the composition and amount of the waste gas. Additionally, temperature, moisture, and particulate content have to be considered.

Table 2.3 Overview on odor treatment processes

Process	**Options**
Adsorption	Different adsorbents (activated carbon, activated alumina, silica gels, zeolites, etc.)
Absorption	Physical absorption, chemical absorption
Biological waste gas treatment	Bioscrubbers, biotrickling filters, biofilters
Waste gas incineration	Thermal afterburners, catalytic incinerators, regenerative thermal oxidation (RTO)
Non-thermal oxidation processes	Ozone, UV, non-thermal plasma

Temperature is the main limiting factor for biological systems. Normally, the temperature should not exceed 40°C. However, there are biological systems that may deal with higher temperatures, like thermophilic bio-scrubbers. High gas temperatures may also reduce the efficiencies of adsorption and absorption and also increase volatility of the odorous substances. Moisture content of the gase influences the selection of an odor treatment system. Although biofilters need air input saturated with water vapor for a successful operation, very moist gas streams may have a negative effects on selected adsorption systems.

Adsorption

The attachment of the molecules of the odorous compounds to solid surfaces is an adsorption mechanism. Four adsorbents including activated carbon, activated alumina, silica gels and zeolites are commonly used. The first three of these are amorphous adsorbents with a non-uniform internal structure. However, zeolites are crystalline and have an internal structure of regularly spaced cavities with interconnecting pores of definite size (Buonicore, 1992a). Recently, research has focused on the design of engineered, specific adsorbents (Cartellieri et al., 2005).

Adsorbers are mostly designed as fixed bed reactors, with the gas passing through a stationary bed in industrial applications. Simultaneous adsorption and desorption is required for continuous operation of adsorbers. This can be achieved by parallel operation of several adsorbers or by using an adsorber wheel (Fischer, 2001). Regeneration of the adsorbent is usually conducted by means of hot gas or steam.

Adsorption may also be an enrichment step before thermal gas treatment (Anguil, 1998). It can also be combined with other technologies, like biofiltration. This combination may be especially suitable for companies with varying exhaust air concentrations, e.g., due to discontinuous production, because biofilters tend to be less effective under transient conditions. In these cases, the adsorbent can be loaded in times of high raw gas concentrations and desorbed when the inlet concentrations are low, e.g., at night. That way, the biofilter can be loaded with a relatively constant concentration (Paul et al., 2001).

In the process design of the fixed-bed adsorber, the diameter of the adsorber and the adsorbent bed depth are the two critical dimensions, as they influence the superficial velocity and the pressure drop of the adsorber. To avoid fluidized bed conditions due to high air velocities and uneconomical pressure losses, for continuous operation a superficial velocity between 0.1 and 0.5 m s^{-1} has been proven to be practicable (VDI 3674, 1998).

Absorption

During the absorption process, waste gas compounds are dissolved in a scrubbing liquid. Mass transfer is mainly controlled by the solubility of the substances and the gas–liquid interfacial surface (Buonicore, 1992). The solubility is affected by selection of a suitable solvent, as discussed by Freudenthal et al. (2005). Packed columns are used commonly to provide a large interfacial surface. Other devices which are used include jet and venturi scrubbers, plate columns and spray scrubbers (Fischer, 2001; Buonicore, 1992). Accumulation of the waste gas components in the scrubbing liquid would result in ending the mass transfer after establishment of equilibrium according to Henry’s law. Thus, the scrubbing liquid must either be exchanged or regenerated (Fischer, 2004). Regeneration of the scrubbing liquid can be conducted by means of stripping with air or steam.

Chemicals are added into the scrubbing liquid that will react with the dissolved waste gas compounds in many applications. The use of oxidants is the most common application in chemical scrubbing. Besides ozone (O_3) and hydrogen peroxide (H_2O_2), mainly sodium hypochlorite (NaOCl) is used because it is both relatively inexpensive and easy to handle. For the removal of ammonia, particularly from piggeries, sulfuric acid scrubbers have been successfully applied. This process is often is combined with a subsequent biofilter to remove remaining odors (Hahne and Vorlop, 2001). Acidic substances, like hydrogen sulfide (H_2S) can be treated with caustic scrubbers using diluted sodium or potassium hydroxide. This way, organic sulfur compounds can also be removed (Dammann et al., 2001).

Biological treatment systems

Biological waste gas treatment systems rely on the activity of microorganisms, which are able to degrade organic contaminants from the air stream. The microorganisms feed on odorous substances and oxidize them to CO_2 and H_2O or other odorless products.

There are two biological systems commonly used for the treatment of odorous emissions; (1) Biofilters, (2) Bioscrubbers/biotrickling filters.

Biofilters can be described as biochemical fixed bed reactors where the waste gas is treated while passing a biofilter bed. Microorganisms settle on its surface and form a biofilm in which the airborne substances are absorbed. An important criterion for bio-filter media is to provide optimum environments for the microorganisms, thus an essential property is the ability to store water. Additional criteria are a low pressure drop to assure an even air distribution and a large specific surface for the mass transfer and the microorganisms to settle on. Frequently used biofilter media are compost, peat, root wood, bark, wood chips (normally used as bulking agent) and different kinds of combinations (VDI 3477, 2002).

One of the key parameters of biofiltration is the moisture content of the biofilter material. The optimal range for biologically active organic media is between 40% and 60% (VDI 3477, 2002; Kennes and Thalasso, 1998). To avoid drying of the filter media, the waste gas should be saturated with water vapor. Anyway, adding too much water should be avoided as it results in clogging and consequently in an increasing pressure drop, a limitation of the mass transfer, and possibly in anaerobic zones (Kennes and Thalasso, 1998). Biofilters may be designed as open to the atmosphere or enclosed (VDI 3477, 2002).

Biofilter beds are up to 2 m deep. In open biofilters the air passes through the bed in an up-flow direction. Enclosed biofilters are less affected by weather conditions than open filters, and also offer a better moisture distribution, as they can be operated under down-flow conditions.

Traditionally, biofilters were used to treat waste gases from sewage treatment plants, composting facilities and rendering plants, which mainly contain biological intermediate degradation products (Schlegelmilch et al., 2005b). In recent years, further applications have been opened to this technology including in food and tobacco producing and processing industries (Eitner, 1992; Kersting, 1992), as well as the treatment of waste gases containing industrial solvents and other volatile organic compounds (Fell, 2002; Herzog and Thißen, 1997).

In bioscrubbers and biotrickling filters, the microorganisms generally are suspended in a scrubbing liquid but may additionally be immobilized on packing material. The most important component of these devices is the absorption column where the mass transfer between gaseous and aqueous phase takes place, and thus the airborne substances are made available to the microorganisms. Usually packing materials are installed to enhance the contact surface of both phases. In most applications the gaseous and the aqueous phases are distributed in counter flow to each other. However, if no packing materials are installed; cross-flow systems often are used. Once the odorous substances are dissolved in the scrubbing liquid, if degradable they are removed by the microorganisms. The degradation process may take place in the liquid, usually water, or in the biofilm that grows on the packing materials. These internals not only enhance the surface for the mass transfer but also provide an additional surface for the microorganisms to settle.

During the adaptation phase the microorganisms start to grow and form a biofilm which has a large effect on the degradation efficiency of the scrubber. Attention has to be paid to the fact that clogging of the scrubber might be a problem. To avoid clogging, the packed bed should have large pores and should be cleaned frequently.

The Bioscrubber/biofilter combination system combines the advantages of both technologies. The bioscrubber acts as a humidifier and degrades a high portion of the odor load. It also shows a buffering effect (Schlegelmilch et al., 2005b), which prevents high concentrations of odorous substances from entering the biofilter, which otherwise might lead to a rise in temperature in the biofilter material due to increasing degradation processes.

Thermal waste gas treatment

Thermal treatment can be basically applied to any exhaust air. However, since the concentration of VOCs is often low, the addition of natural gas or a pre-concentration, e.g., by adsorption, is usually required.

For thermal treatment, catalytic and non-catalytic techniques are applied. Catalytic processes can be operated at lower temperatures, resulting in considerably lower energy demand. On the other hand, the costs for the catalyst itself have to be taken into account. In addition, for non-catalytic processes, energy costs can be significantly reduced by using advanced systems with heat recovery.

Non-thermal oxidation technologies

Besides thermal oxidation, several ‘‘cold’’ oxidation techniques for the treatment of odorous exhaust air, like UV treatment or non-thermal plasma, have been investigated in the last few years.

UV treatment is successfully used for sterilization of drinking water or treatment of persistent wastewater components. The technology is based on the UV induced formation of highly reactive radicals and ions which can oxidize organic molecules. Repeated efforts were conducted to apply the positive experience from water and wastewater treatment to waste gas treatment. However, significant efficiencies were only measured when high performance UV radiators were used, resulting in a very high energy demand not considered suitable for treatment of odorous waste gas (Fischer, 2001, 2004).

The non-thermal plasma technology uses strong alternating electrical currents or microwave radiation to induce highly activated molecules. Like with UV radiation, reactive radicals and ions are subsequently formed and react with odorous compounds. The ‘‘ionised air’’ can be generated in an additional air flow that is merged with the main waste gas flow, or directly in the main flow. Both non-thermal plasma and UV radiation result in the formation of excess ozone, which has to be removed by a subsequent catalyst (Fischer, 2001).

Studies on odor control technologies

Ranau et al. (2005) conducted a study to determine the efficiency of different treatment systems for the reduction of odorous emissions, a gas chromatographic method followed by simultaneous mass spectrometry and olfactometry (GC–MS/O) was developed. The collected samples from a coffee bean roasting and a fat and oil processing plant were analyzed. At the coffee bean roasting plant, cooling gases were analyzed prior to and after treatment in a full scale bioscrubber. The GC–MS/O analysis showed that the amounts of aldehydes and ketones decreased after treatment of cooling gases of coffee bean roasting in the bioscrubber, whereas the contents of the heterocyclic compounds, like pyridine and the pyrazines, and acetophenone and guaiacol remained almost unchanged. The amounts of dimethyl disulfide, 3-hydroxy-2-butanone, and the carboxylic acids increased after bioscrubber treatment.

Furthermore, the performance of each stage of a combined experimental plant for the treatment of exhaust air of the fat and oil processing was investigated. This treatment plant consisted of a bioscrubber, a biofilter, and an activated carbon adsorber. The important odor-active compounds of the exhaust air of fat and oil processing were the typical fat oxidation products (aldehydes, ketones) and with lower importance 2-pentylfuran, a few terpenes and aromates. Again, the key odor-active compounds, aldehydes and ketones, were degraded in the bioscrubber. Further degradation of aliphatic, unsaturated, methylated, and cyclic alkanes, as well as aromates, terpenes, and furans by the biofilter was observed. After the last treatment stage, the activated carbon filter, only small amounts of aliphatic, unsaturated, methylated, and cyclic alkanes and aromates remained in the waste gas (Ranau et al., 2005).

A study was carried out in order to present odor removal efficiencies of biological waste gas treatment systems. In the study, biofilter/bioscrubber combinations were used and different biofilter materials were tested. Odorous substances in the waste gas were identified, and their reduction in the different systems was measured. The biofilter proved to be mainly responsible for efficient odor degradation. The filter media of screened compost was very effective, and proved to be a low cost biofilter material for odor degradation purposes. Screened compost showed higher degradation rates than a coke–compost mixture. The results of this study are also presented that enclosed systems have advantages when compared to conventional open single bed biofilters (Schlegelmilch et al., 2005b).

Most odorants found in waste gas of solid waste and wastewater treatment facilities are biodegradable, and biological treatment techniques, such as biofiltration, are considered to be effective in controlling these odors (Frechen, 1993). A study was conducted to evaluate the removal efficiencies of butyric acid, which was selected to represent volatile fatty acids found in compost waste gas. The experiments were based on a laboratory-scale biofilter using contaminated airstreams with concentration of 25 and 50 ppm and different packing materials. Results indicate that butyric acid can be effectively removed at efficiencies nearing 100% by both compost and compost-perlite filled biofilters at all times during a run period extending 2000 h (Otten et al., 2004).

In investigations at several plants using non-thermal plasma technology, Fischer (2004) measured efficiencies between 0% and nearly 100%. The results were strongly depending on the composition of the waste gas and process technology. The results of applying a non-thermal ionisation system show that a removal of the identified main odour causers (limonene, a-pinene and dimethyl disulfide) in the waste gas of the biological waste treatment is possible under optimal process configurations (Steinberg et al., 2004).

2.4. Odor regulations

United States: In the United States, odors are regulated by states and by local governments. There are no federal regulation for odors. For example, in Massachusetts, there is a draft odor policy for composting facilities, which requires that new or expanding facilities should not exceed 5 dilutions/threshold (D/T) at the property line. Some states have hydrogen sulfide standards and other states have D/T limits. Many states have general rules that stipulates that odors do not create a nuisance. Nuisance is usually defined as interfering unreasonably with the comfortable enjoyment of life and property or the conduct of business.

Germany: The Directive on Odor in Ambient Air sets an impact odor concentration of 1 OU m^{-3}, which is the limit impact concentration, and then limits the percentage of time during which a higher impact concentration may be tolerable, which is insubstantial annoyance. The time percentages are 15%, and 10% for industrial area and residential areas, respectively.

The Netherlands: The odor regulations in the Netherlands have the objective to keep the population free from annoyance. The aim in 2000 was that not more than 12% of the population would be annoyed by industrial odors. The percentage of people strongly annoyed by industrial odors should drop below 3% in the future. The percentage results are renewed every year.

Japan: National laws regarding odor prevention in Japan were first established in 1972 and have been modified several times up to the present. There are some emission standards concerning both odor concentration and odor-causing substances. As main cause substances of odor pollution, 22 substances are the targets for regulation at the present. The head of a local self-governing body or a prefecture has the authority of issuing improvement advices or commands for correcting the environment around factories and offices that have discharged odor substances.

Turkey: Although, there is no current regulation in effect for odor measurements in Turkey, a draft regulation was prepared within the scope of a LIFE project "Odorous Emissions and Immissions Management Policy in Turkey" conducted between years 2002-2005 (LIFE Project, Final Report, 2005). The draft regulation sets not only emission limits but also limits the odor percentage time similar to German regulation. The time percentages are 20%, and 15% for industrial area and residential areas, respectively. Three sets of emission limits are defined in the regulation. Odor emissions with a concentration below 1000 OU m^{-3} are allowed, odor concentrations between 1000-10000 OU m^{-3} are allowed if there is no immision problem (exceedence of odorous hour limit) in the neighborhood. If complaints exist, the immissions are measured and if the odor level is above the limits mentioned above the facility will be forced to reduce its odor emission. Odor emissions with a concentration above 10000 OU m^{-3} will be forbidden and the facility has to minimize its odor emission via constructing an odor control system (Atimtay et al., 2004).

CHAPTER THREE
MATERIALS AND METHODS

This chapter describes the materials and methods used for determination and characterization of odors. Sampling sites, sampling techniques and instruments (olfactometer, GC-MS) that were used in the thesis are discussed.

3.1 General overview

Three succesful sampling and measurement periods were accomplished during the thesis. Sampling and analysis were conducted on different days of May 2005, September 2005 and June 2006. The time schedule of these periods were presented in Table 3.1. These sampling sites were as follows: (1) Harmandalı landfill, (2) Aliağa town (3) wastewater treatment plant of Izmir city (Çiğli-Izmir), (4) a rendering plant (Buca–İzmir), and (5) university campus located in non-industrial and non-urban area (Buca–İzmir). The sampling sites are presented in Fig. 3.1. Sampling and analyses were accomplished in Landfill and Aliağa at all sampling periods. Izmir WWTP was added to the study schedule later, in June 2006 period. Rendering plant measurements were done only at May 2005 period. For other sampling periods, sampling was not allowed from the facility due to privatization. Dokuz Eylül University Tınaztepe campus was selected as a non-urban and non-industrial area and measurements were done only for comparison. So in September 2005 and June 2006 periods measurements were not conducted.

Odor concentrations were concentrations were determined by olfactometric measurements and 72 organic gases in the odorous air around them were analyzed.

The characteristics of the study sites, their locations and the points from which samples were taken are described below.

Table 3.1 Time schedule of the sampling periods with respect to the urban and industrial facilities during the thesis

Sampling site	**May 2005**	**September 2005**	**June 2006**
Landfill	+	+	+
Aliağa	+	+	+
Izmir WWTP	-	-	+
Rendering plant	+	-	-
Campus site	+	-	-

\+ sampling was accomplished

\- sampling was not accomplished

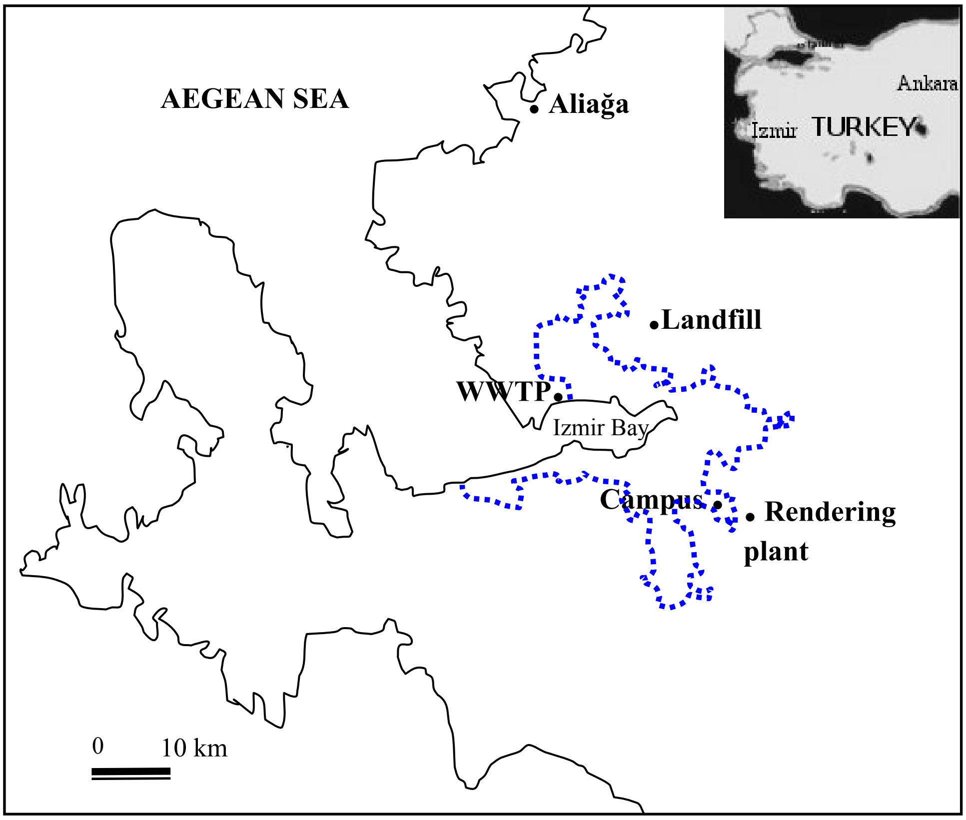

Figure 3.1 Locations of the sampling sites in the thesis (blue dots shows the borders of Izmir Greater Municipality)

3.2 Site descriptions

3.2.1 Landfill.

Harmandalı MSW site is the main landfill in Izmir. It has been in operation since 1990 and receives commercial, industrial and municipal wastes. The capacity of the landfill is 3000 ton day^{-1} of domestic, medical and industrial wastes and wastewater treatment sludge. The site does not accept hazardous wastes.

The field sampling was conducted on May 6 2005, September 1, 2005 and May 29, 2006 to represent the beginning of the hot and dry summer season in the area that has a typical Mediterranean climate. The average temperatures were 19ºC in May 2005, 25ºC in September 2005 and 36ºC in May 2006 and the relative humidity was 55% in both May 2005 and September 2005 sampling days.

Sampling was accomplished at six sampling points in the landfill during this study (Figure 3.2). Five sampling points were visited in the sampling protocol. First four of them were the same sampling sites. Fifth sampling site were visited in May 2005 and September 2005 while the sixth one was visited only in May 2006. This was also presented in Table 3.2.

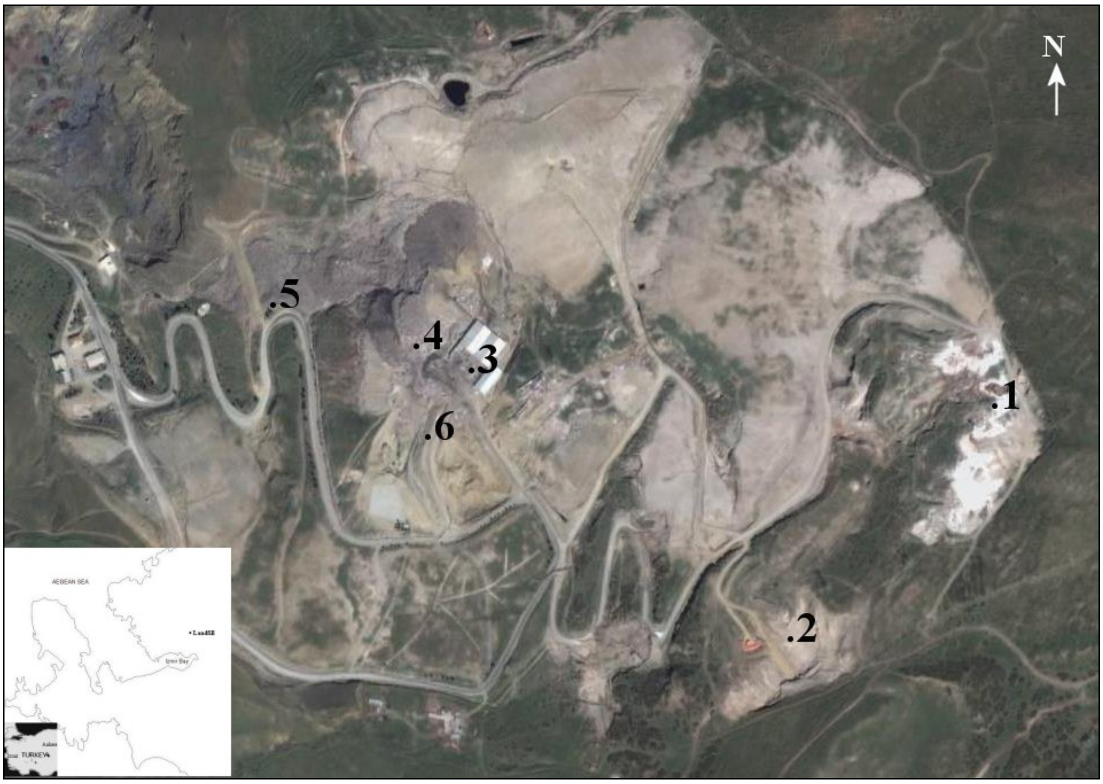

Figure 3.2 Sampling points in the landfill

Table 3.2 Time schedule of the sampling periods at the landfill

Sampling point	May 2005	September 2005	May 2006
1	+	+	+
2	+	+	+
3	+	+	+
4	+	+	+
5	+	+	-
6	-	-	+

+ sampling was accomplished
- sampling was not accomplished

Sites 1 and 2 were selected to represent the areas where thickened sludge from the Izmir municipal wastewater treatment plant and industrial solid wastes and the medical wastes were disposed, respectively. The third, fourth and fifth points were at the domestic solid waste disposal area. Site 3 was the raw waste collection area of the municipal wastes and all the machinery and truck operations were continuing during sampling days. Site 4 was a domestic site where solid wastes were dumped just before the sampling day and were still open at the top. Site 5 was the point that solid wastes were disposed earlier. These three of the municipal waste burial areas were selected to represent different stages and ages of solid waste management. The sixth sampling point was the headspace of the leachate.

3.2.2 Aliağa town

Aliağa town is located 45 km north of Izmir and have electric arc steel furnaces and rolling mills, a large petroleum refinery, a petrochemical complex and numerous industrial facilities such as liquified petroleum gas storage tanks and filling units and ship dismantling facilities. Sampling was conducted at especially close points to refinery and petrochemical industry (Figure 3.3)

Petroleum refineries and petrochemical plants are generally large industrial installations and their operation is associated with the emission of various organic compounds into the atmosphere, mainly originating from the production processes, the storage tanks and the waste areas (Kalabokas et al., 2001). In petrochemical industries, most of the organic compounds are derived from petroleum fractions, and actually from only a few basic hydrocarbons such as methane, ethane, propane, benzene, toluene, and xylene predominate in the air (Crosby, 1998). Petroleum refining is the physical, thermal and chemical separation of crude oil into its major distillation fractions. The primary products of the industry fall into three major categories (EPA, 1995): fuels (i.e. motor gasoline, diesel and distillate fuel oil, liquefied petroleum gas); finished non-fuel products (i.e. solvents, lubricating oils); and chemical industry feedstocks (i.e. naphtha, propane, butane, benzene, toluene and xylene).

First and second sampling periods were carried out on May 12 and September 6 2005, respectively. The refinery has a large capacity of nearly 10,000 tons crude per year and next to it a petrochemical complex consisting of 17 different chemical plants, with numerous liquified petroleum gas storage tanks and filling units in between. Both the refinery and petrochemical plants have many flares and a high number of smokestacks.

In May 2005, three points have been chosen for sampling the odors and the chemical gases. The first point was the entrance of the refinery that was near to the liquified gas filling stations. Second one was at the border of the refinery and petrochemical plant. Third one was at a point just downwind of the flares at the border of the refinery which was chosen as the most odorous point during the field work. In September 2005, sampling was conducted at eight points. First three were the same as in May. Other five points were as follows; (4) Horozgediği village at the south of Aliağa, (5) main entrance of petrochemical complex, (6) ship dismantling area, (7) ENKA sports center, 8) north of Aliağa and the industries (Aliağa quarantine).

Third sampling period was carried out on June 6, 2006 and sampling was conducted at six sampling points. Four sampling points [sampling points (1), (2), (3), (5)] were the same as in September 2005 period. The fifth sampling point (9) was the tank area of the refinery where products were stored. The sixth sampling point (10) was at the center of Aliağa town which represents an urban sampling point.

Four sampling points [sampling points (4), (7), (8), (10)] were chosen as residental sampling points where industrial facilities did not exist. These points also represented the neighboring locations of the refinery and petrochemical complex so that the impacts of these industries could be identified.

Table 3.3 Sampling point definitions and time schedule of the sampling periods in Aliağa with respect to sampling points

Sampling point	Sampling point	2005 May	September 2005	June 2006
1	Refinery main gate	+	+	+
2	Refinery-petrochemical complex border	+	+	+
3	Clauss plant area	+	+	+
4	Horozgediği	-	+	-
5	Petrochemical complex main gate	-	+	+
6	Ship dismantling area	-	+	-
7	ENKA sports center	-	+	-
8	Aliağa quarantine	-	+	-
9	Tank field	-	-	+
10	Urban-Aliağa	-	-	+

+ sampling was accomplished
- sampling was not accomplished

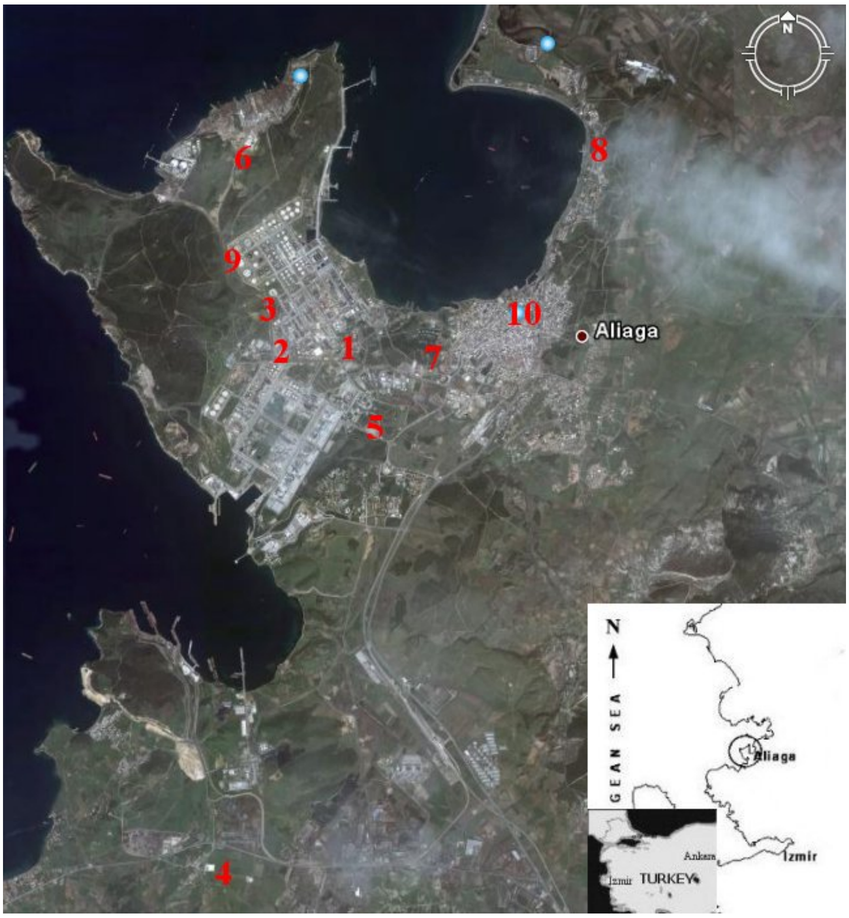

Figure 3.3 Sampling points at Aliağa

3.2.3 The Wastewater Treatment Plant of Izmir

Izmir WWTP was in operation since 2001 and has been treating 7 m^3 s^{-1} wastewater during this study. It is a domestic treatment plant which accepts industrial wastewaters after pretreatment up to a quality acceptable according to the sewer standards. Samples were collected from different units of the WWTP of Izmir (Figure 3.4). The sampling points were fine screens, primary settling unit, aeration pond, sludge collection basin and sludge drying area. Sampling was conducted on June 1, 2006. The average air temperature during sampling was 33ºC and the sampling date was selected randomly. Samples were collected between 10:00 a.m. and 14:00 p.m.

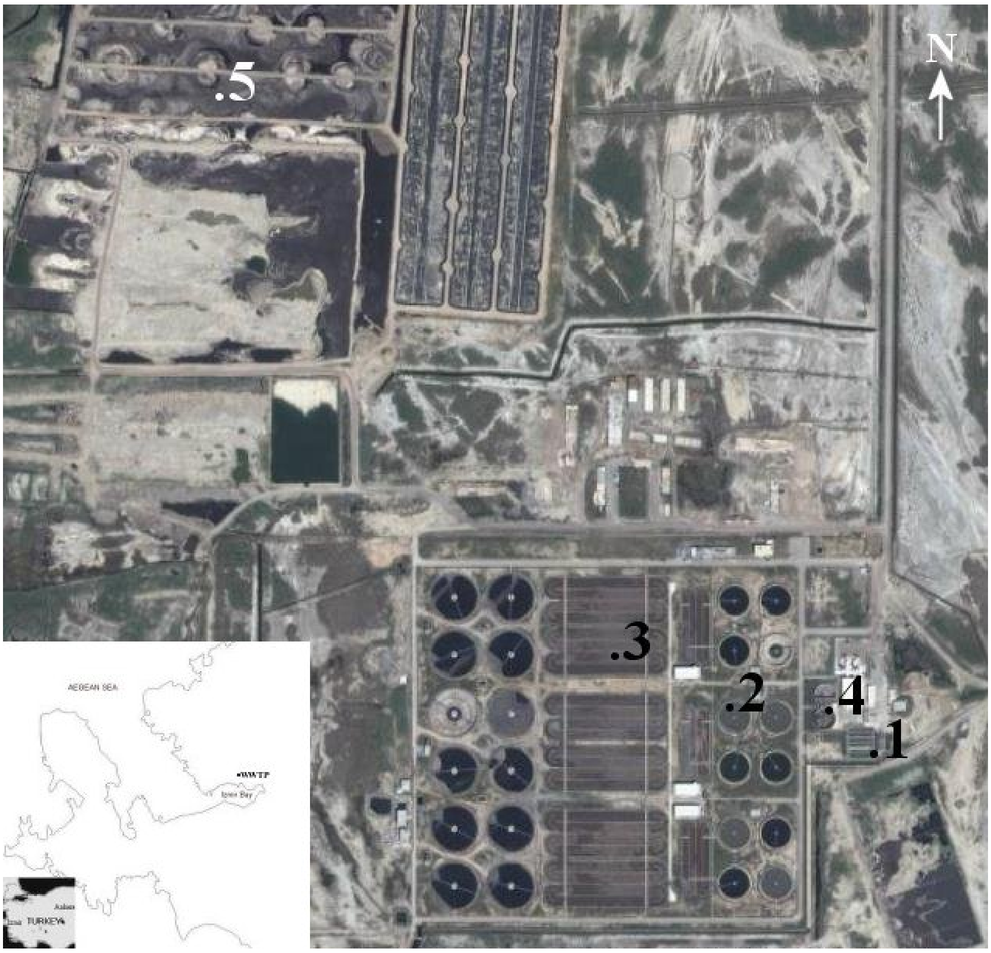

Figure 3.4 Treatment units and sampling points of WWTP

3.2.4 Rendering plant

This is a large complex about 10 km south of the city and has a capacity of 700 cattle and 7000 sheep per day. It includes a live animal stockyard, slaughterhouse, meat processing and packaging, rendering and wastewater treatment plant units. Capacity of the rendering unit alone is 10 tons day^{-1}. In this study this industrial complex is named after the rendering unit as it is the predominant source of odor nuisance. Sampling at this site was carried out on 2 May 2005. Although traffic did not exist in the facility during sampling at the site, a busy express way is located about 500 m upwind of the plant. A previous olfactometric study at this site indicated very serious odor problems due to the lack of adequate odor control devices for emissions from the rendering unit.

There has been seven points at which air sampling was carried out at the rendering site. First one was located at the wastewater treatment plant of the facility. Headspace air over the water surface in the equalization basin was directly sampled using the odor sampler. At this unit chlorination is applied to treated wastewaters. Also the air from outdoors of the management building located 100 m downwind of rendering plant and the rendering plant indoor air were sampled. The fourth sampling point was at the rendering unit stack, and emission odor sampling technique was applied (VDI, 1987). A fifth point located at 40 m upwind of rendering plant was chosen to represent the incoming air towards the rendering unit. Air from the livestock area where live animals were kept is sampled at the sixth point. The final sampling point was selected at the complex borderline with the neighboring fish market building.

3.2.5 Campus site.

Campus site sampling was done at the air pollution measurement platform which is located in a growing coniferous forest at about 10 km southeast of the urban center of İzmir. This station is selected mainly for comparing the findings in odorous compounds from other urban and industrial activity sites with the air at a background area in the Kaynaklar Campus of the Dokuz Eylul University that is located rather far from the city. There is subtantial traffic density near this study site as it is about 500 m to the expressway. This area is located at the 3 km north of the rendering plant. In order to see the impact of varying intensity of traffic the odor measurements and the chemical analyses were repeated in the morning, noon and evening hours on 10 May 2005.

3.3 General overview of the methods

Fig. 3.5 shows the categorization of sensory and analytical test methods for an odorous sample evaluation in general.

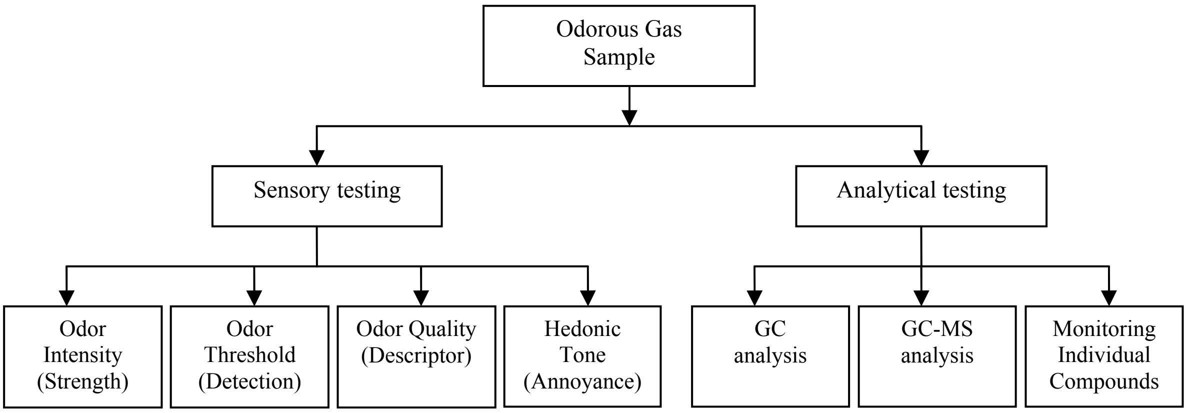

Figure 3.5 The categorization of test methods for odorous gas samples

The main two types of measurements described above were performed during the thesis. Sensory (olfactometric) method of measurements, which employs the human nose as detector was used to determine the odor concentrations of the samples. The analytical part was used for identification and quantification of the chemical mixture in odorous samples that concern the physical and chemical properties of odorous compounds. Instruments of these measurements are olfactometer for sensory measurements, and thermal desorption followed by GC-MS for analytical measurements. The relationship between the two sets of data belonging to the same odorous sample was analyzed.

3.3.1 Sensory measurements

3.3.1.1 Sampling method for odor analysis

Three samples were collected from the air adjacent to the surfaces of the area odor sources such as landfill covers and WWTP units using a specially designed hood at each sampling point. Sampling was carried out following the recommendations described in the European Standard EN 13725 (CEN, 2003). Air samples were drawn into Nalophan® bags of 5 liter capacity by means of a special sampler working with the lung principle. The sampler draws the air directly into the bag by evacuating the atmospheric pressure vessel in which it was placed. Odor and taste free Nalophan® bags that are impermeable to water and organics were used in sampling only for once. PTFE (polytetrafluoroethylene) sampling tubes were used as input and connection lines. Samples were transported to the olfactometry laboratory and analyzed within 24 hours.

3.3.1.2 Olfactometric Analysis

The odor concentrations of the samples were measured by dynamic olfactometry. An ECOMA TO7 yes/no olfactometer (Honigsee, Germany) (Figure 3.6) was used throughout the tests to determine the odor concentrations of the samples following the protocols described in the European standard EN 13725 (CEN, 2003). These tests were carried out inside an odor-free, clean laboratory with selected and trained panelists. Each sample was diluted several times differing from each other by a factor of two and presented to the panelists three times. Dilutions were made using odor-free air supplied by a compressor fitted with carbon filters and an air dryer.

The olfactometer is a computer controlled semi-automatic instrument with four panel member places and computes the odor concentration by means of a special computer program based on the perception response data of the panelists. This method employs a “yes/no” technique and determines how many times a sample must be diluted with odor-free air to be at the threshold of detection by 50% of the panel. At this instance, the required number of dilution defines the odor concentration in odor units per cubic meter (OU m^{-3}). Example results of the olfactometer results are given in Appendix-B.

The olfactometer is in principle a dilution system where a sample of odorous air is diluted with neutral air. Panel members judge for the presence of odor in the diluted sample. Two gas jet pumps are operated by neutral air one for each measurement range. The air sample is drawn from the sample-bag through a pre-mixing unit and flow meters. The flow rate of odorous air is controlled in steps by needle valves.

In the gas jet pump the odorous air is mixed thoroughly with the odorless air. The mixture flows via the rotary slide valve to the sniffing ports. While one panel member is provided with mixed air (diluted sample air) the opposite panel members receives neutral air. The panel members who are in the expiration phase (2 per time) are provided with a minimal flow of neutral air.

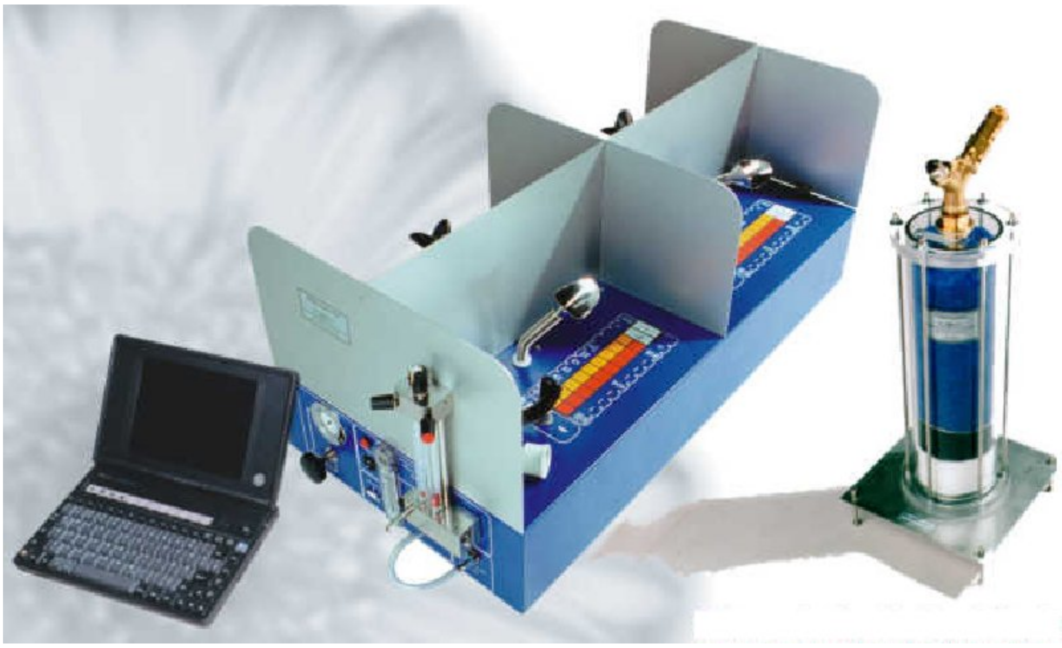

Figure 3.6 ECOMA TO7 yes/no olfactometer

The central switch-over valve switches over from neutral air to the mixture between two breathing phases. The breathing frequency is given by optical signals. The procedures are run simultaneously for the four panelists. The duration of a measurement sequence is thereby hold to a minimum.

The total measurement program is computer controlled and runs automatically. It includes several measurement sequences; recovery breaks for the panel members and includes clean air flushing functions for the dilution unit.

The panel members are supplied with mixed gas. The concentration starts at low threshold and increases. With the first odor impression the button “yes, it smells” has to be pushed; this indicates that the odorant concentration is reached. The result for example of 4 panel members who proved there odor impression in 3 rounds the odorant concentration gives a multiple of the threshold of the odorant concentration in odor units per cubic meter (OU m^{-3}).

3.3.2 Analytical measurements

3.3.2.1 Sampling method for VOCs

Gas samples were collected into Nalophan® bags and were transported to the laboratory. Then, gases were passed through the adsorbent tubes via silicone tubing connected to a vacuum pump (Rena 301, Rena OEM, France). Sampling flow rate and sample volume were 100 ml min^{-1} and 2-3 liters, respectively. The flow rate was measured using a rotameter (Gilmont, Barnant Inc., USA). The rotameter calibration was checked occasionally (at three flow rates in duplicate, n=6) using a primary standard (soap-bubble meter). The average percent difference between two flow meters was<2.5%.

For each sampling period, duplicate tubes obtained from sampling bags were separately analyzed. For May 2005 and September 2005 sampling period, the concentrations of VFAs and volatile organic compounds (VOCs) were determined and for June 2006 sampling period, the concentrations of VOCs and RSCs were determined. RSCs were studied only in June 2006 sampling period due to the analytical difficulties that were met in May 2005 and September 2005. The sample tubes were refrigerated and analyzed within 1-3 days as recommended (Peng & Batterman, 2000).

Grab sampling by Nalophan® bags has been commonly used to collect gas samples. Samples collected in bags are either directly introduced to the analytical systems or concentrated using techniques like solid phase micro extraction (SPME) or adsorbent tubes-thermal desorption (TD). Some recent applications using grab sampling with Nalophan® bags include the analysis of odorous gas emissions from composting plants (gas sample-proton transfer reaction-mass spectrometry) (Biasoli et al., 2004), waste gases and landfill gases (SPME-GC-MS) (Davoli et al., 2003; Kleeberg et al., 2005; Pierucci et al., 2005), VOC emissions from apple tree (TD-GC-MS) (Vallat et al., 2005), VOCs emissions from moss roses (solid-liquid extraction-GC-MS) (Caisard et al., 2006), fig tree emissions (solid-liquid extraction-

GC-MS) (Grison-Pige et al., 2001), volatiles from maize (solid-liquid extraction-GC-FID) (Hoballah et al., 2004), mushroom composting emissions (TD-GC-MS) (Noble et al., 2001). The use of Nalophan® bags for odor sampling is recommended by the European Standard EN 13725 (CEN, 2003) due to their inertness. A recent study indicated that gas mixtures containing ppbv concentrations of several chlorinated and aromatic hydrocarbons could be safely stored for several days in Nalophan® bags without any significant loss (Gorgenyi et al., 2000).

3.3.2.2 Adsorbent selection for VOCs

Different adsorbents are commercially available and the user is faced with the difficulty of selecting an appropriate adsorbent from the great variety of materials on the market. The adsorbent used for adsorptive enrichment in combination with thermal desorption should have the characteritics to guarantee an accurate determination of VOCs; complete enrichment of the analytes of interest, complete and fast desorption of the analytes, homogenous and inert surface to avoid artifact formation, low affinity to water to avoid displacement and hydrolysis reactions, low adsorption capacity for other inorganic constituents of air and multiple usability (Dettmer & Engewald, 2002; USEPA, 1999).

In this study, Tenax TA (60/80 mesh, Supelco, Bellefonte, PA, USA), and Carboxen 1000 (Supelco, Bellefonte, PA, USA) were chosen as sorbents following the recommendations described in the Compendium Method of TO-17 (USEPA, 1999) since they cover the suitable range for a wide range of VOCs at temperatures of our applications.

Tenax TA is a porous polymer resin based on 2,6-diphenylene-oxide. It is the most widely used adsorbent resin for use with purge and trap thermal desorption for applications such as trapping VOCs in air. It has been specifically designed for the trapping of volatiles and semi-volatiles and has very low levels of impurities (Calogirou et al., 1996).

3.3.2.3 Adsorbent tubes

Glass adsorbent tubes (6 mm OD, 17.8 mm length) were prepared in the laboratory according to the ambient air sampling methods recommended by USEPA (1999). Each tube was packed at the upstream (sampling) end with 3 mm silanized glass wool followed by a series of sections of 150 mg Tenax TA (60/80 mesh) (Supelco, Bellefonte, PA, USA), 3 mm silanized glass wool, 100 mg Carboxen 1000 (Supelco, Bellefonte, PA, USA) and finally 3 mm silanized glass wool at the downstream end (Figure 3.7). Filled tubes were conditioned at 260°C for 1 h with a 50 ml min^{-1} reverse flow (opposite to the sampling direction) of high purity nitrogen prior to use. Second conditioning was also done in GC-MS under Helium flow. Ends of the conditioned tubes were first closed with PTFE caps and each tube was placed into tightly capped special tube containers prior to use and after sampling. Silica gel and activated charcoal were placed to the bottom section of the tube containers for humidity and contamination control, respectively.

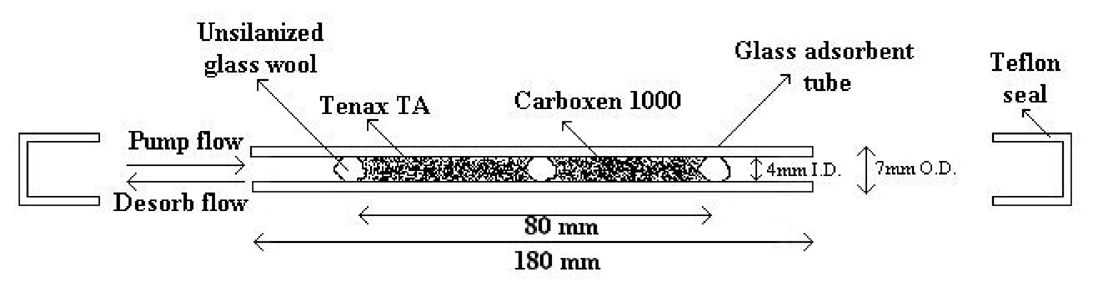

Figure 3.7 Example of construction of adsorbent tubes

3.3.2.3 Analytical method, Thermal Desorption, Gas Chromatography-Mass Spectrometer (TD-GC/MS)

The combination of gas chromatography (GC) for separation and mass spectrometer (MS) for detection and identification of the components of a mixture of compounds has been used commonly as an analytical tool in the research and commercial analytical laboratories.

In this study, samples were analyzed with a gas chromatograph (GC) (Agilent 6890N, Agilent, Wilmington, DE, USA) equipped with a mass selective detector (Agilent 5973 inert MSD, Agilent, Wilmington, DE, USA) and a thermal desorber (Tekmar, Aerotrap 6000, USA). The thermal desorber was modified by replacing the original fused silica transfer line (0.32 mm I.D.) causing flow restriction through the GC inlet with a glass-lined inert steel tubing (0.7 mm I.D., Alltech). The cryogenic internal trap operating with liquid nitrogen was replaced with an adsorbent (100 mg Tenax, Supelco, Bellefonte, PA, USA) to fill the ambient trap. The cooling for the internal trap was provided by a vacuum pump drawing air at room temperature through the liquid nitrogen line at a rate of 15 l min^{-1}. VOC samples were desorbed for 5 min at 225°C using helium flow at the rate of 40 ml min^{-1}. Internal trap temperature during sample desorption was 35°C. The trap was desorbed for 1 min at 240°C. Then, it was baked for 10 min at 250°C. Valve oven and transfer line temperature of the thermal desorber was 200°C.

The chromatographic column was HP5-MS (30 m, 0.25 mm, 0.25 µm) and the carrier gas was helium at 1 ml min^{-1} flowrate and 36 cm s^{-1} linear velocity. The split ratio was 1:40. The inlet temperature was 240°C. Temperature program for VOCs and RSCs were as follows: initial oven temperature 40°C, hold for 3 min, 40°C to 120°C at 5°C min^{-1}, hold 1 min. Ionization mode of the MS was electron impact (EI). Ion source, quadropole, and GC/MSD interface temperatures were 230, 150, and 280°C, respectively. The MSD was run in selected ion monitoring mode. Compounds were identified based on their retention times (within ±0.05 minutes of the retention time of calibration standard), target and qualifier ions. Identified compounds were quantified using the external standard calibration procedure. The operating conditions are also summarized in Table 3.4.

During the analyses of VOCs, VFAs and reduced sulfur compounds (RSCs) calibration standards were prepared individually. Five levels (0.4, 2, 5, 10 and 20 µg ml^{-1}) of VOC solutions were prepared in methanol as the calibration standards. Five levels of standard solutions with varying VFAs (i.e., 12, 30, 60, 180, and 300 µg ml^{-1} for acetic acid) were prepared in deionized (DI) water. Seven levels of standard solutions (1 to 100 µg ml^{-1}) were prepared in methanol and used for calibration for reduced sulfur compounds (RSC). To calibrate the system preconditioned thermal desorption tubes containing 150 mg Tenax TA and 100 mg Carboxen 1000 were spiked with 1 µl of the calibration standard and the system was run at specified conditions. In all cases linear fit was good with $r^2 > 0.99$.

Table 3.4 Operating conditions for the analytical system

Gas Chromatography	**Operating Conditions**
Column	HP5-MS (30 m, 0.25 mm, 0.25 µm film thickness)
Carrier gas	Helium, 1ml min^{-1}, 36 cm s^{-1} linear velocity
Inlet	Split/splitless, Split ratio 1:40
Inlet temperature	240°C
Temperature program VOCs + RSCs	Initial oven temperature 40°C, hold 3 min, 40°C to 120°C, 5°C /min, hold 1 min
VFAs	Initial oven temperature 50°C, hold 1 min, 50°C to 225°C, 35°C /min, hold 2.5 min
Thermal Desorber	
Sample desorb flow	40 ml min^{-1}
Sample desorb	5 min at 225°C
Internal trap temperature during sample desorb	35°C
Trap desorb	Preheat to 240°C, desorb for 1 min at 240°C
Trap bake	10 min at 250°C
Valve oven and transfer line temperature	200°C
Mass Selective Detector	
Ionization mode and energy	Electron impact (EI), 70 eV
Detection mode	Selected ion monitoring (SIM)
Ion source and quadropole temperatures	230 and 150°C
Tuning compound	PFTBA
GC/MSD interface temperature	280°C

3.3.3 H_2S sampling and analysis

Analysis of H_2S was in accordance with the NIOSH method 6013 (NIOSH, 1994). This method is applicable for ambient H_2S measurements and the maximum concentration that will be measured in the method is given as 20 mg m^{-3} and the accuracy of the method was given as ±11.8%. Odorous gas samples were passed through a gas sampling train and H_2S was held in special sampling tubes consisting of two separate sections filled with coconut shell charcoal of 400 mg and 200 mg. In the sampling train a 0.5 µm pore size Zefluor prefilter was fixed in order to eliminate entrance of particles into the tube. During sampling a gas flow rate of 1 l min^{-1} was maintained using a mass-flow controlled vacuum pump and a total of 20 l air was passed through the sampler during a sampling period of 20 minutes. This flow rate is recommended by NIOSH-6013 ambient air sampling method for H_2S determination in the air. If a higher flow rate was used, breakthrough of the adsorbent could have endangered the sampling procedure. And a lower flow rate would take longer time and considering the ambient temperature on the sampling day, this could have risked loss of H_2S due to evaporation. During sampling air temperature was 30^{O}C. All air volumes were corrected for 20^{O}C.

Hydrogen sulfide was determined separately in both sections of the sampling tube and the results were summed up. After extraction of H_2S into water from the activated carbon in the tubes and following the hydrogen peroxide oxidation of sulfides into sulfates in the aqueous solution, sulfate concentrations were found by ion chromatography. For this the ion chromatograph Dionex, with an IonPac AG9-HC column, and ASRS-ULTRAII anion self-regenerating suppressor was used. For this analysis 10 mM Na_2CO_3 was used as eluent at 1 mL min^{-1} flow rate.

3.4. Quality control and quality assurance

The system performance was confirmed daily by analyzing a midrange calibration standard. The relative standard deviation from the initial calibration was <10%. Analytical precision determined from three pairs of duplicate samples ranged between 2-5%.

Instrumental detection limits for VOCs (~5 pg for a split ratio of 1:40) were determined by linear extrapolation from the lowest standard in the calibration curve using the area of a peak having a signal/noise ratio of 3. Six blank thermal desorption tubes (3 for VFAs and 3 for VOCs) for May and September 2005 sampling period were analyzed as process blanks in order to determine the level of contamination during sample handling and preparation. The limit of detection (LOD, pg) of the method was defined as the mean blank mass plus three standard deviations (LOD=mean blank+3 SD) (Thomas et al., 2006; Sofuoglu et al., 2004). LOD values for different compounds ranged between 5-15230 pg and 5-3843 pg for May 2005 and September 2005 sampling periods, respectively. Instrumental detection limits were used for the compounds that were not detected in blanks. In general, VOCs in the samples were substantially higher than the blanks. Sample quantities exceeding the LODs were quantified and corrected by subtracting the mean blank amount from the sample amount. For VFA analyses, no blanks were detected and therefore blank correction was not necessary for May 2005 and September 2005 sampling periods.

For May-June 2006 sampling period, the system performance was confirmed daily by analyzing a midrange calibration standard again. Six blank thermal desorption tubes (3 for RSCs and 3 for VOCs) for this sampling period were analyzed as process blanks in order to determine the level of contamination during sample handling and preparation. LOD values ranged between 5-3541 pg in this period. Generally, VOCs in the samples were substantially higher than the blanks. Sample quantities exceeding the LODs were quantified and corrected by subtracting the mean blank amount from the sample amount. For RSCs analyses, no blanks were detected except for carbon disulfide (CS_2).

To check if there was breakthrough for three samples a back-up tube was connected in series with the sample tube during sampling from the Nalophan® bags. Back-up tubes were found to contain similar quantities of the compounds as the blanks indicating that the breakthrough from the sample tubes was not a problem during sampling.

For H_2S, throughout sampling and analysis high purity DI water, standards and analytical grade laboratory reagents were used in sampling, extraction and all laboratory handling and procedure on the samples. Together with the samples and standards, a suitable number of blanks consisting of unexposed filters and tubes were taken to the field and brought back unopened and unused. Also aliquots of the laboratory reagents and water were analyzed for blanks. Six blanks were run to allow the calculation of standard deviation to be used in the determination of the limit of detection (LOD) of the procedure. The calculated detection limit for H_2S determinations was below 0.1 mg m^{-3}, too.

Instrumental detection limit of ion chromatography was below 0.5 mg l^{-1} for sulfate readings. Blank correction of the measurements was made by using the average blank value. Aqueous standards were prepared to obtain 0.5, 3.75, 7.5, 15, 30 mg l^{-1} as sulfate. These concentrations were chosen to be within the range expected from the samples. Aqueous sulfate concentrations were converted to and expressed as H_2S concentrations in units of µg m^{-3} using the method recommended in NIOSH method 6013.

3.5. Data analysis

For the evaluation of measurement results three different analysis methods were applied to the overall datasets of the results. Two of them were statistical methods: (1) Regression analysis, (2) Correlation analysis. The last one was odorous component contribution analysis.

3.5.1 Regression analysis

Regression analyses were applied to evaluate the relationship between odor and chemical concentrations of the samples. This aimed at modeling the relationships between variables and determines the magnitude of those relationships. The models can be used to make predictions. Regression analysis models the relationship between one or more interrelated variables (also called explained variables or predicted variables) (usually named Y), and the independent variables (also called explanatory variables or control variables) usually named $X_1,...,X_p$).

Linear regression assumes the best estimate of the response is a linear function of some parameters. Simple linear regression and multiple linear regression are the two methods for modeling the relationship between two or more random variables using a linear equation. Simple linear regression refers to a regression on two variables while multiple regression refers to a regression on more than two variables. In this thesis, both types of regression models were used and the results of these analyses were presented and discussed in the following sections.

3.5.2 Correlation analysis

Correlation analysis was applied to describe the degree of relationship between odor and chemical concentrations of the samples. Correlation is the ratio of the covariance of two variables to the product of their standard deviations. The resulting correlation coefficient is a unitless number that ranges between −1.0 and +1.0. A value of −1.0 represents a perfect inverse relationship between the two variables, whereas +1.0 occurs when the two variables react in exactly the same way as their values change. A correlation coefficient of zero suggests that the two variables are independent of each other. In this thesis, "Pearson r correlation" (http://rem.jrc.cec.eu.int/atmes2/21b.htm) was used and the results of the correlation analysis are presented in the following sections.

3.5.3 Odorous component contribution analyses

For pure compounds contribution of different components in odors is dependent on two parameters; concentration of the component and odor threshold of the pure compound. A unitless number defined as "odor activity value (OAV)" showing the odor contribution of a measured component is established by dividing the concentration of the odorous compound to its odor threshold (Qian & Reineccius, 2003). For a mixture of odorous gases, a comparison of the ratios of individual components gives an idea on the relative significance of different components in the odor level. One should note that higher ratios may be due to high concentrations of less odorous components or low concentrations of highly odorous substances, or both.

The calculation of “odor activity value” on the basis of odor thresholds from the literature allowed the identification of the key odorous compounds present in the investigated samples. OAV describes the potential contribution of each single component to the cumulative odor impression (Freudenthal et al., 2005).

Calculation of the OAV is made for each single component for which an odor threshold concentration by using the equation described below: ,

$$OAV_i = \frac{VOC_i}{OT_i} \tag{3}$$

Where: OAV_i: odor activity value of compound *i*, VOC_i: concentration of quantified compound *i*, OT_i: odor threshold concentration of compound *i*.

CHAPTER FOUR
RESULTS AND DISCUSSION

This chapter presents the measurement results and evaluation of olfactometric and analytical measurement results are given in this chapter. Measurement results and evaluations were given individually for all sampling sites.

4.1 Results of landfill measurements

4.1.1 VOC composition and concentrations

In three sampling campaigns, the odorous emissions from landfill were consisted of several compounds. Fifty-three VOCs were detected in May 2005, 48 VOCs in September 2005 and 46 VOCs in May 2006 sampling campaigns. Concentration ranges and aritmethic mean values of the identified and quantified compound are also given in Table 4.1. The measured VOCs are classified as monoaromatics (e.g. benzene, toluene), halogenated compounds (e.g. chlorobenzene, trichloroethene), aldehydes (e.g. hexanal, propanal), ketones (e.g. acetone), VFAs (e.g. acetic acid, formic acid), esters (e.g. butyl acetate, butyl formate). H_2S, CS_2, dimethyl sulfide (DMS), dimethyl disulfide (DMDS) were also present in the composition of odorous gas.

In May 2005, the abundant group was ketones (25% of total VOC concentrations) followed by monoaromatics (21%), aldehydes (20%), volatile fatty acids (VFAs) (17%), halogenated compounds (14%) and esters (2%). In September 2005, aldehydes had the highest concentration (37% of total VOC concentrations) and ketones (36%), monoaromatics (13%), halogenated compounds (6%), VFAs (5%), and esters (1%) followed them. Total VOC concentration is defined as the sum of the concentrations of identified and quantified compounds in $\mu g\ m^{-3}$.

The VOC concentrations at the landfill were much higher than at the other sampling sites in May 2006 sampling campaign and at sampling point #1 which is the burial site of industrial wastes and the wastewater sludges. Concentrations unusually reached up to mg m^{-3} levels. This may be due to the burial of industrial wastes containing unusually high amounts of these compounds. Thus results of this sampling point at this campaign were discarded as it did not represent the usual odor levels and quality of the environment. So the evaluations were done for the results of other four sampling points. In May 2006, the most abundant group was monoaromatics (41% of total VOC concentrations) followed by ketones (19%), halogenated compounds (18%), aldehydes (16%) and RSCs (4%).

Aldehydes and ketones are carbonyls that are generated from incomplete oxidation of organic matter and are emitted during the initial disposal stage. A variety of aromatic compounds are among the most abundant trace components in landfill gases. The aromatics usually have special toxicological significance since they include benzene and benzene derivatives. Toluene was the most abundant aromatic compound occuring immediately after waste deposition, probably coming from direct volatilisation. The level and diversity of aromatic compounds tended to increase under anaerobic conditions. Chlorinated organics in the landfill might be related to the residues of cleaning and disinfection agents widely used in urban and industrial sources. The waste degradation processes usually produce substantial amounts of these VOCs, and as a consequence, the differences in their levels are dependent upon both their concentration in the refuse material and the waste decomposition stage reached in the degradation process (Houghton et al., 1991).

Table 4.1 VOC concentrations (ranges and mean values) in landfill

	Concentration range (μg m^{-3})		
	May 2005	**September 2005**	**May 2006**
Formic acid	3.44-43.71 (24.22)	11.10*	n.s.
Acetic acid	0.17-5.34 (1.92)	n.d.	n.s.
Propionic acid	0.19-3.52 (1.86)	n.d.	n.s.
Isobutyric acid	0.50-6.61 (3.56)	n.d.	n.s.
Butyric acid	0.06-4.39 (2.22)	n.d.	n.s.
Isovaleric acid	0.05-6.05 (2.34)	0.20*	n.s.
Valeric acid	0.07-4.99 (1.86)	0.37*	n.s.
Isocaproic acid	2.84*	n.d.	n.s.
Caproic acid	1.37-2.91 (2.14)	0.14-0.34 (0.22)	n.s.
Heptanoic acid	0.25-8.85 (3.39)	0.30-1.30 (0.73)	n.s.
Acrolein	0.48-2.02(1.04)	1.25-2.66(1.83)	4.3*
Butanal	0.43-1.70(1.01)	0.34-1.33(0.59)	2.2*
Crotonaldehyde	0.05-0.38(0.14	0.01-0.15 (0.09)	0.1-13.2(7.1)
Decanal	0.66-1.49 (0.97)	1.25-9.42(3.95)	2.9-16.3(9.9)
Heptanal	0.16-1.51(0.73)	0.18-.64(0.32)	1.7-18.5(7.5)
Hexanal	0.47-5.94(2.59)	0.45-3.55(1.32)	4.4-288.4(97.8)
Nonanal	0.64-2.16 (1.57)	1.28-5.01(2.64)	8.4-44.7(19.4)
Octanal	0.27-2.28(1.54)	0.53-1.42(0.82)	1.6-26.8(13.2)
Pentanal	0.15-1.92 (0.75)	0.26-0.87(0.44)	1.3-44.2(19.0)
Propanal	4.16-38.55 (21.13)	5.15-13.45(8.49)	48.8-445.8(190.2)
Butyl Acetate	0.12-7.54(2.70)	0.09-0.42(0.21)	5.6-49.3(21.1)
Butyl formate	0.03-0.10(0.06)	0.03-0.12(0.05)	1.5*
Butyl Propionate	0.11*	0.10*	n.d.
Methyl propionate	n.d.	0.18*	2.5-8.3(5.0)
Vinyl acetate	0.01-2.29(0.51)	0.08-1.79(0.65)	0.3*
Benzene	0.09-0.59(0.29)	0.34-1.06(0.53)	0.9-5.7(3.2)
Ethylbenzene	0.21-4.94(2.03)	0.15-0.76(0.45)	1.1-136.6(44.5)
o, m - Xylene	0.35-10.16(4.33)	0.22-1.11(0.73)	1.8-305.9(93.3)
p-Xylene	0.34-9.55(3.59)	0.15-1.01(0.62)	1.9-320.6(97.1)
Styrene	0.67-14.44(3.88)	0.13-0.40(0.24)	1.0-241.0(66.7)
Toluene	1.56-47.42(18.97)	1.51-11.18(4.76)	12.5-1975.4(603.3)
1,1,1-Trichloroethane	0.02-0.05(0.04)	0.02-0.10(0.04)	0.1-0.2(0.1)
1,1,2,2-Tetrachloroethane	n.d.	n.d.	n.d.
1,1,2-Trichloroethane	0.05-0.08(0.06)	n.d.	0.4*
1,1-Dichloroethane	0.0014-0.01(0.006)	0.02*	0.1*
1,1-Dichloroethene	0.12-0.37(0.27)	0.04-0.70(0.22)	0.6*
1,2-Dichlorobenzene	0.03-0.08(0.05)	0.02-0.09(0.04)	0.02-0.05(0.03)

Data in brackets represent the average concentrations; n.d., not detected; n.s., not studied

* Identified only at one sampling site

Table 4.1 VOC concentrations (ranges and mean values) in landfill (cont.)

	Concentration range (μg m^{-3})		
	May 2005	**September 2005**	**May 2006**
1,2-Dichloroethane	0.01-1.22(0.30)	0.01*	0.2-1.9(0.8)
1,2-Dichloropropane	n.d.	n.d.	n.d.
1,3-Dichlorobenzene	0.002-0.01(0.005)	0.02*	n.d.
1,4-Dichlorobenzene	0.08-0.40(0.25)	0.07-0.21(0.14)	1.1-40.6(14.9)
Bromodichloromethane	n.d.	n.d.	0.1*
Bromoform	n.d.	n.d.	n.d.
Carbon tetrachloride	0.12-0.23(0.17)	0.10-0.15(0.13)	1.1-2.8(1.5)
Chlorobenzene	0.01-0.12(0.04)	0.009-0.014(0.01)	0.07-0.13(0.1)
Chloroform	0.03-0.16(0.08)	0.03-0.13(0.06)	0.3-10.1(3.3)
cis-1,3-Dichloropropene	0.03-0.07(0.05)	n.d.	n.d.
cis-1,4-Dichloro-2-butene	n.d.	n.d.	n.d.
Dibromochloromethane	n.d.	n.d.	n.d.
Iodomethane	0.001-0.02(0.02)	0.02-0.03(0.02)	0.2-0.8(0.5)
Methylene chloride	1.62-7.95(4.42)	0.68-2.58(1.43)	22.3-68.1(38.2)
Tetrachloroethene	0.05-9.16(2.37)	0.02-1.02(0.50)	0.3-1219.7(307.4)
trans-1,2-Dichloroethene	n.d.	0.11*	n.d.
trans-1,3-Dichloropropene	0.085-0.09 (0.09)	n.d.	n.d.
trans-1,4-Dichloro-2-butene	n.d.	0.004*	n.d.
Trichloroethene	0.18-62.91(13.06)	0.11-1.95(0.81)	1.5-8.3(4.4)
2-Butanone	n.d.	n.d.	n.d.
2-Hexanone	0.04-0.80(0.27)	0.06-0.22(0.10)	5.1*
4-Methyl-2-pentanone(MIBK)	0.03-0.42(0.21)	0.05-0.18(0.08)	2.1-5.8(3.9)
Acetone	7.95-67.60(37.17)	11.20-28.57(19.94)	102.7-808.4 (364.2)
Cyclohexanone	0.08-9.13(3.15)	0.004*	1.8-111.8(30.6)
Acrylonitrile	0.09-0.20(0.14)	0.03-0.04(0.034)	0.1-0.2(0.1)
Pyridine	n.d.	n.d.	n.d.
Hydrogen sulfide	n.s.	n.s.	44-113(86.5)
Methyl mercaptan	n.s.	n.s.	n.d.
Ethyl mercaptan	n.s.	n.s.	n.d.
Dimethyl sulfide	n.s.	n.s.	0.1-41.4(12.5)
Carbon disulfide	0.41-5.05 (1.51)	0.24-2.36(1.15)	9.7-64.7(25.7)
2-methyl-2-propanethiol	n.s.	n.s.	n.d.
n-propyl mercaptan	n.s.	n.s.	n.d.
Dimethyl disulfide	n.s.	n.s.	0.6-375.4(80.1)
Tetrahydrothiophene	n.s.	n.s.	n.d.

Data in brackets represent the average concentrations; n.d., not detected; n.s., not studied

* Identified only at one sampling site

High levels of monoaromatics were identified and quantified in May 2005 and September 2005 samples (Figure 4.1). Toluene had the highest average concentration in this group and was exceeded only by formic acid and propanal in these sampling campaigns. In May 2006, monoaromatics had significant concentrations. Compared to other two sampling campaigns the concentration levels of monoaromatics were 5 to 150-fold in some cases.

Sixteen chlorinated compounds were detected in May 2005 and September 2005 samples, and fifteen compounds were detected in May 2006. In May 2005, the average concentrations of some chlorinated species such as chloroform, carbon tetrachloride, chlorobenzene, trichloroethene, tetrachloroethene were 0.08, 0.17, 0.04, 13.06 and 2.37 µg m^{-3}, respectively (Figure 4.1). In May 2006, the average concentrations of chloroform, carbon tetrachloride, chlorobenzene, trichloroethene, tetrachloroethene were 3.8, 5.9, 0.3, 4.39 and 252 µg m^{-3}, respectively (Figure 4.1). In May 2006 samples, the average concentrations were much higher than May and September 2005 samples. Tetrachloroethene is present in the textiles, dry cleaning workplaces, and chemical manufacturing units. Trichloroethene is used as a degreaser, extraction, and cleaning solvent for household, commercial and industrial uses. Thus, their residuals might have reached the landfill along with the domestic, commercial and industrial wastes. Compared to monoaromatic compounds, the concentrations of chlorinated species were relatively lower in samples.

High levels of aldehydes and ketones were observed at each sampling point in both three sampling campaigns with the maximum levels of at sampling sites 3 and 4. Especially in May 2006 samples, high concentrations were found (Table 4.1; Figure 4.1). Propanal has a pungent, suffocating and unpleasant odor characterizing the landfill gas emissions. Propanal was found above the odor threshold of 3.6 µg m^{-3} (USEPA, 1992) at all sampling points.

Some esters were also identified and quantified (Table 4.1). However, the concentrations of these compounds were relatively lower compared to other VOC groups. For example, concentrations of butyl acetate were 2.70 and 0.21 µg m^{-3} in

May and September 2005, respectively. In May 2006 samples, butyl acetate concentrations were higher than May and September 2005 samples; maximum values reaching to 21.5 and 49.3 µg m^{-3} at sampling points #3 and #4, respectively. Acrylonitrile concentrations were even lower in all sampling periods (0.034, 0.14 and 0.1 µg m^{-3}).

As it can be seen from the Table 4.1 and Fig. 4.1, in May 2006 samples all the concentrations were much higher than the other sampling campaigns. This may be due the hot weather during the sampling day. Before sampling day also four or five very hot days were seen in the region. This increase might have originated from the decomposition of wastes on these warm days. It is well known that the rate of decomposition of wastes increases with increasing temperatures ending in more odor complaints at hot seasons.

In May 2005, VFAs as a full list were found only at the medical waste burial point of the landfill. Formic and isobutyric acids were the most abundant volatile fatty acids in the landfill burial points with the concentrations of 24.22 and 3.56 µg m^{-3}, respectively (Figure 4.1). In September 2005, the concentration of formic acid was relatively lower and it could be detected at one site only. VFA concentrations were very low or some of them could not be detected in September in contrast to the most of them were found at all sampling sites in May 2005 (Figure 4.1). The VFA is a good indicator of waste decomposition process. The decrease in concentrations of these VOCs was probably due to their lower content in the wastes because of loss by evaporation during a long and hot period. For this reason In May 2006, VFAs were not studied.

Benzene-to-toluene (B:T) ratio has been commonly used as an indicator of traffic emissions. A B:T ratio of 0.5 was reported from studies on vehicle exhaust (Scheff and Wadden, 1993). Recent urban air measurements have also showed B:T ratios were ranging between 0.22-0.5 (Elbir et al.,2007; Wang et al., 2002; Muezzinoglu et al., 2001) (Table 4.2). Therefore B:T ratios around 0.5 may indicate that the ambient VOC concentrations are mainly affected by traffic emissions. On the other hand, landfills have significantly lower B:T ratios such as 0.1 in USA as reported by LaRegina et al., (1986). Benzene-to-toluene ratios measured in this study were 0.015, 0.11 and 0.022 in May 2005, September 2005 and May 2006, respectively indicating the presence of more toluene than benzene in landfills compared to traffic exhaust rich urban areas.

Table 4.2 Comparison of average benzene and toluene levels (µg m^{-3}) and B:T ratios in ambient air at selected locations and landfill

Benzene	Toluene	B:T	Site	Reference
0.23	18.97	0.015	Izmir (landfill)	This study (May 2005)
0.53	4.76	0.11	Izmir (landfill)	This study (September 2005)
13.4	603.6	0.022	Izmir (landfill)	This study (May 2006)
3.31	15.39	0.22	Izmir (urban)	Elbir et al., 2007
37.6	102	0.37	Izmir (urban)	Muezzinoglu et al., 2001
52.8	528	0.1	USA (landfill)	LaRegina et al., 1986
33.8	62	0.5	Guangzhou (urban)	Wang et al., 2002

RSCs were only studied in May 2006 sampling campaign due to analytical reasons. Identified and quantified RSCs were H_2S, CS_2, DMS and DMDS. The concentration values were reported in Table 4.3 and Fig.4.2.

Table 4.3 Identified and quantified RSCs in the landfill samples (µg m^{-3})

Sampling point	1	2	3	4	6
Hydrogen sulfide	113.0	89.0	44.0	100.0	n.d.
Dimethyl sulfide	9.4	0.1	8.6	41.4	3.1
Carbon disulfide	64.7	11.4	9.7	16.7	n.d.
Dimethyl disulfide	375.4	2.1	5.1	17.5	0.6

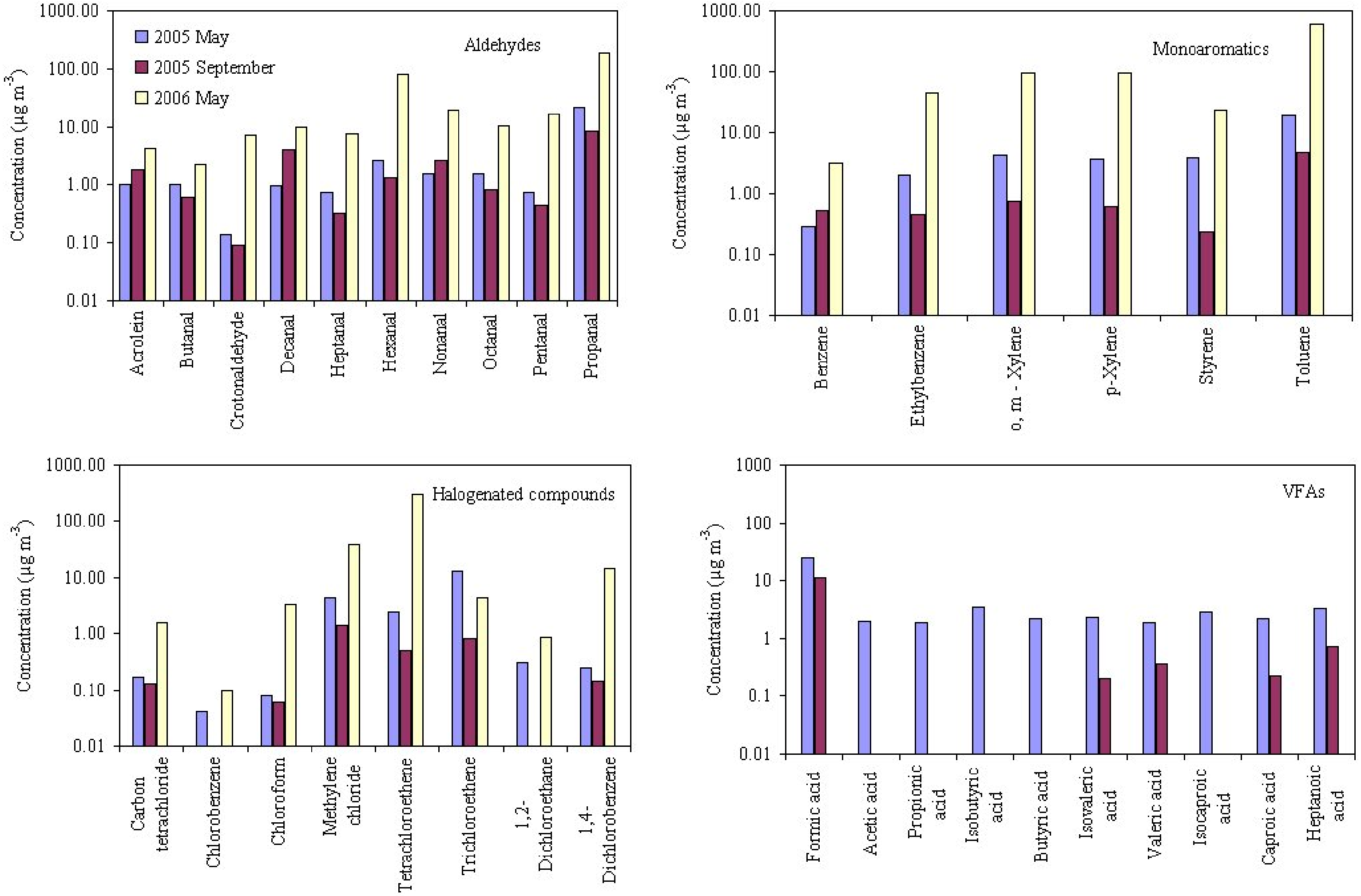

Figure 4.1 Seasonal variations of concentrations of aldehydes, monoaromatics, halogenated compounds and VFAs in landfill

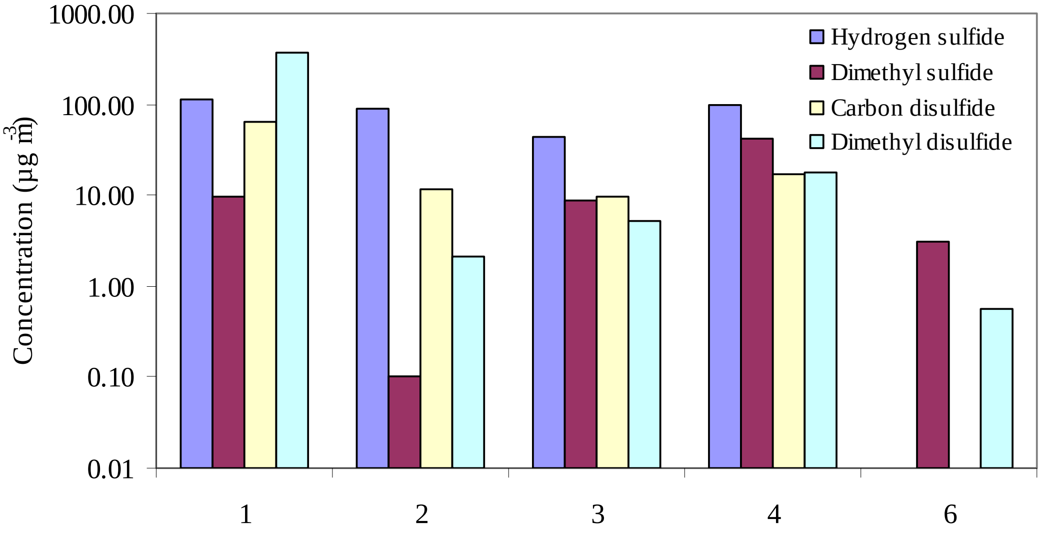

Figure 4.2 RSCs levels of May 2006 samples in landfill

4.1.2 Odor and Total VOC concentrations

The results of olfactometric and chemical analysis for the three sampling campaigns are given in Table 4.4. For May 2005 samples, olfactometric concentrations varied between 1416-116027 OU m^{-3} with a geometric mean value of 47886 OU m^{-3} and the total VOC concentrations (TVOC), which is defined as the sum of the concentrations of identified and quantified compounds, were between 69-258 µg m^{-3} (arithmethic average, 156 µg m^{-3}). For September 2005 samples the olfactometric and TVOC concentrations varied between 1070-111980 OU m^{-3} (average, 29684 OU m^{-3}) and 43-101 µg m^{-3} (average, 56 µg m^{-3}), respectively. For May 2006 samples, olfactometric concentrations varied between 1120-127000 OU m^{-3} with a mean value of 24280 OU m^{-3} and TVOC concentrations varied between 514-165336 µg m^{-3} (average, 34872 µg m^{-3}).

Table 4.4 Odor (OU m^{-3}) and TVOC concentrations (μg m^{-3}) of the sampling campaigns in the landfill

	May 2005		September 2005		May 2006	
Sampling point	Odor	TVOC	Odor	TVOC	Odor	TVOC
1	3765	118±10	3380	56±5	*	*
2	1416	69±2	1070	36±2	1120	514±27
3	116027	258±13	111980	101±6	57000	1213±79
4	35928	207±11	29270	43±2	127000	6071±394
5	82292	127±9	2720	44±4	-	-
6	-	-	-	-	20080	564±55

* not evaluated;

\- not sampled

Total VOC concentrations in May 2005 and September 2005 have shown similar patterns. In September 2005, TVOC concentrations were relatively lower at all sampling locations with slightly decreasing odor concentrations (Figure 4.3). A significant decrease in odor concentration was observed only at sampling point #5. This decrease was probably because during the May sampling there was an ongoing waste burial while the site was covered with soil during the September sampling.

The variations of TVOC concentrations and odor of May 2006 sampling campaign was also presented in Fig. 4.4 including sampling points 2, 3, 4, 6. The fifth sampling point point was not sampled in May 2006 sampling period because dumped wastes were covered with soil in this period.

The results of chemical analysis of the three sampling campaigns with respect to the chemical groups are also presented in Table 4.5.

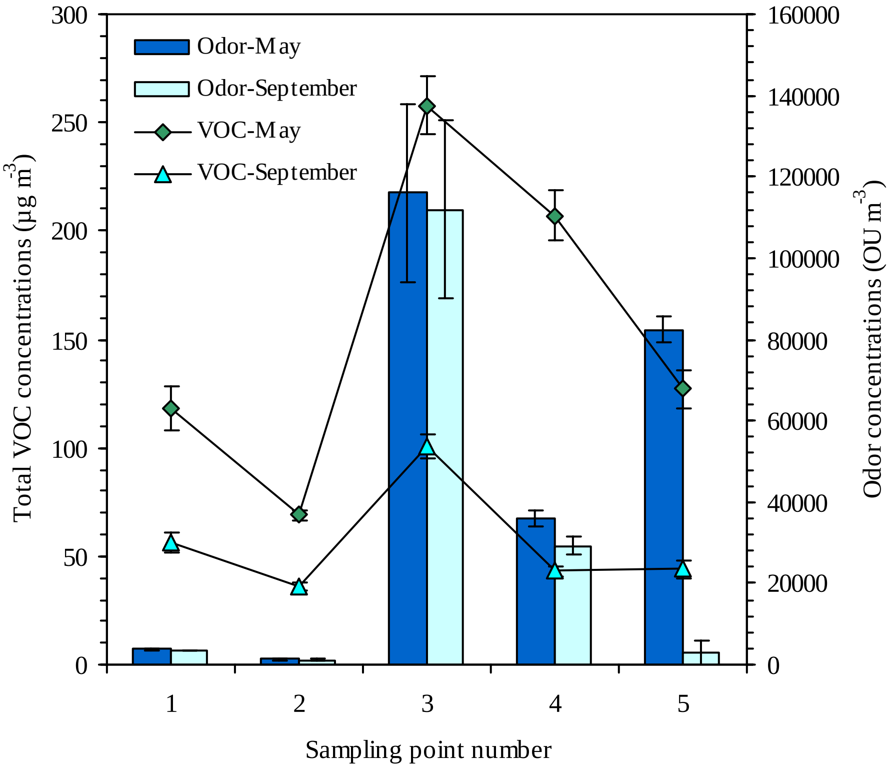

Figure 4.3 Variations of odor and TVOC concentrations in May 2005 and September 2005 samples in landfill

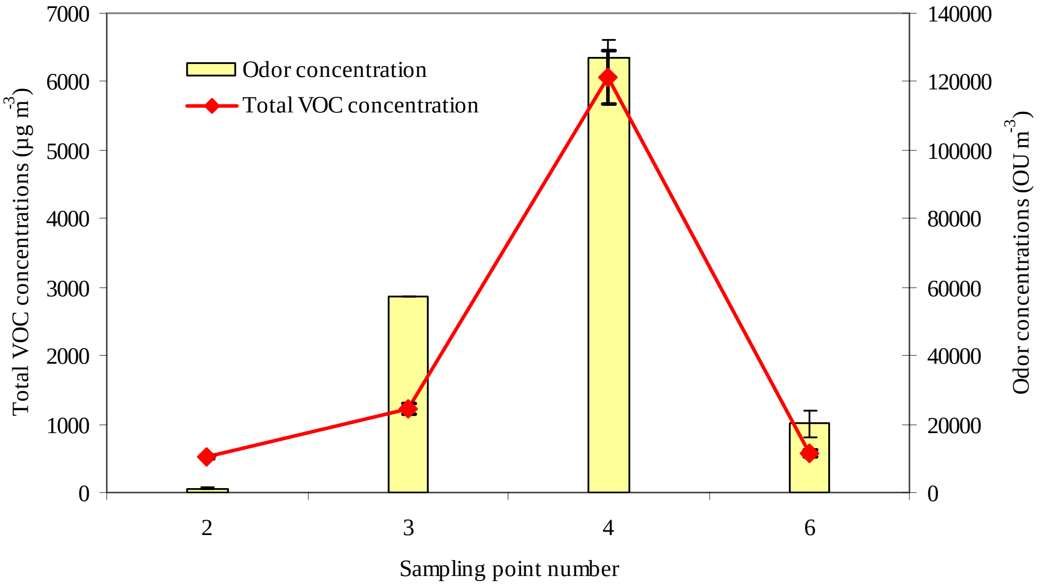

Figure 4.4 Variations of odor and TVOC concentrations in May 2006 samples in landfill (5th point was not sampled)

Table 4.5 Concurrent data sets of the olfactometric odor concentrations (OU m^{-3}) and chemical concentrations (μg m^{-3}) for sampling campaigns in landfill

Sampling Campaign	Sampling point	Odor concentration	TVOC concentration	Acids	Aldehydes	Esters	Halogenated compounds	Monoaromatics	Ketones	RSC
2005 May	1	3765±153	118±10	0.11±0.04	18±3	1±0.23	74±16	6±0.53	19±11	n.s.
	2	1416±219	69±2	45±2	9±1	0.17±0.06	2±0.42	4±0.83	8±4	n.s.
	3	116027±21939	258±13	38±9	48±12	10±4	17±3	76±13	68±48	n.s.
	4	35928±2050	207±11	45±22	34±7	5±2	5±0.54	67±18	50±19	n.s.
	5	82292±3215	127±9	1±0.04	48±9	0.42±0.14	7±1	13±2	52±25	n.s.
2005 September	1	3380±400	56±5	n.d	19±4	0.26±0.01	5±0.70	6±2	25±14	n.s.
	2	1070±425	36±2	1±0.37	14±2	0.19±0.05	1±0.19	5±0.58	12±6	n.s.
	3	111980±20817	101±6	12±6	37±4	1±0.09	6±0.79	15±4	29±17	n.s.
	4	29270±2309	43±2	2±0.5	18±2	1±0.21	3±0.50	8±2	11±6	n.s.
	5	2720±800	44±4	0.30	14±4	2±1	2±0.29	3±0.54	23±13	n.s.
2006 May	2	1120±231	514±27	n.s.	87±17	8.42±5	39±8	60±6	217±61	103±43
	3	57000±0	1213±79	n.s.	218±48	30±9	93±16	546±153	260±142	67±18
	4	127000±5196	6071±394	n.s.	883±165	55±27	1317±427	2822±748	819±464	176±39
	6	20080±4041	564±55	n.s.	178±42	8.14±2	37±11	32±10	304±146	4±2

n.s., not studied; n.d., not detected

4.1.3. Relationship between the odor and TVOC concentration

The characterization of VOCs at landfills (Davoli et al., 2003) and odor assessment based on the dispersion of odors (Sarkar et al., 2003) were previously reported. However, previous studies did not investigate the relationship between landfill odor and VOC concentrations.

The relationship between concentrations of odors and total VOCs measured in this study was statistically analyzed. Linear regression analyses results are presented in Table 4.6 including the regression formulae, R^2 and P values. Evaluations were done for %95 confidence level and for a statistically significant relation P values should be smaller or equal to 0.05. According to these results, there were statistically significant relationships between odor and TVOC concentrations in September 2005 and May 2006. Results indicate that 86% and 90% of the variance in odor concentrations could be explained by TVOC concentrations in September 2005 and May 2006 samples, respectively. No significant relation was found in May 2005 samples.

For the overall dataset (May 2005, September 2005 and May 2006) results of linear regression analysis indicated that 27% of the variance in odor concentrations can be explained by TVOC concentrations (Figure 4.5).

The relationships of odor concentrations with the concentrations of different groups of chemicals were further examined using a step-wise multiple regression analysis. It was found that the concentrations of aldehydes, ketones, and esters are the best estimators, explaining 96% of the variability in odor concentrations ($r^2 = 0.96$, $n = 10$, $P<0.01$) in May 2005 and September 2005 samples.

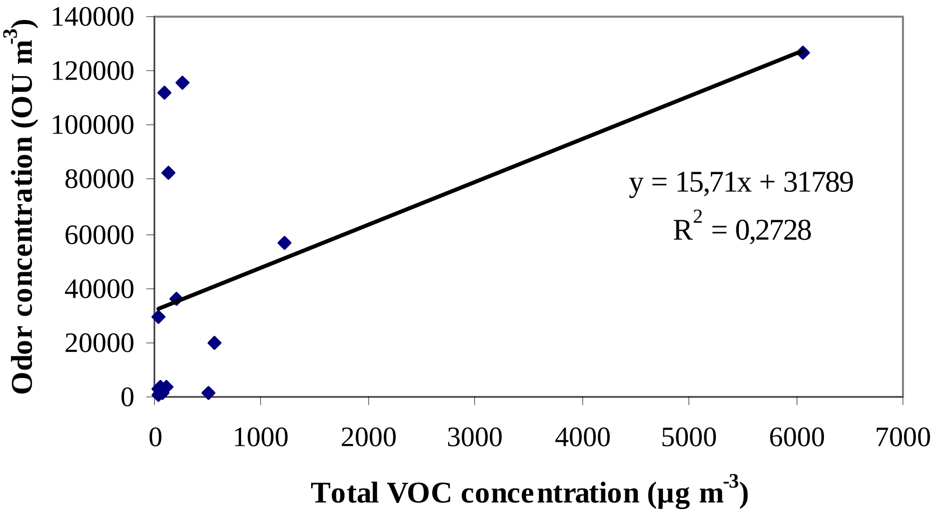

Figure 4.5 The relationship between odor and total VOC concentration for all dataset

In addition, a correlation matrix was calculated for different variables and Pearson coefficients are given as a measure of relationship between groups of variables. The results are given in Table 4.7. There are statistically significant correlations ($P<0.05$) between odor and TVOC, aldehyde, monoaromatic and ester concentrations.

Table 4.6 The relationships between odor and TVOC concentrations in sampling campaigns in landfill

Sampling campaign	n	Formula	R^2	*P* value
May 2005	5	$OC = 484\ C_{TVOC} - 27420$	0.53	0.16
September 2005	5	$OC = 1681.7\ C_{TVOC} - 64492$	0.86	0.02*
May 2006	4	$OC = 19.74\ C_{TVOC} + 10028$	0.90	0.05*
May 05+September 05+May 06	14	$OC = 15.71\ C_{TVOC} + 31789$	0.27	0.05*
May 05+September 05 (Aldehydes+ketones+esters)	10	$OC = 6089.6\ C_{alde} - 3380.8\ C_{ketones} + 8363.2\ C_{esters} - 34890$**	0.96	0.01*

*statistically significant

**$C_{aldehydes}$ is the total concentrations of aldehydes, $C_{ketones}$ is the total concentrations of ketones, C_{esters} is the total concentrations of esters

Table 4.7 Pearson correlation coefficients between the different compound groups and odor in the all samples (n=14) in landfill

	Odor	TVOC	VFAs	Aldehydes	Esters	Halogenated compounds	Monoaromatics	Ketones	RSC
Odor	1	0.52*	0.23	0.53*	0.54*	0.51	0.54*	0.46	0.82
TVOC		1	0.63	0.99*	0.94*	0.99*	0.99*	0.95*	0.82
VFAs			1	0.22	0.58	0.18	0.69	0.37	-
Aldehydes				1	0.95*	0.97*	0.98*	0.97*	0.76
Esters					1	0.89*	0.94*	0.94*	0.77
Halogenated compounds						1	0.99*	0.91*	0.83
Monoaromatics							1	0.92*	0.83
Ketones								1	0.74
RSC									1

***** Statistically significant ($p<0.05$)

4.1.4. Evaluations based on odorous component contribution analyses

The odor activity values (OAVs) of the compounds in composition of the odorous gas emissions of the landfill are presented in Appendix-D. Example calcuation for OAVs are also given in Appendix-C. Among the identified and quantified 53 compounds; a few different compounds have OAVs above 1 indicating that odor thresholds were exceeded and these compounds were the key odorants in the samples. Most of the compounds have OAVs below 1 so they are not important as odorants. Therefore their evaluations were done for individual components of the VOCs in this section and they are not added to the evaluations.

Propanal which is an odorous aldehyde was the most abundant odorous compound that was found in the sampling points. Especially in May and September 2005 sampling periods propanal and similar aldehyde compounds were found to be responsible for the odor in the landfill. On the other hand, valeric, formic and butyric acids (VFAs) were the key odorants at the medical waste burial site in May 2005 sampling period. Toluene and formic acid were also effective in the municipal solid waste dumping sites in May 2005 sampling period. Fig 4.6 illustrates the odorous component contributions in May 2005 sampling period. The percent contributions in the figure were the ratio of OAV of the compound to the total OAVs of the odorous compounds given.

In September 2005 sampling period, aldehyde compounds were dominating the odor concentrations at all sampling locations (Fig. 4.7). The contributions of other odorous compounds were not significant in this sampling period. The contributions of monoaromatic compounds were not important in these sampling periods.

In May 2006 sampling period propanal and similar aldehyde compounds were still dominating the odor concentrations but significant contributions of hydrogen sulfide and monoaromatic compounds especially toluene were seen, too. Especially at medical waste burial site hydrogen sulfide was the second abundant odorous compound and the contributions of hydrogen sulfde were also present at raw waste dumping sites (Site 3 and Site 4). At these raw waste dumping sites toluene was also dominating the odors together with propanal. Fig 4.8 presents the odorous component contributions in May 2006 sampling period.

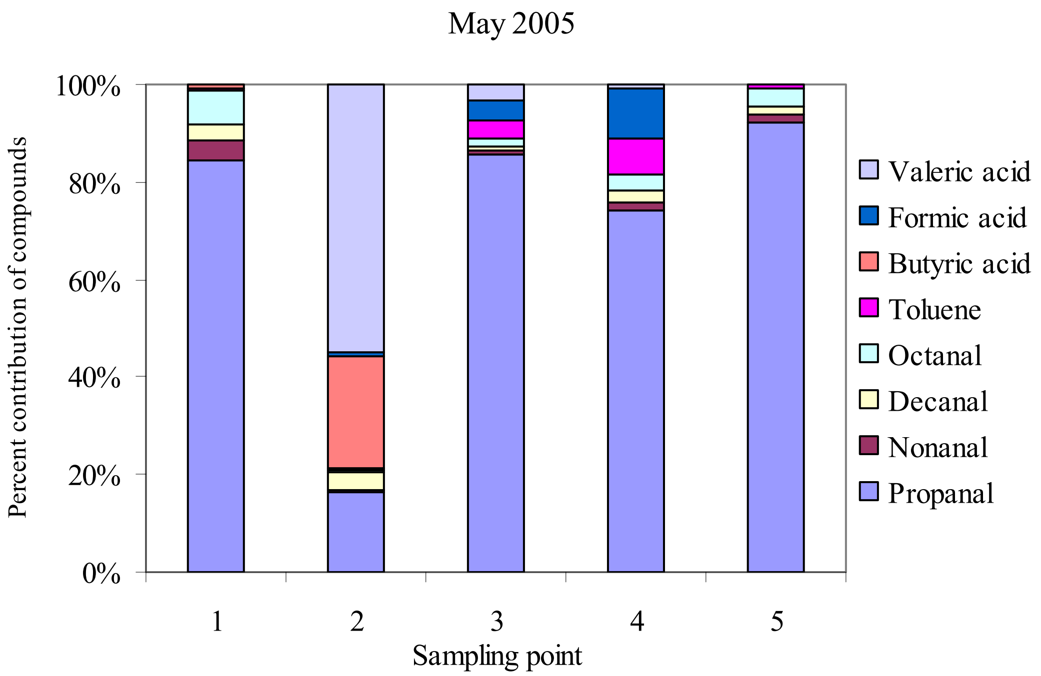

Figure 4.6 Odorous component contributions in May 2005 sampling period in landfill

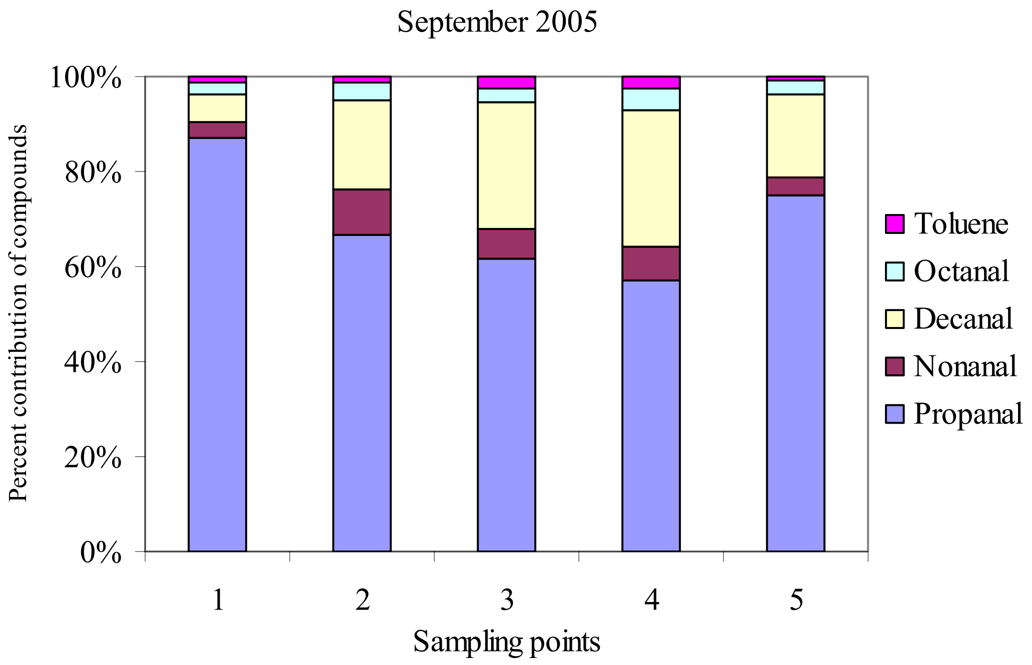

Figure 4.7 Odorous component contributions in September 2005 sampling period in landfill

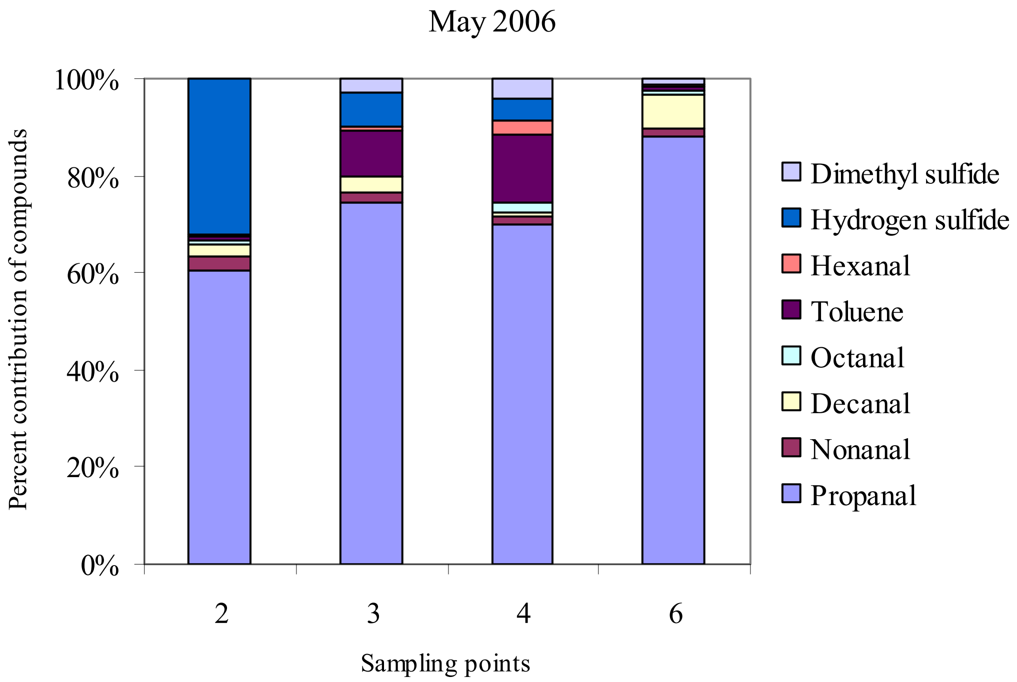

Figure 4.8 Odorous component contributions in May 2006 sampling period in landfill

Among the identified and quantified 53 compounds, 11 compounds were found to be the key odorants in the landfill. The dominance of aldehyde compounds might be due to their unpleasant and suffocating vegetable and fruity odor characteristics and low odor threshold concentrations. Most significant contributions were notable especially in municipal waste dumping sites.

After finding the key odorants in the landfill, the relationships between odor concentrations and concentrations of these odorants were investigated. Linear regression analysis were performed for odor concentrations versus OAVs of propanal and toluene. Statistically significant correlations were found between odor and propanal concentrations (r^2 = 0.27, n = 14, P<0.05) (Figure 4.9) and between odor and toluene concentrations (r^2 = 0.29, n = 14, P<0.05) (Figure 4.10)

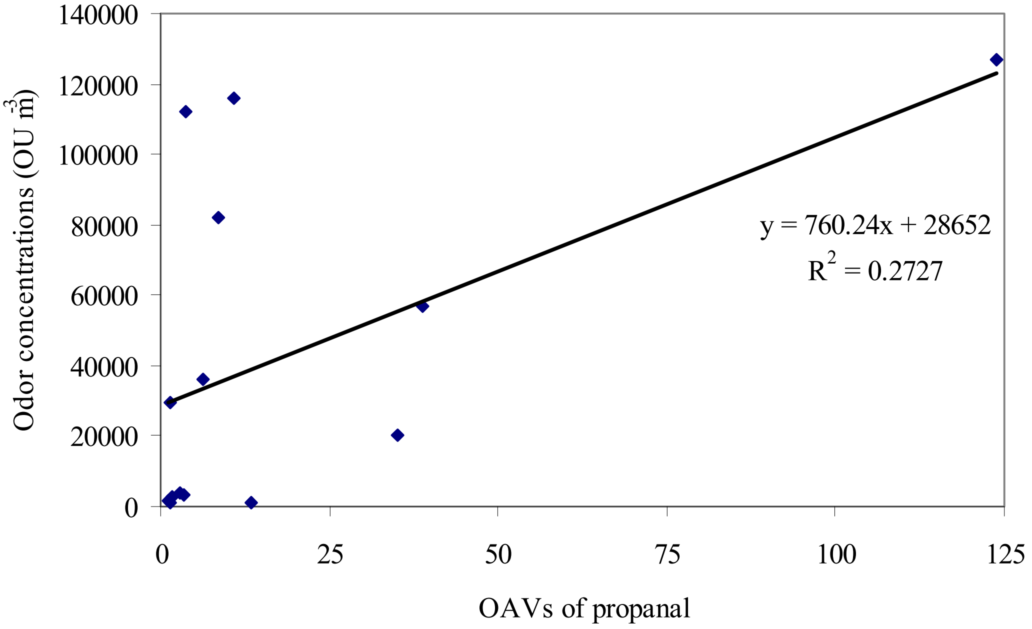

Figure 4.9 Relationship between odor concentrations and OAVs of propanal in landfill samples

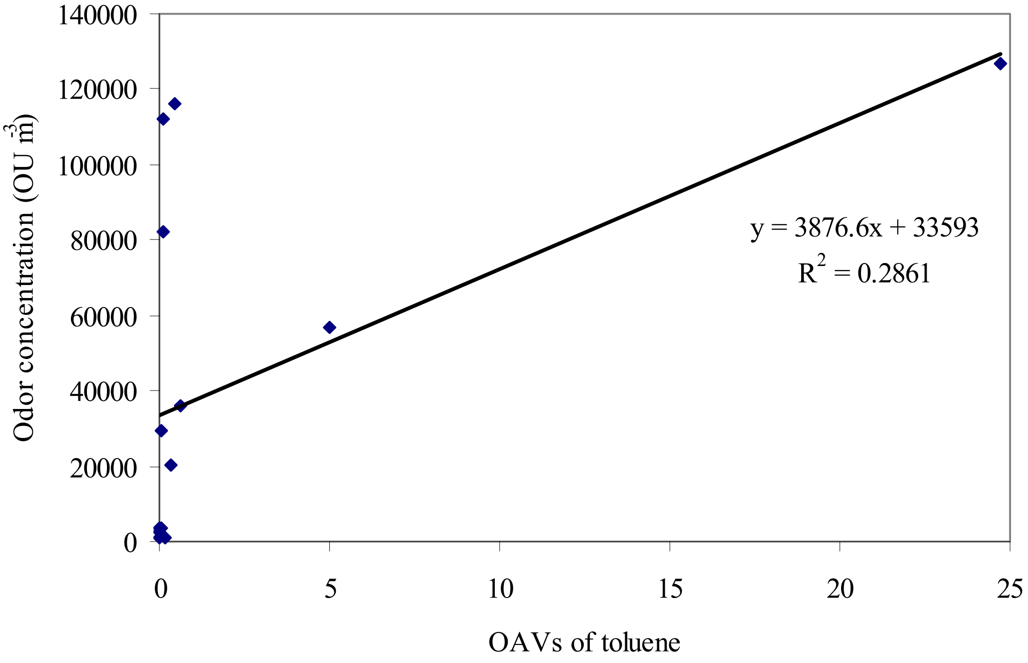

Figure 4.10 Relationship between odor concentrations and OAVs of toluene in landfill samples

4.2 Results of Aliağa measurements

4.2.1 VOC composition and concentrations

In all of the sampling campaigns, the odorous samples from ambient air of Aliağa have consisted of several compounds. The total numbers of VOCs identified and quantified were 43, 38 and 45 VOCs in May 2005, September 2005, and June 2006 sampling campaigns, respectively. Concentration ranges and mean values of each identified and quantified compound are also given in Table 4.8. The measured VOCs were classified as monoaromatics (e.g. benzene, toluene), halogenated compounds (e.g. chlorobenzene, trichloroethene), aldehydes (e.g. hexanal, propanal), ketones (e.g. acetone), VFAs (e.g. acetic acid, formic acid), esters (e.g. butyl acetate, butyl formate). Reduced sulfur compounds (RSC) such as H_2S, CS_2, dimethyl sulfide (DMS), dimethyl disulfide (DMDS) were also present in the composition of odorous gas.

In May 2005, the abundant group was monoaromatics (55% of total VOC concentrations) followed by ketones (18%), aldehydes (14%), halogenated compounds (7%), volatile fatty acids (VFAs) (5%) and esters (1%).

In September 2005, the compositions of the odorous gas samples were different from May samples. In September, aldehydes had the highest concentration (41% of total VOC concentrations) followed by ketones (27%), monoaromatics (18%), halogenated compounds (6%), and esters (2%). In September 2005, VFAs were not found in the samples. And in June 2006, the abundant group was monoaromatics (42% of total VOC concentrations) followed by halogenated compounds (21%), aldehydes (17%), ketones and RSCs (9%) and esters (2%).

The seasonal variations of concentrations of monoaromatics, halogenated compounds and aldehydes in Aliağa are presented in Fig. 4.11.

Table 4.8 VOC concentrations (ranges and mean values) of ambient air of Aliağa

	Concentration range (µg m^{-3})		
	May 2005	**September 2005**	**June 2006**
Acrolein	1.13-4.64 (2.42)	0.95-4.06 (3.58)	1.39-14.78(7.61)
Butanal	0.24-0.45 (0.34)	0.31-0.99 (0.57)	0.20-0.86(0.56)
Crotonaldehyde	0.06-0.07 (0.06)	0.07-0.18 (0.11)	0.05-3.59(2.10)
Decanal	0.33-0.87 (0.62)	0.24-1.21 (0.67)	2.01-5.54(3.52)
Heptanal	0.22-0.24 (0.23)	0.20-1.53 (0.83)	0.18-0.54(0.37)
Hexanal	0.65-1.45 (0.93)	0.12-1.55 (0.63)	0.68-2.70(1.87)
Nonanal	0.41-0.88 (0.69)	0.19-1.94 (0.92)	1.24-3.89(2.98)
Octanal	0.15-0.59 (0.40)	0.41-2.67 (1.10)	0.41-1.75(1.02)
Pentanal	0.20-0.40 (0.31)	0.36-2.04 (1.01)	0.23-0.80(0.50)
Propanal	5.19-7.42 (5.94)	1.64-7.30 (4.50)	7.19-16.60(10.89)
Butyl Acetate	0.04-0.05(0.05)	0.03-0.35 (0.09)	0.11-6.76(2.05)
Butyl formate	0.05*	0.02-0.03 (0.02)	n.d.
Butyl Propionate	n.d.	0.01*	n.d.
Methyl propionate	n.d.	n.d.	n.d.
Vinyl acetate	0.04-0.32 (0.13)	0.14-0.86 (0.32)	0.15-1.60(0.81)
Benzene	1.29-22.17 (8.27)	0.23-2.65 (0.90)	0.38-95.51(17.73)
Ethylbenzene	0.67-1.63 (1.00)	0.11-066 (0.37)	0.23-16.79(5.29)
o, m - Xylene	1.98-5.53 (3.19)	0.19-1.51 (0.72)	0.56-52.43(23.03)
p-Xylene	0.92-13.77 (5.22)	0.11-0.77 (0.44)	0.36-37.81(16.51)
Styrene	0.45-1.05 (0.67)	0.15-0.40 (0.29)	0.04-2.55(0.52)
Toluene	3.42-76.20 (27.79)	0.69-13.98 (3.37)	1.41-57.60(15.85)
1,1,1-Trichloroethane	0.05*	0.02-0.02 (0.02)	0.03-0.09(0.05)
1,1,2,2-Tetrachloroethane	0.02-0.02 (0.02)	n.d.	n.d.
1,1,2-Trichloroethane	n.d.	n.d.	0,14
1,1-Dichloroethane	0.02-0.04 (0.03)	0.01-0.02 (0.01)	0.03-0.06(0.04)
1,1-Dichloroethene	0.01-0.01 (0.01)	0.04-.04 (0.04)	0.68-3.92(1.73)
1,2-Dichlorobenzene	0.01-0.68 (0.24)	0.003-0.01 (0.006)	0.02-0.05(0.03)
1,2-Dichloroethane	0.12-2.22 (0.89)	0.02-0.52 (0.12)	0.02-0.14(0.07)
1,2-Dichloropropane	n.d.	n.d.	n.d.
1,3-Dichlorobenzene	0.003-0.03 (0.01)	n.d.	0,02
1,4-Dichlorobenzene	0.09-0.73 (0.34)	0.02-0.06 (0.04)	0.53-6.12(4.59)
Bromodichloromethane	n.d.	n.d.	0,01
Bromoform	0.01*	n.d.	0.01-0.02(0.01)
Carbon tetrachloride	0.09-0.13 (0.10)	0.09-0.14 (0.12)	1.74-5.41(3.18)
Chlorobenzene	0.01-0.02 (0.01)	0.01-0.02 (0.02)	0.03-0.07(0.05)
Chloroform	0.02-0.03 (0.03)	0.03-0.05 (0.04)	0.08-0.19(0.14)
cis-1,3-Dichloropropene	n.d.	n.d.	n.d.

Data in brackets represent the average concentrations; n.d., not detected; n.s., not studied
* Identified only at one sampling site

Table 4.8 VOC concentrations (ranges and mean values) of ambient air of Aliağa (cont.)

	Concentration range (µg m^{-3})		
	May 2005	**September 2005**	**June 2006**
cis-1,4-Dichloro-2-butene	n.d.	n.d.	n.d.
Dibromochloromethane	n.d.	n.d.	0,01
Iodomethane	n.d.	n.d.	n.d.
Methylene chloride	0.89-6.35 (3.12)	0.51-2.04 (1.28)	16.56-47.86 (30.14)
Tetrachloroethene	0.03-0.08 (0.05)	0.02-0.04 (0.04)	0.01-0.22(0.10)
trans-1,2-Dichloroethene	n.d.	n.d.	n.d.
trans-1,3-Dichloropropene	n.d.	n.d.	n.d.
trans-1,4-Dichloro-2-butene	0.002*	n.d.	0,03
Trichloroethene	0.13-1.53 (0.62)	0.06-0.53 (0.17)	0.18-0.90(0.51)
2-Butanone	n.d.	n.d.	n.d.
2-Hexanone	0.05*	0.03-0.09 (0.06)	0,1
4-Methyl-2-pentanone	0.01-0.03 (0.02)	0.02-0.12 (0.05)	0,1
Acetone	10.78-20.32 (14.85)	6.39-15.89 (10.19)	11.05-19.52 (16.16)
Cyclohexanone	n.d.	n.d.	0.10-0.12(0.11)
Acrylonitrile	0.38-0.48 (0.43)	0.37-0.73 (0.51)	0,02
Formic acid	3-8 (6)	n.s.	n.s.
Acetic acid	0.11-0.12 (0.11)	n.s.	n.s.
Methyl mercaptan	n.s.	n.s.	n.d.
Ethyl mercaptan	n.s.	n.s.	n.d.
Dimethyl sulfide	n.s.	n.s.	0.05-0.63 (0.23)
Carbon disulfide	0.28-0.32 (0.30)	0.43-1.44 (0.92)	1.22-21.04(8.28)
2-methyl-2-propanethiol	n.s.	n.s.	n.d.
n-propyl mercaptan	n.s.	n.s.	n.d.
Dimethyl disulfide	n.s.	n.s.	0.03-0.72(0.26)
Tetrahydrothiophene	n.s.	n.s.	n.d.
Hydrogen sulfide	n.s.	n.s.	3-14 (9)

Data in brackets represent the average concentrations; n.d., not detected; n.s., not studied
* Identified only at one sampling site

Petroleum refineries and petrochemical plants emit high quantities of many organic vapors and gases into the atmosphere. These compounds mainly originate from the production processes, the storage tanks and the waste areas. Along with regulated stack emissions, fugitive emissions are also important in these industries. The differences in the airborne levels of these compounds around these facilities in Aliağa are dependent upon the changes in production processes of petrochemicals and petroleum refining as well as meteorological factors. As expected, monoaromatics and halogenated compounds are mainly related to the significant impact of the petroleum industries in May 2005 and June 2006 period. But in September 2005 period the concentration levels of monoaromatics were much lower. This triggered the high levels of aldehyde and ketones in September 2005 period. The difference might be related to changes in production processes of refinery and petrochemical plant.

Monoaromatics had significant concentrations in May 2005 and June 2006 samples (Figure 4.11). High levels of benzene and toluene were measured in the samples. Benzene is a known carcinogen and exposure to 1 µg m^{-3} produces a lifetime risk of $4*10^{-6}$ for leukaemia (WHO, 1987). Usually, 5 µg m^{-3} is considered as a practical limit (ENDS, 1996). Benzene levels in excess of this limit were found at some sampling points in Aliağa and maximum value measured was up to 95.51 µg m^{-3}. This may present a significant health hazard to the community in Aliağa.

Fifteen chlorinated compounds were detected in May 2005, 12 chlorinated compounds were detected in September 2005 samples and 18 chlorinated compounds were detected in June 2006 samples. 1.2 Dichloroethane is produced in vinyl chloride process of the petrochemical complex located in Aliağa area as an intermediate compound of the reaction between ethylene and Cl_2. 1.2 Dichloroethane is also a gasoline additive used as a lead scavenger (Barletta et al., 2002) and might have originated from the petroleum refinery nextdoor or from the heavy traffic around.

In September 2005, the average concentrations of some chlorinated species such as chloroform, carbon tetrachloride, chlorobenzene, trichloroethene, tetrachloroethene and 1.2 Dichloroethane were 0.05, 0.12, 0.02, 0.17, 0.04 and 0.12 µg m^{-3}, respectively (Figure 4.9). In May 2006, the average concentrations of chloroform, carbon tetrachloride, chlorobenzene, trichloroethene, tetrachloroethene and 1.2 Dichloroethane were 0.14, 3.18, 0.05, 0.51, 0.10 and 0.07 µg m^{-3}, respectively (Figure 4.11). Compared to monoaromatic compounds, the concentrations of chlorinated species were relatively lower in this study.

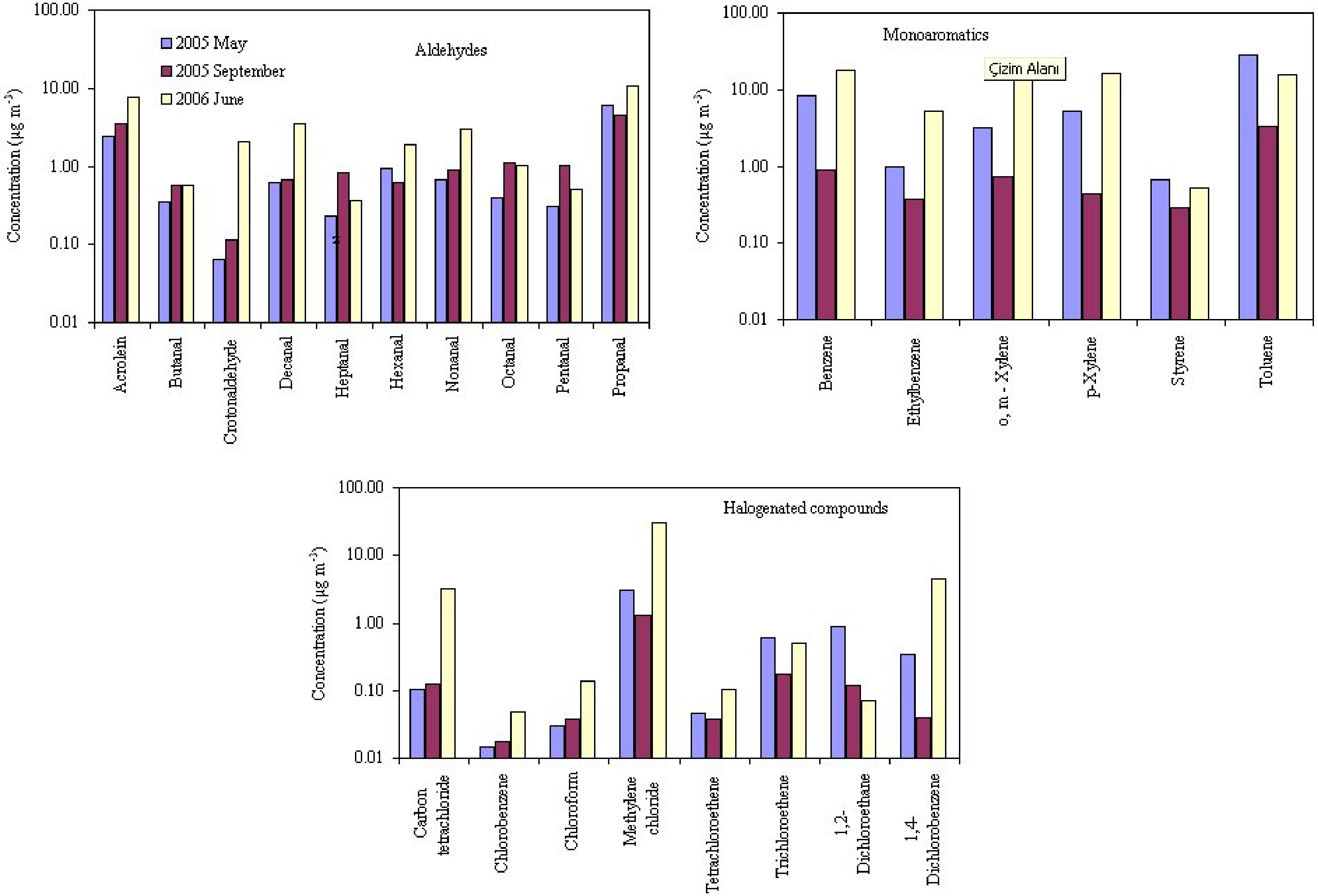

Figure 4.11 Seasonal variations of concentrations of monoaromatics, halogenated compounds, aldehydes in Aliağa

High levels of aldehydes and ketones were observed at each sampling point in all sampling campaigns. Among them Propanal has been leading. This gas has a pungent, suffocating and unpleasant odor characterizing the industrial emissions. Propanal was found above the odor threshold of 3.6 µg m^{-3} (USEPA, 1992) in almost all sampling points in Aliağa (Figure 4.11). Acetone at high concentrations was the abundant ketone in the odorous gas samples.

Some esters and acrylonitrile were also identified and quantified in Aliağa. However, the concentrations of these compounds were relatively low compared to other chemical groups. For example, concentration range of butyl acetate was 0.11 to 6.76 µg m^{-3} in June 2006 samples. Acrylonitrile was found in all sampling campaigns but its concentration level was much lower compared to other compounds.

In June 2006 samples, H_2S, CS_2, DMS and DMDS were found with average concentrations of 9 µg m^{-3}, 8 µg m^{-3}, 0.23 µg m^{-3}, 0.26 µg m^{-3}, respectively. These concentrations were relatively lower than the levels that were measured in the landfill and WWTP in the study.

The concentrations of the compounds were shown to have similar patterns in May 2005 and September 2005 sampling periods in Aliağa. However, the concentrations were much higher in June 2006 sampling period. In this period, concentration values were increased 10-fold in some cases.

Similarly high levels of benzene, toluene and xylene (BTX) concentrations were reported in literature. Srivastava et al. (2006) reported mean BTX concentrations as 45.31, 1.12 and 29.16 µg m^{-3} at residential areas, respectively. Lin et al. (2004) conducted a study to find the ambient air concentrations of benzene, toluene, ethylbenzene and xylene (BTEX) of a petroleum refinery. The authors reported BTEX concentrations at a range of 6-2155 µg m^{-3}, 53-2958 µg m^{-3}, 11-725 µg m^{-3}, 10-292 µg m^{-3}, respectively. However these studies did not include odor measurements.

As discussed in Section 4.1.1 benzene-to-toluene (B:T) ratio has been used as an indicator of traffic emissions. B:T ratios around 0.5 may indicate that the ambient VOC concentrations are mainly affected by traffic emissions. The evaluations related to B:T ratios were done by using the results of sampling points 4, 7, 8 and 10 because these points were residential points and were mainly affected by traffic. As Aliağa is a town with large petroleum industries, there might be many benzene sources close to the other sampling points which are classified as industrial points in section 3.2.2. Benzene-to-toluene ratios measured in this study were 0.55 and 0.27 in September 2005 and June 2006 period, respectively indicating the ambient VOC concentrations are mainly affected by traffic emissions (Table 4.9).

Table 4.9 Comparison of average benzene and toluene levels (µg m^{-3}) and B:T ratios in ambient air at selected locations

Benzene	Toluene	B:T	Site	Reference
0.59	1.8	0.55	Aliağa	This study (September 2005)
0.38	1.41	0.27	Aliağa	This study (June 2006)
3.31	15.39	0.22	Izmir (urban)	Elbir et. al.,
37.6	102	0.37	Izmir (urban)	Muezzinoglu et. al., (2001)

4.2.2 Spatial distribution of odor and VOCs

As shown in Fig. 3.1 sampling and analysis were carried out at ten points in Aliağa. Six points were located at industrial regions while remaining (sampling points: 4, 7, 8, 10) were chosen as residential points. Sampling point 4 was at the south of Aliağa and about 15 km far from the refinery and petrochemical complex while sampling point 8 was in the north and about 5 km far from the industries. Sampling points 7 and 10 were near to the industries; especially the point 7 was very close to the industries. The concentration variations of odor, monoaromatics, some of the halogenated compounds, aldehydes and acetone in different points were presented in Fig. 4.12. It was found that the VOC levels of residential points were lower than the industrial points. Same pattern was seen in odor concentrations except the sampling point 7. This meant that being so close to the industries, this point was affected by them in prevailing winds of south-westerly.

The average odor concentrations of the sampling points were between 10 and 438 OU m^{-3}. Odor concentrations of the industrial points were higher than the residential ones. Besides, these odor concentration levels might create serious odor annoyance in the community. Especially the neighborhood of the point 7 (ENKA sports center) were exposed high levels of odor. As shown in Fig. 4.12, odor level of Aliağa center (point 10) was in agreement with Aliağa quarantine (point 8). These points were less affected by the industries.

Apart from the other VOCs, high monoaromatic concentrations appeared in the industrial points. Among these sampling points, points 2, 3, and 5 have much higher concentrations because both of them were located at the central of the industries. Under the northwesterly winds, the concentrations of these three points were increasing seriously. The sampling point (point 6) located upwind of the industries had lower concentrations than the central points. The sampling point 5, which was very close to petrochemical complex, had the highest odor and VOC concentrations. It was possible that the point 5 located at the downwind direction as well as receives not only petrochemical complex emissions but also the refinery emissions.

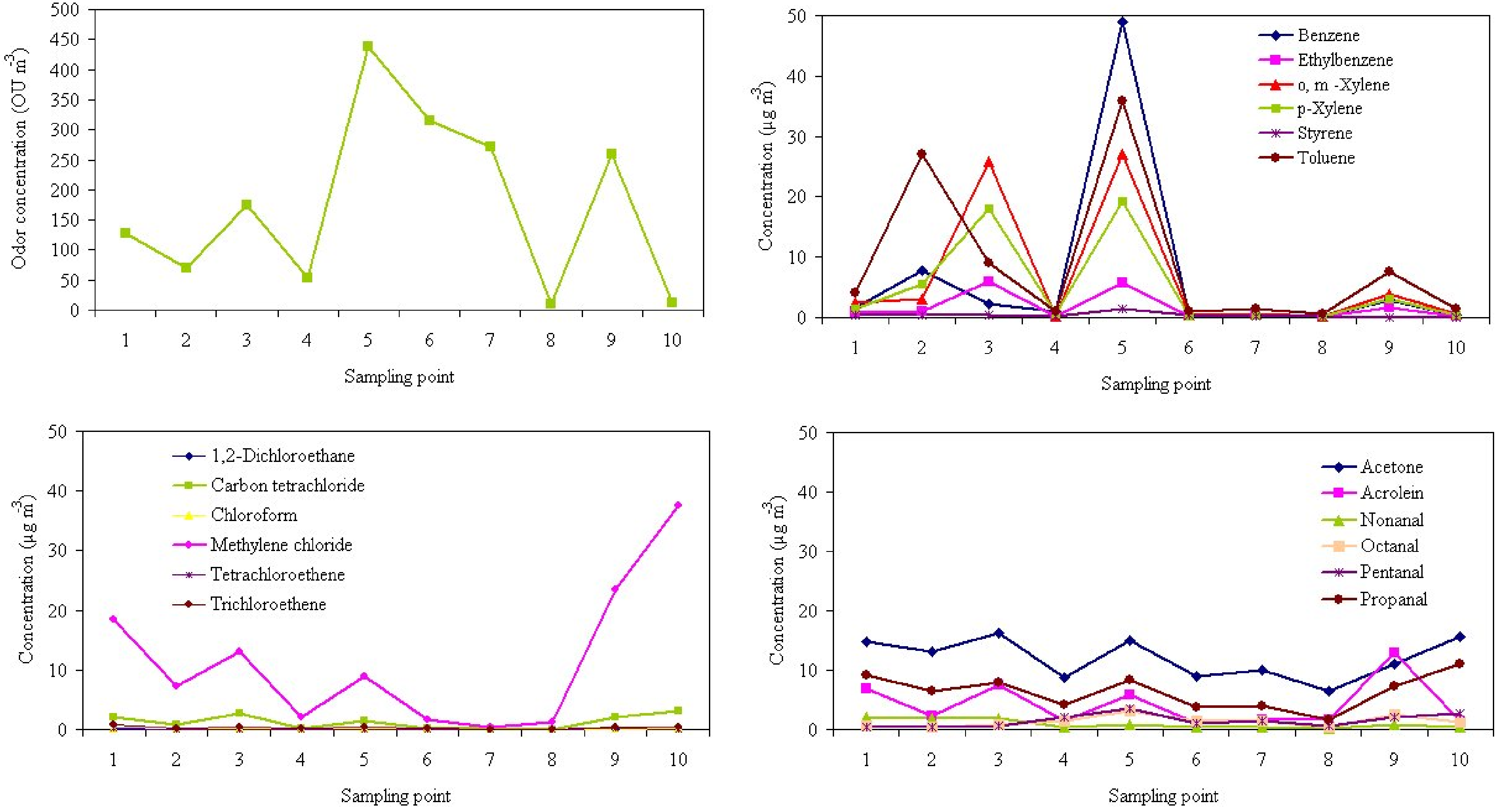

Figure 4.12 Spatial average concentration variations of odor, monoaromatic, halogenated compounds and aldehydes from point to point sampling in Aliağa

4.2.3 Odor and TVOC concentrations

The results of olfactometric and chemical analysis of the three sampling campaigns are given in Table 4.10 and Fig. 4.13. For May 2005 samples, olfactometric concentrations varied between 30-83 OU m^{-3} (mean value 43 OU m^{-3}) and the TVOC concentrations varied between 47-156 µg m^{-3} (mean value 84 µg m^{-3}). For September 2005, the olfactometric and TVOC concentrations ranged between 10-362 OU m^{-3} (average, 121 OU m^{-3}) and 16-60 µg m^{-3} (average, 33 µg m^{-3}) and for June 2006, olfactometric concentrations varied between 13-626 OU m^{-3} with a mean value of 178 OU m^{-3} and TVOC concentrations varied between 86-355 µg m^{-3} (average, 187 µg m^{-3}).

The results of chemical analysis of the three sampling campaigns with respect to the chemical groups and the odor concentrations are presented in Table 4.11.

In September 2005 and June 2006, both odor concentrations and TVOC concentrations have shown similar patterns. In June 2006, both odor and TVOC concentrations were higher than the other two sampling campaigns. In September 2005, TVOC concentrations were relatively lower.

Table 4.10 Odor (OU m^{-3}) and TVOC (µg m^{-3}) concentrations of the Aliağa samples

	May 2005		September 2005		June 2006	
	Odor	TVOC	Odor	TVOC	Odor	TVOC
Refinery main gate	32	39±3	146	40±2	452	169±9
Refinery-petrochemical complex border	83	152±19	65	30±2	63	86±4
Clauss plant area	30	47±5	288	37±2	626	305±16
Horozgediği	-	-	54	27±2	-	-
Petrochemical complex main gate	-	-	362	60±4	530	355±20
Ship dismantling area	-	-	314	24±2	-	-
ENKA sports center	-	-	271	26±2	-	-
Aliağa quarantine	-	-	10	16±1	-	-
Tank field	-	-	-	-	260	112±5
Urban-Aliaga	-	-	-	-	13	94±7

- not studied

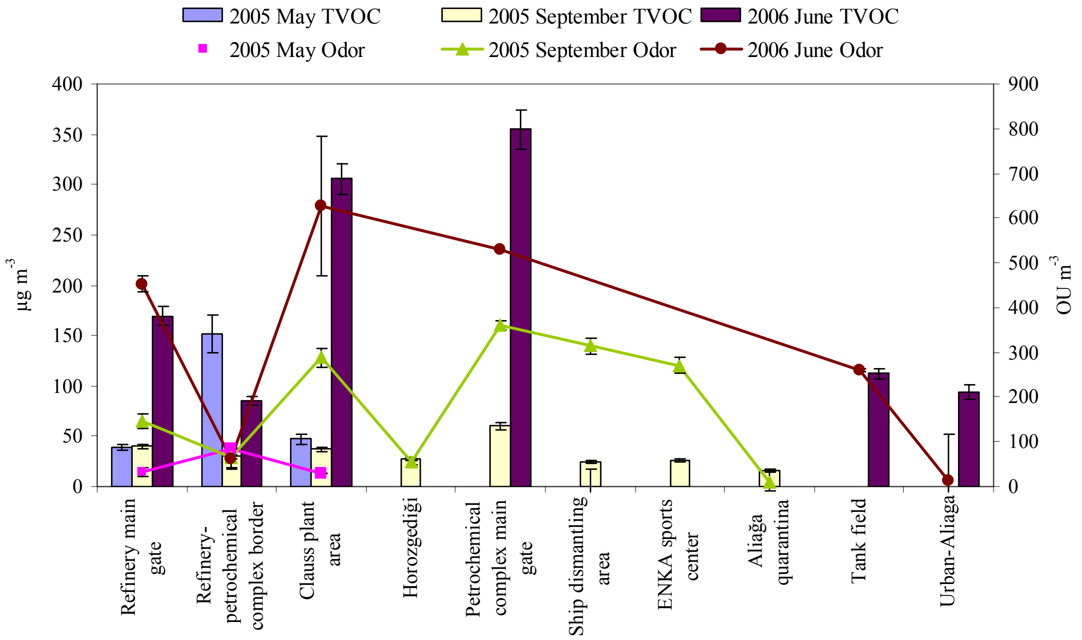

Figure 4.13 Variations of odor and TVOC concentrations in May 2005, September 2005 and June 2006 samples in Aliağa

Table 4.10 Concurrent data sets of the odor concentrations (OU m^{-3}) and chemical concentrations (µg m^{-3}) for three sampling campaigns in Aliağa

Sampling Campaign	Sampling point number	Sampling points	Odor	TVOC	VFAs	Aldehydes	Esters	Monoaromatics	Halogenated compounds	Ketones	RSCs
May 2005	1	Refinery main gate	32±10	47±3	8*	10±2	0.14±0.007	9±1	9±2	11±6	n.s.
	2	Refinery-petrochemical complex border	83±6	155±19	4±2.5	12±2	0.08±0.004	12029±	6±0.75	13±9	n.s.
	3	Clauss plant area	30±0	47±5	0.11*	14±2	0.37±0.18	9±1	2±0.24	20±14	n.s.
September 2005	1	Refinery main gate	146±55	40±2	n.s.	17±2	0.50±0.21	8±1	2±0.45	13±7	n.s.
	2	Refinery-petrochemical complex border	65±8	30±2	n.s.	14±2	0.22±0.09	4±1	1±0.33	10±7	n.s.
	3	Clauss plant area	288±121	37±2	n.s.	20±3	1±0.57	6±1	2±0.35	9±6	n.s.
	4	Horozgediği	54±4	27±2	n.s.	12±1	0.24±0.11	3±0.41	3±0.62	9±5	n.s.
	5	Petrochemical complex main gate	362±80	60±4	n.s.	22±3	1±0.07	20±5	2±0.35	16±11	n.s.
	6	Ship dismantling area	314±156	24±2	n.s.	10±1	0.32±0.12	2±0.33	2±0.52	9±5	n.s.
	7	ENKA sports center	271±150	26±2	n.s.	11±1	0.39±0.16	4±0.48	1±0.16	10±7	n.s.
	8	Aliağa quarantine	10±3	16±1	n.s.	6±0.6	0.22±0.06	1±0.22	2±0.37	6±4	n.s.
June 2006	1	Refinery main gate	452±40	169±9	n.s.	46±6	2±0.74	15±2	60±13	21*	24±10
	2	Refinery-petrochemical complex border	63±8	86±4	n.s.	21±2	1±0.27	9±1	26±6	16±11	13±5
	3	Clauss plant area	626±23	305±16	n.s.	36±5	8±4	170±29	49±10	20*	23±7
	5	Petrochemical complex main gate	530±104	355±20	n.s.	34±3	4±3	257±34	31±5	14±8	15±4
	9	Tank field	260±156	112±5	n.s.	33±4	2±0.72	19±3	32±7	11±8	15±5
	10	Urban Aliağa	13±3	94±7	n.s.	18±3	n.d.	3±0.48	43±10	16*	14±4

n.d.,not detected; n.s., not studied; *detected only in one sampling point

4.2.4. Relationship between the odor and total VOC concentration

The relationship between concentrations of odors and total VOCs measured in Aliağa samples was statistically analyzed. Linear regression analyses were performed on the dataset. Results including the formula, R^2 and P values are presented in Table 4.12. There were statistically significant relationships between odor and TVOC concentrations in June 2006 samples. Results indicated that 77% of the variance in odor concentrations could be explained by TVOC concentrations in May 2006 samples. No significant relation was present in May 2005 and September 2005 samples.

Table 4.12 The relationships between odor and TVOC concentrations in the samples of Aliağa measurements

Sampling campaign	n	Formula	R^2	*P* value
May 2005	3	$OC = 0.47\ C_{TVOC} + 10.72$	0.99	0.06
September 2005	8	$OC = 5.87\ C_{TVOC} – 2.18$	0.34	0.13
June 2006	6	$OC = 1.91\ C_{TVOC} – 33.67$	0.77	0.02*
May 05+September 05+June 06	17	$OC = 1.39\ C_{TVOC} + 79.42$	0.50	0.001*

* statistically significant

For the overall dataset result of linear regression analysis indicated a statistically significant relationship between odor and TVOC concentrations as 50% of the variance in odor concentrations can be explained by the TVOC concentrations (r^2= 0.51, n=17, $P<0.01$) (Figure 4.14).

The relationships of odor concentrations with the concentrations of different groups of chemicals were further examined using a step-wise multiple regression analysis. It was found that the concentrations of aldehydes and monoaromatics were the best estimators, explaining 68% of the variability in odor concentrations (r^2 = 0.68, n = 17, $P<0.05$) in all the dataset.

In addition, a correlation matrix was calculated for different variables and Pearson coefficients are given as a measure of relationship between groups of variables. The results are given in Table 4.13. There are statistically significant correlations

($P<0.05$) between odor concentrations and TVOC, aldehyde, ester and monoaromatic concentrations.

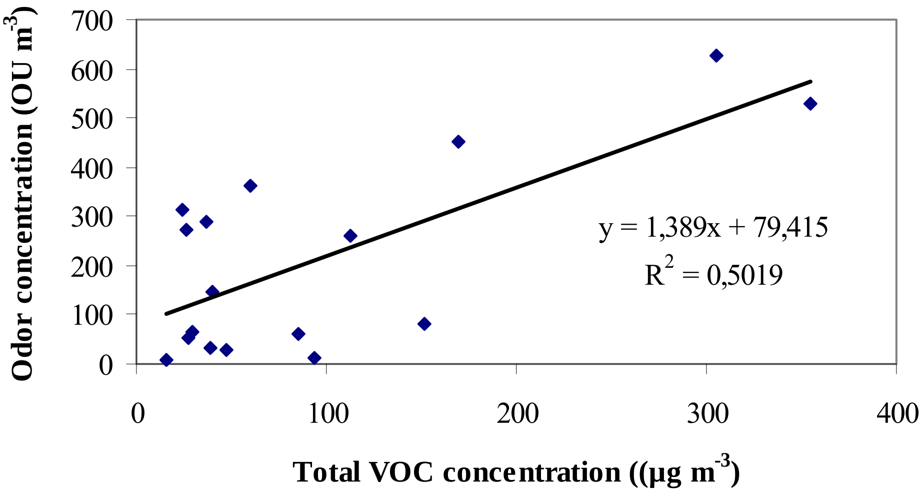

Figure 4.14 The relationship between odor and TVOC concentration for all dataset

4.2.5. Evaluations based on odorous component contribution analyses

As discussed before contributions of different components in sensed odor levels are dependent on two parameters; concentration of the component and threshold level of the pure compound. A unitless number showing the odor activity of measured components is established by dividing the concentration of the odorous compound to its odor threshold (Qian & Reineccius, 2003). Like for landfill samples, same evaluations were done for Aliaga samples. The odor contribution ratios of the compounds in composition of the odorous gas emissions of the Aliaga samples are presented in Appendix-D.

Among the identified and quantified 45 compounds 6 compounds were found to be key odorants in Aliağa. Propanal was the abundant odorous compound that was found in the sampling points and propanal and such aldehyde compounds especially decanal were dominating the odor concentrations of the three sampling periods. Toluene was also effective in odor concentrations at the sampling points 2 and 5 which were very close to the refinery and petrochemical complex. For June 2006 sampling period significant contributions of hydrogen sulfide were obtained. Fig. 4.15 and Fig. 4.16 show the contributions of odorous compounds for the sampling periods of September 2005, and June 2006, respectively. As mentioned before the contributions of these compounds were due to their low odor threshold concentrations. The contributions of other chemical groups were not significant because of their high odor threshold concentration levels.

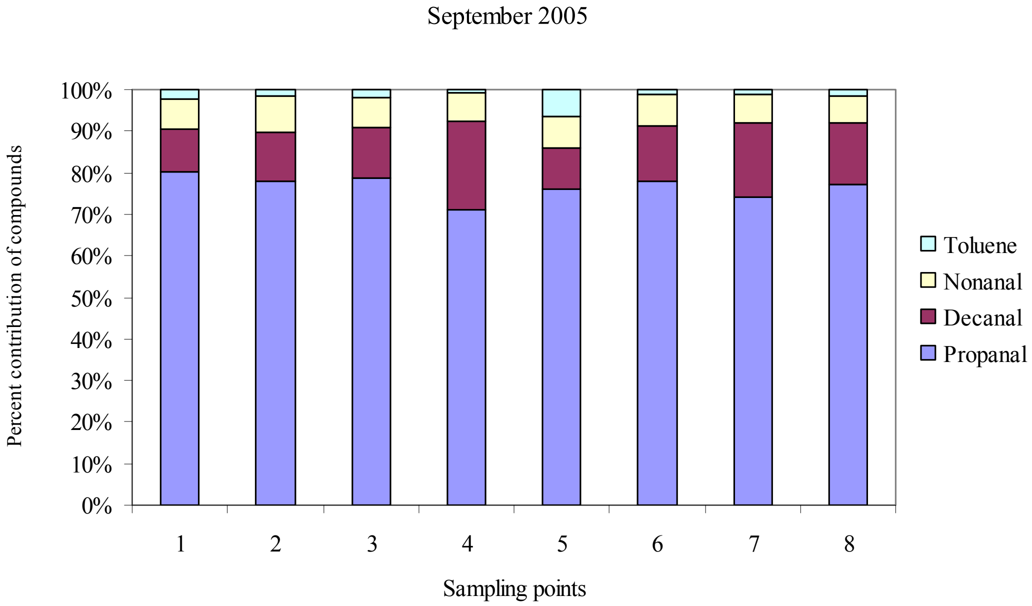

Figure 4.15 Odorous component contributions in September 2005 sampling period in Aliağa

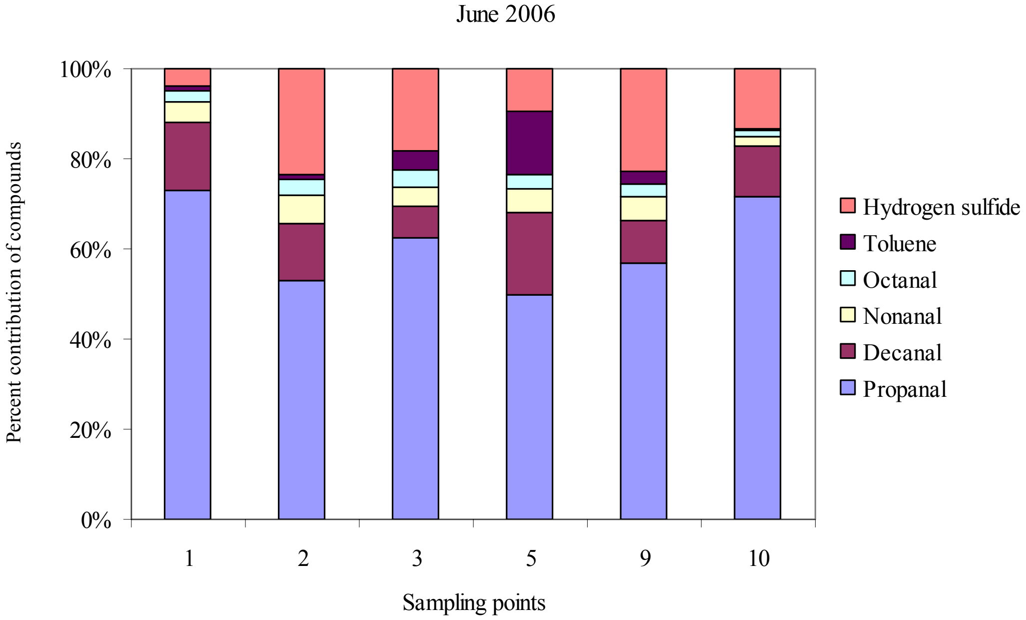

Figure 4.16 Odorous component contributions in June 2006 sampling period in Aliağa

The relationship between concentrations of odors and OAVs of propanal was statistically analyzed. It was found that the concentrations of propanal was the best estimator, explaining 33% of the variability in odor concentrations ($r^2 = 0.33$, n = 17, $P<0.05$) in the samples (Figure 4.17).

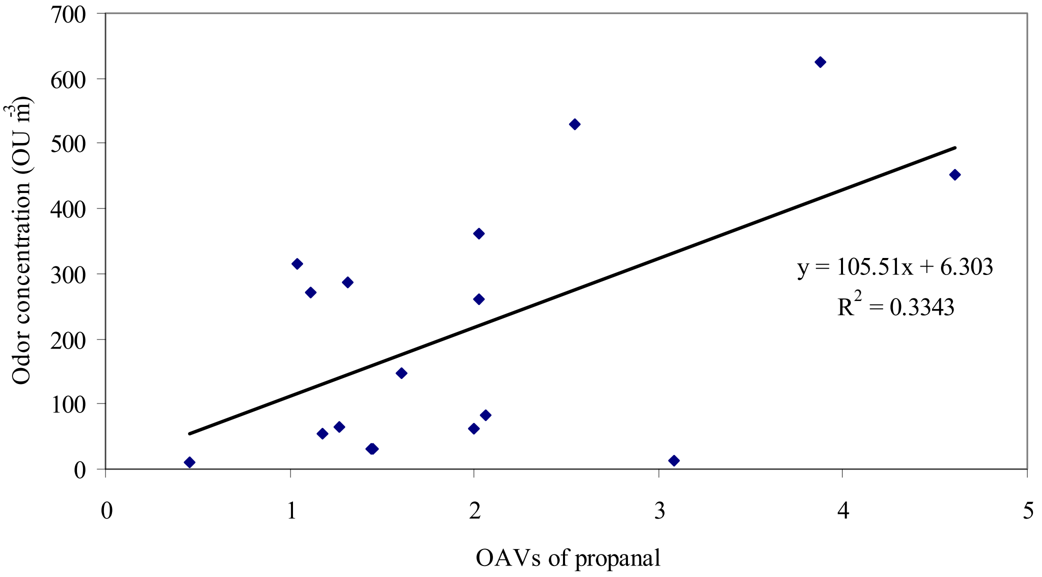

Figure 4.17 Relation between odor concentrations and OAVs of propanal for Aliağa samples

Table 4.13 Pearson correlation coefficients between the different compound groups and odor in Aliağa

	Odor concentration	Total VOC concentration	VFAs	Aldehydes	Esters	Monoaromatics	Halogenated compounds	Ketones	RSC
Odor	1	0.71*	0.03	0.75*	0.78*	0.70*	0.15	0.37	0.72
Total VOC		1	-0.008	0.73*	0.84*	0.90*	0.56*	0.52*	0.39
VFAs			1	-0.99	-0.74	0.99	-0.008	-0.95	n.a.
Aldehydes				1	0.70*	0.55*	0.37	0.64*	0.81
Esters					1	0.80*	0.26	0.47	0.58
Monoaromatics						1	0.19	0.29	0.14
Halogenated							1	0.42	0.88*
Ketones								1	0.80*
RSC									1

* statistically significant (*P*<0.05); n.a. not available

4.3 Results of WWTP measurements

4.3.1 VOC composition and concentrations

The odorous emissions from WWTP were consisted of several compounds. Fourthy-eight VOCs were detected in May 2006 sampling period. Analytical results for the odorous compounds with respect to the sampling locations are given in Table 4.14. The measured VOCs are classified as monoaromatics (e.g. benzene, toluene), halogenated compounds (e.g. chlorobenzene, trichloroethene), aldehydes (e.g. hexanal, propanal), ketones (e.g. acetone), esters (e.g. butyl acetate, butyl formate) and RSCs [H_2S, CS_2, dimethyl sulfide (DMS), dimethyl disulfide (DMDS)]. VFAs were not studied in WWTP due to analytical reasons.

The most abundant group was monoaromatics (57% of total VOC concentrations) followed by RSCs (12%), esters and halogenated compounds (10%), ketones (6%), and aldehydes (5%).

H_2S is not only malodorous and corrosive but also highly toxic. Tomar and Abdullah (1994) reported that long-term exposure to a concentration of 300 µg m^{-3} H_2S in air can cause death and human exposure to concentrations exceeding 2000 µg m^{-3} can be fatal within a few minutes. At H_2S concentration levels of 10 to 30 µg m^{-3} in air long term exposure causes eye and respiratory symptoms and headache (Marthilla et al., 1994). Accepted odor threshold level of H_2S is 0.1 µg m^{-3}. Apparently the World Health Organization (WHO) guideline value for H_2S of 150 µg m^{-3} (daily mean) is too high a figure to prevent the adverse health effects (Haahtela et al, 1992).

DMDS and DMS are emitted from both terrestrial and marine ecosystems. These substances are irritating to the skin, eyes and the respiratory tract and may cause effects on the central nervous system, but the toxicity of DMDS and DMS have not been well established.

Table 4.14 VOC concentrations (mg m^{-3}) of the WWTP with respect to treatment units

Component	**Screens**	**Primary settling**	**Aeration basin**	**Sludge basin**	**Sludge area**
1,1,1-Trichloroethane	0.34	2.16	82.06	21.27	0.69
1,1,2,2-Tetrachloroethane	n.d.	n.d.	n.d.	n.d.	n.d.
1,1,2-Trichloroethane	n.d.	n.d.	n.d.	n.d.	n.d.
1,1-Dichloroethane	0.05	0.20	2.22	1.67	0.08
1,1-Dichloroethene	n.d.	9.22	66.02	n.d.	n.d.
1,2-Dichlorobenzene	0.04	0.08	0.03	0.10	0.07
1,2-Dichloroethane	0.05	0.09	0.76	0.36	0.05
1,2-Dichloropropane	n.d.	n.d.	2.15	1.94	n.d.
1,3-Dichlorobenzene	n.d.	0.01	0.01	0.01	n.d.
1,4-Dichlorobenzene	7.13	8.04	11.96	8.52	5.76
2-Butanone	n.d.	n.d.	n.d.	n.d.	n.d.
2-Hexanone	n.d.	0.41	n.d.	n.d.	0.31
2-methyl-2-propanethiol	n.d.	n.d.	n.d.	n.d.	n.d.
4-Methyl-2-pentanone(MIBK)	n.d.	0.14	n.d.	1.78	n.d.
Acetone	61.57	98.57	60.53	76.54	135.33
Acrolein	n.d.	5.44	n.d.	n.d.	4.99
Acrylonitrile	0.05	0.05	n.d.	n.d.	0.19
Benzene	0.62	1.40	1.30	3.10	0.55
Bromodichloromethane	0.13	0.31	0.83	0.14	0.04
Bromoform	0.03	0.03	0.02	0.00	n.d.
Butanal	n.d.	1.83	0.23	1.63	2.88
Butyl Acetate	3.14	6.17	2.41	698.04	4.61
Butyl formate	0.08	0.07	0.12	0.44	0.06
Butyl Propionate	n.d.	n.d.	n.d.	n.d.	n.d.
Carbon disulfide	3.06	9.82	n.d.	2.86	1.77
Carbon tetrachloride	1.59	1.60	1.51	1.26	2.59
Chlorobenzene	0.08	0.14	0.11	0.26	0.14
Chloroform	1.19	4.62	32.75	13.74	4.23
Cis-1,3-Dichloropropene	n.d.	n.d.	n.d.	n.d.	n.d.
Cis-1,4-Dichloro-2-butene	n.d.	n.d.	n.d.	n.d.	n.d.
Crotonaldehyde	0.14	0.29	0.10	0.21	0.12
Cyclohexanone	0.14	1.16	n.d.	n.d.	0.00

n.d, not detected

Table 4.14 VOC concentrations (mg m^{-3}) of the WWTP with respect to treatment units (cont.)

Component	**Screens**	**Primary settling**	**Aeration basin**	**Sludge basin**	**Sludge area**
Decanal	3.69	7.68	3.17	4.79	2.59
Dibromochloromethane	0.09	0.15	0.25	0.05	0.01
Dimethyl disulfide	1.43	2.05	0.62	119.60	11.41
Dimethyl sulfide	0.59	1.24	0.66	21.04	10.04
Ethanethiol	0.22	n.d.	n.d.	n.d.	n.d.
Ethylbenzene	1.22	3.35	1.90	409.18	1.70
Heptanal	1.86	3.02	1.65	n.d.	1.68
Hexanal	4.77	10.53	3.98	6.11	5.66
Hydrogen sulfide	180	328	23	43	63
Iodomethane	n.d.	0.02	0.18	0.25	0.12
Methyl mercaptan	n.d.	n.d.	n.d.	9.18	n.d.
Methyl propionate	n.d.	n.d.	n.d.	n.d.	n.d.
Methylene chloride	16.09	25.07	32.07	36.43	91.74
Nonanal	6.38	9.14	2.98	3.72	4.73
n-propyl mercaptan	n.d.	n.d.	n.d.	n.d.	n.d.
o, m -Xylene	2.60	6.81	3.80	935.36	4.01
Octanal	2.04	6.99	3.35	8.17	1.80
Pentanal	0.68	1.44	0.59	1.03	1.02
Propanal	35.65	55.38	27.28	40.70	83.40
p-Xylene	2.65	7.25	3.91	1254.74	4.32
Styrene	0.30	0.70	0.46	12.04	0.33
Tetrachloroethene	3.27	1.79	40.63	12.91	0.94
Tetrahydrothiophene	n.d.	n.d.	n.d.	n.d.	n.d.
Toluene	12.56	23.68	14.47	1356.93	10.00
trans-1,2-Dichloroethene	n.d.	n.d.	n.d.	n.d.	n.d.
trans-1,3-Dichloropropene	n.d.	n.d.	n.d.	n.d.	n.d.
trans-1,4-Dichloro-2-butene	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroethene	1.86	4.05	34.88	78.21	1.97
Vinyl acetate	n.d.	n.d.	0.85	n.d.	n.d.

n.d., not detected

Hydrogen sulfide was the dominant volatile RSC emitted from Izmir WWTP. The concentration range was wide: the minimum level was measured at the aeration unit (23 µg m^{-3}), while the maximum was measured at the primary settling unit (328 µg m^{-3}). The average concentration of measured H_2S was 127 µg m^{-3}. The concentrations of H_2S in the treatment units of WWTP were above the odor threshold level. Measured H_2S in the primary settling unit was higher than the WHO guideline value which might affect the human health in long term exposure. Maximum H_2S concentrations measured in this study were found to be lower than the data found in previous studies. Devai and DeLaune (1999) found a maximum value of H_2S as 502.3 mg m^{-3} at WWTP in Baton Rouge. In another study, H_2S concentration levels of 15 to 38 mg m^{-3} were measured in the influent collection tank headspace in a WWTP in Tokyo (Hwang et al., 1995). But similar values were also reported in these studies.

DMDS, which was a methylated sulfur compound, was the second most abundant RSC in the gas samples. The concentration of DMDS (range 0.62 to 119.62 µg m^{-3}) was generally lower in all samples than H_2S except for sludge basin unit where DMDS was at its maximum. At this location it was more than double the H_2S. Concentrations similar to the levels in this study have been reported from a dairy (concentration range of 0.8 to 9.9 µg m^{-3}) (Filipy et al., 2006) and from the hog barns of swine facilities (concentration range of 0.5 to 8.6 µg m^{-3}) in North Carolina (Blunden et al., 2005).

DMS, which was another methylated sulfur compound, represented lower percentage (4% of RSC) among the RSCs measured in the samples. Maximum measured DMS was in the sludge basin with the concentration value of about 21µg m^{-3}. Cheng et al. (2005) reports high levels of DMS (up to 999 µg L^{-1}). But concentrations similar to levels measured in this study were found from a dairy (concentration range of 0.18 to 2.6 µg m^{-3}) (Filipy et al., 2006) and from the hog barns of swine facilities (concentration range of 0.6 to 40 µg m^{-3}) in North Carolina (Blunden et al., 2005).

CS_2 was present at relatively low concentrations in the gas samples obtained from Izmir WWTP. The minimum concentration (1.77 µg m^{-3}) was measured in sludge area of the WWTP, while the maximum was (9.82 µg m^{-3}) measured in primary settling unit. CS_2 was a component in photochemical reactions in the atmosphere, including smog formation (Vairavamurthy et al., 1992). CS_2 has a characteristic odor (sulfidy, ethereal) and is toxic to humans. Short-term exposure of CS_2 between 600 and 1500 µg m^{-3} could cause death (International Occupational Safety and Health Information Centre (CIS)). The measured CS_2 concentrations in this study were far below these values.

Methyl mercaptan and ethyl mercaptan were found in only one treatment unit of Izmir WWTP. The concentration values of methyl mercaptan and ethyl mercaptan were 9.18 µg m^{-3} and 0.22 µg m^{-3}, respectively. This does not mean that there is no methyl mercaptan and ethyl mercaptan in Izmir WWTP. Our GC configuration can not be suitable for mercaptan analysis. Devai and DeLaune (1999) reported similar values (8 µg m^{-3}) of methyl mercaptan in the WWTPs of Baton Rouge, Louisiana. Methyl mercaptan causes odor nuisances at very low levels because the odor threshold level (0.0003 µg m^{-3}) is very low and can also irritate the respiratory track and cause toxicity.

These malodorous RSCs irritate the eyes, the skin and the respiratory tract and all of them have different odor characteristics. The chemical structures and odor characteristics of identified RSCs are shown in Table 4.15.

Table 4.15 Chemical structures and odor characteristics of identified RSCs

Compound	Structure	Sensory description
Hydrogen sulfide	H_2S	rotten egg, sewage-like
Dimethyl sulfide	CH_3SCH_3	canned corn, cooked cabbage
Dimethyl disulfide	CH_3SSCH_3	vegetal, cabbage, onion-like at high levels
Carbon disulfide	CS_2	sweet, ethereal, slightly green, sulfidy
Methyl mercaptan	CH_3SH	rotten cabbage
Ethyl mercaptan	CH_3CH_2SH	decayed cabbage

Monoaromatics had significant concentrations in the samples of Izmir WWTP (Figure 4.18). Toluene had the highest average concentration in this group. The maximum concentration of toluene was measured in sludge basin with the value of 1356.93 µg m^{-3}. Xylene concentrations were also high. Benzene and toluene were commonly referred as traffic originated pollutants and a B:T ratio of 0.5 was reported from studies on vehicle exhaust. But B:T ratios were below 0.1 indicated the presence of more toluene compared to traffic exhaust rich urban areas. B:T ratios around 0.1 were found in landfills (LaRegina et al., 1986). The B:T ratios were found between 0.002 to 0.009 in the Izmir WWTP.

High levels of halogenated VOCs were found in the composition of odorous gas composition. Eighteen chlorinated compounds were detected in the study. The average concentrations of some chlorinated species such as 1,1,1-trichloroethane, 1,4-dichlorobenzene, carbon tetrachloride, chloroform, methylene chloride, tetrachloroethene, trichloroethene were 21.30, 8.28, 1.71, 11.30, 40.28, 11.91 and 24.20 µg m^{-3}, respectively (Figure 4.15). Tetrachloroethene is present in the textiles, dry cleaning workplaces, and chemical manufacturing units. Trichloroethene is used as a degreaser, extraction, and cleaning solvent for household, commercial and industrial uses. Butyl acetate is commonly used as a solvent in the production of lacquers and other products and methylene chloride is used as paint stripper. Carbon tetrachloride is used in fire extinguishers and refrigeration. 1,1,1-Trichloroethane had many industrial and household uses, including use as a solvent to dissolve other substances, such as glues and paints; to remove oil or grease from manufactured metal parts; and as an ingredient of household products such as spot cleaners, glues, and aerosol sprays.

Chloroform, the most well known trihalomethane (THM) may not only cause central nervous system depression, but may also cause hepatotoxicity, nephrotoxicity, teratogenicity and carcinogenicity. THMs are the by-products of water and pretreated wastewater chlorination. Chloroform in the odorous samples of WWTP might be related to the chlorinated and brominated compounds that are widely used household cleaning agents. Compared to monoaromatic compounds, the concentrations of chlorinated species were lower in samples.

These high levels of monoaromatic and chlorinated compound concentrations could be originated from fugitive industrial discharges especially considering there was a huge industrial organized district very close to the treatment plant.

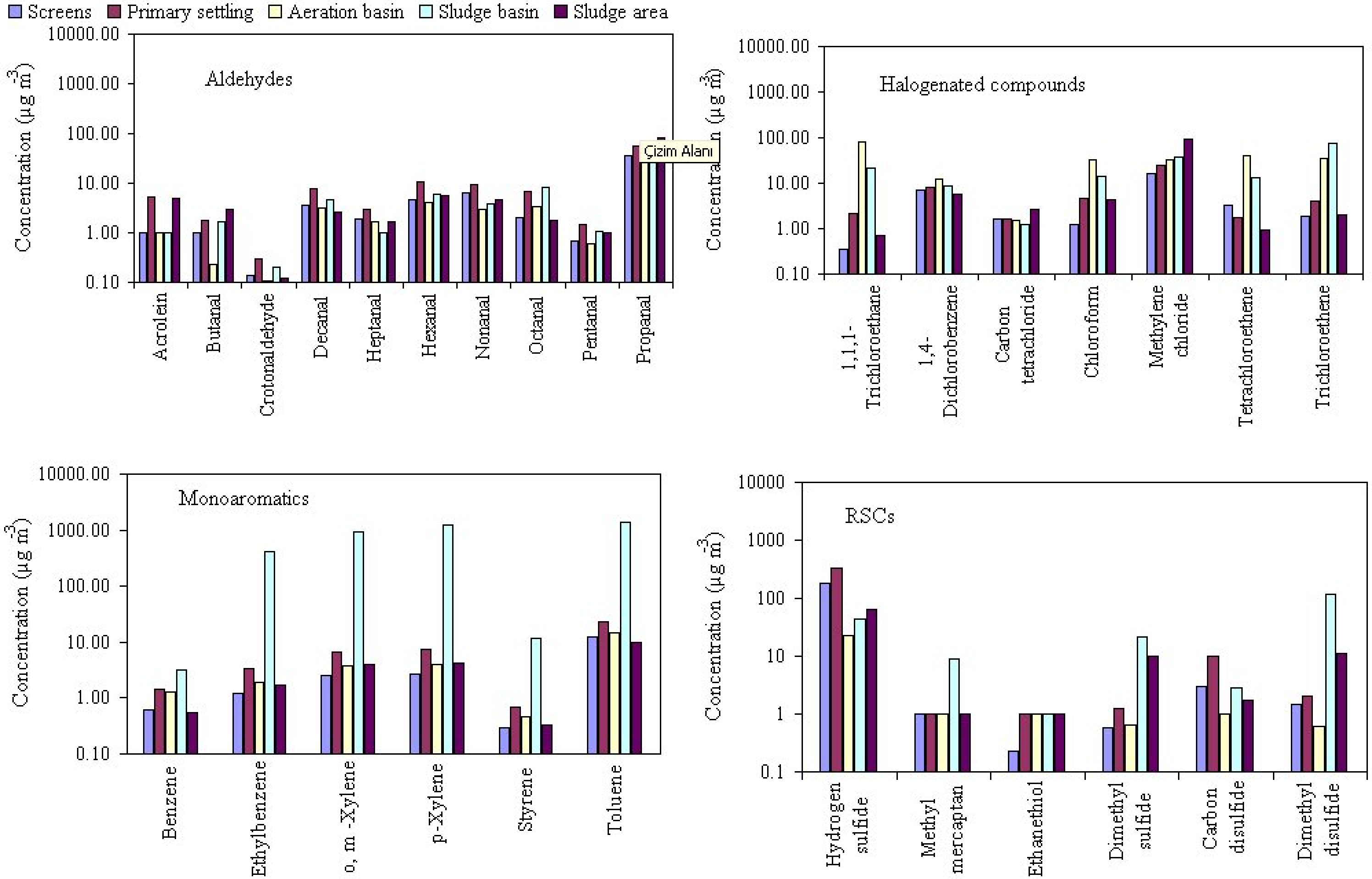

Figure 4.18 Variations of concentrations of aldehydes, halogenated compounds, monoaromatics, and RSCs in gases released from WWTP

4.3.2 Odor and TVOC concentrations and the relationship in between

The results of olfactometric and chemical analysis are given in Table 4.16 and Fig. 4.19. Olfactometric concentrations varied between 3730-37290 OU m^{-3} with a mean value of 8830 OU m^{-3} and the TVOC concentrations varied between 357-5187 µg m^{-3} (average, 1425 µg m^{-3}).

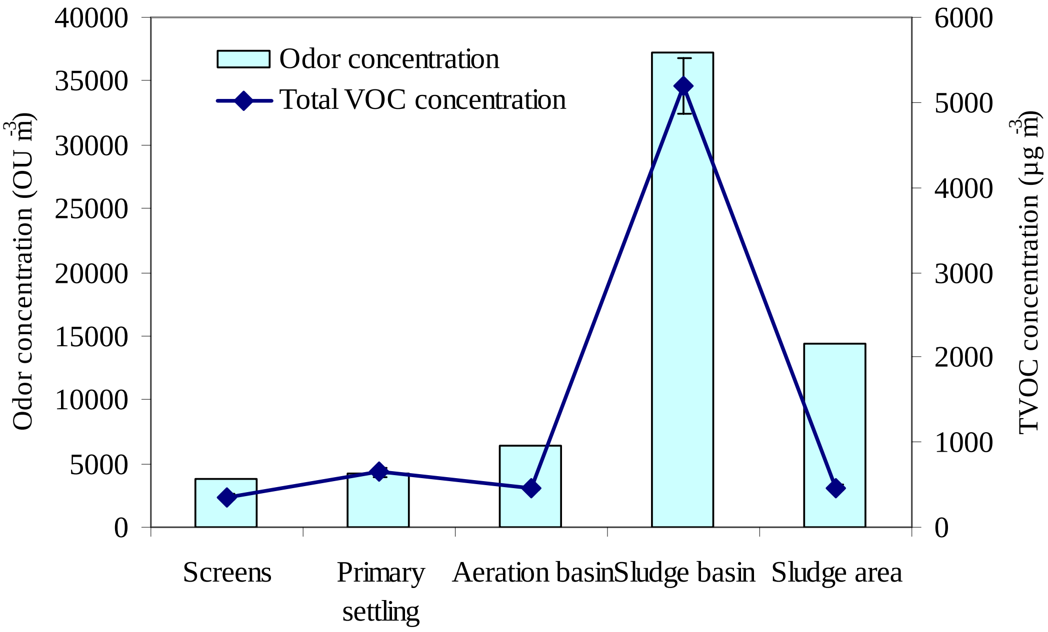

Figure 4.19 Odor and TVOC concentrations of the samples in WWTP

The relationship between concentrations of odors and total VOCs measured in the study was statistically analyzed. A correlation matrix was calculated for different variables and Pearson coefficients were given as a measure of relationship between groups of variables (Table 4.17). There were statistically significant correlations (P<0.05) between odor concentrations and total VOC and monoaromatic concentrations.

Linear regression analysis performed between odor and TVOC concentrations indicated that 90% of the variance in odor concentrations can be explained by the TVOC concentrations (r^2= 0.90, n=5, P<0.05).

Table 4.16 Concurrent data set of the odor concentrations (OU m^{-3}) and chemical concentrations (µg m^{-3}) of WWTP

Sampling point	Odor concentration	TVOC concentration	Aldehydes	Esters	Halogenated compounds	Monoaromatics	Ketones	RSC
Screens	3730±231	357±31	55±12	3±2	32±4	20±5	62±43	185±80
Primary settling	4160±208	650±51	102±16	6±4	58±6	43±9	100±49	341±162
Aeration basin	6430±351	466±20	43±9	3±1	308±25	26±5	61*	24±13
Sludge basin	37290±2309	5187±332	66±13	698±493	177±20	3971±65	78±53	196±48
Sludge area	14460±3055	465±29	109±26	5±3	108±24	21±4	136±95	86±28

* identified only in aeration basin

Table 4.17 Pearson correlation coefficients between the different compound groups and odor in WWTP (bolds were statistically significant (*P*<0.05))

	Odor concentration	TVOC concentration	Aldehydes	Esters	Halogenated compounds	Monoaromatics	Ketones	RSC
Odor concentration	1	**0,95**	0,00	**0,95**	0,24	**0,95**	0,08	-0,03
TVOC concentration		1	-0,14	**0,99**	0,20	**0,99**	-0,14	0,17
Aldehydes			1	-0,17	-0,53	-0,16	0,94	0,42
Esters				1	0,20	**0,99**	-0,15	0,14
Halogenated compounds					1	0,20	-0,33	-0,68
Monoaromatics						1	-0,16	0,14
Ketones							1	0,09
RSC								1

4.3.3 Evaluations based on odorous component contribution analyses

Table 4.18 indicates the odor contribution ratio of several compounds in composition of the odorous gas emissions studied in Izmir WWTP. From Table 4.23 it can be seen that among the selected 29 compounds; 10 compounds were the key odorants in samples (Figure 4.20). Hydrogen sulfide was the abundant odorous compound that was found in primary treatment units; screens and primary settling tanks. In the next treatment units H_2S was losing its importance and other odorous compounds were dominating in the odors. Propanal was one of them and dominating the odors in aeration basin and sludge area. Propanal and such aldehyde compounds were found in these units due to the oxidation of organic materials. Toluene was dominating the odors in sludge collection basin together with propanal. It can be suggested from Table 4.23 that the contribution levels of these compounds varied between pre- and post- activated sludge units.

Based on the information gained from this study, it was found that the concentrations of hydrogen sulfide, propanal and toluene were the best estimators, explaining 99% of the variability in odor concentrations ($r^2 = 0.99$, $n = 5$, $P<0.05$) in the samples. The formula of this relationship obtained from multiple regression analysis is as follows:

$$OC = 592\, C_{propanal} + 1744\, C_{toluene} - 285\, C_{H2S} + 2017 \qquad (4)$$

Where $C_{propanal}$ is the concentrations of propanal, $C_{toluene}$ is the concentrations of toluene, C_{H2S} is the concentrations of hydrogen sulfide.

Table 4.18 Odor threshold concentrations (OTC) and odor contribution levels of some of the studied compounds in the WWTP

Pollutants	**OTC * (μg m^{-3})**	**Screens**	**Primary settling**	**Aeration basin**	**Sludge basin**	**Sludge area**
Hydrogen sulfide	12.30	**14.63**	**26.67**	1.87	3.50	5.12
Methyl mercaptan	3.44	n.d.	n.d.	n.d.	2.67	n.d.
Ethyl mercaptan	2.11	0.11	n.d.	n.d.	n.d.	n.d.
Dimethyl sulfide	5.80	0.10	0.21	0.11	3.63	1.73
Carbon disulfide	48.30	0.01	0.03	n.d.	0.01	0.01
Dimethyl disulfide	303.00	0.03	0.04	0.01	2.48	0.24
Acrolein	400	n.d.	0.01	n.d.	n.d.	0.01
Butanal	12.55	n.d.	0.15	0.02	0.13	0.23
Crotonaldehyde	344	0.00	0.00	0.00	0.00	0.00
Decanal	5.81	0.63	1.32	0.55	0.82	0.45
Heptanal	22.8	0.08	0.13	0.07	n.d.	0.07
Hexanal	57.5	0.08	0.18	0.07	0.11	0.10
Nonanal	13.3	0.48	0.69	0.22	0.28	0.36
Octanal	7.21	0.28	0.97	0.47	1.13	0.25
Pentanal	21.6	0.03	0.07	0.03	0.05	0.05
Propanal	3.6	9.90	15.38	**7.58**	11.31	**23.17**
Benzene	11800	0.00	0.00	0.00	0.00	0.00
Ethylbenzene	400	0.00	0.01	0.00	1.02	0.00
o, m –Xylene	850	0.00	0.01	0.00	1.10	0.00
p-Xylene	570	0.00	0.01	0.01	2.20	0.01
Styrene	140	0.00	0.01	0.00	0.09	0.00
Toluene	80	0.16	0.30	0.18	**16.96**	0.12
1,1,1-Trichloroethane	88000	0.00	0.00	0.00	0.00	0.00
1,4-Dichlorobenzene	730	0.01	0.01	0.02	0.01	0.01
Carbon tetrachloride	11500	0.00	0.00	0.00	0.00	0.00
Chloroform	3000	0.00	0.00	0.01	0.00	0.0
Methylene chloride	4100	0.00	0.01	0.01	0.01	0.02
Tetrachloroethene	12000	0.00	0.00	0.00	0.00	0.00
Trichloroethene	115000	0.00	0.00	0.00	0.00	0.00

n.d.: not detected: * From Appendix A

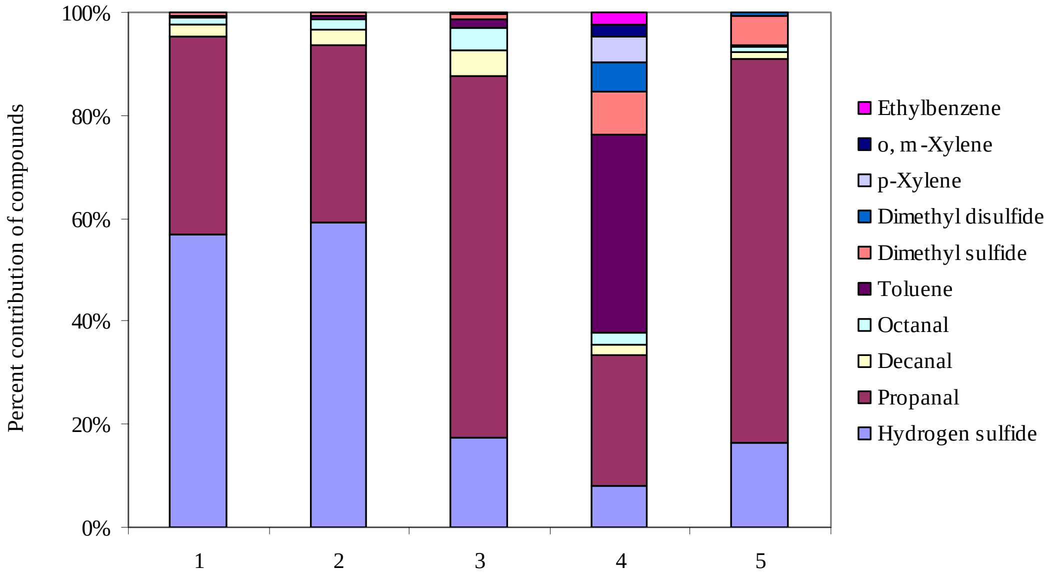

Figure 4.20 Odorous component contributions of WWTP samples

4.4 Results of rendering plant measurements

4.4.1 VOC composition and concentrations

The odorous emissions from rendering plant were consisted of several compounds. Fourthy-seven VOCs were detected in the sampling campaign. Analytical results for the odorous compounds with respect to the sampling locations are given in Table 4.19. The measured VOCs are classified as monoaromatics (e.g. benzene, toluene), halogenated compounds (e.g. chlorobenzene, trichloroethene), aldehydes (e.g. hexanal, propanal), ketones (e.g. acetone), VFAs (e.g. acetic acid, formic acid) and esters (e.g. butyl acetate, butyl formate).

The most abundant group was the aldehydes (26% of total VOC concentrations) followed by ketones (25%), halogenated compounds (23%), monoaromatics (14%), VFA (9%) and esters (1%).

Monoaromatics had low concentrations in the samples. Toluene had the highest average concentration in this group with a value of 4.61 µg m^{-3}.

High levels of halogenated VOCs were found in the composition of odorous gas composition. Seventeen chlorinated compounds were detected in the study. The average concentrations of some chlorinated species such as carbon tetrachloride, chloroform, methylene chloride, tetrachloroethene, trichloroethene were 0.25, 1.33, 8.68, 0.06 and 0.32 µg m^{-3}, respectively. Chlorinated compounds found in the samples and especially at the wastewater treatment plant point were possibly due to impacts of chlorination of the effluents.

High levels of aldehydes and ketones were observed especially at rendering plant unit stack. Propanal and acetone were the abundant compounds in these groups with average concentrations of 7.23 and 12.47 µg m^{-3}, respectively. Unlike from the other results of the sampling sites, identified and quantified odorous compounds of the rendering plant were at low concentrations.

4.4.2 Odor and TVOC concentrations and their relationship

The results of olfactometric and chemical analysis are given in Table 4.20 and Fig. 4.21. Olfactometric concentrations varied between 2200-683000 OU m^{-3} with a mean value of 17480 OU m^{-3} and the total VOC concentrations varied between 19-98 µg m^{-3} (average, 51 µg m^{-3}).

The relationship between concentrations of odors and total VOCs measured in the present study was statistically analyzed by performing linear regression analysis. No statistically significant relationship was found between odor and TVOC concentrations in rendering plant samples ($r^2 = 0.06$, $n = 7$). In this thesis, the reason of insignificant correlation might be due to the lack of the measurements of the sulfur containing compounds. Because, for the emissions of an animal rendering plant treated by biofilter, it was found that the total VOC concentration was a poor estimator for odor concentration. For this type of odor, it was reported previously that concentrations of organic sulfur containing compounds correlated well with odor concentrations (Defoer et al., 2002).

Table 4.19 VOC concentrations (µg m^{-3}) of the Rendering plant samples

Compound	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**
1,1,1-Trichloroethane	0.05	0.05	0.04	0.04	0.03	0.05	0.05
1,1,2,2-Tetrachloroethane	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,1,2-Trichloroethane	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
1,1-Dichloroethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,1-Dichloroethene	1.03	n.d.	0.26	1.55	0.00	n.d.	n.d.
1,2-Dichlorobenzene	0.01	0.01	0.01	0.02	0.01	0.01	0.01
1,2-Dichloroethane	0.16	0.15	0.06	0.16	0.12	0.19	0.23
1,2-Dichloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,3-Dichlorobenzene	0.00	0.00	0.00	0.00	0.01	0.00	n.d.
1,4-Dichlorobenzene	0.18	0.11	0.02	0.13	0.20	0.12	0.24
2-Butanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-Hexanone	0.19	n.d.	0.08	0.23	0.10	0.07	0.04
4-Methyl-2-pentanone	0.12	0.07	0.05	0.13	0.06	0.04	0.03
Acetic acid	n.d.	0.44	n.d.	n.d.	n.d.	0.36	0.36
Acetone	17.04	12.05	9.26	26.13	8.80	9.89	4.10
Acrolein	0.59	0.88	0.59	1.97	0.99	0.59	0.49
Acrylonitrile	0.26	0.23	0.18	0.29	0.21	0.22	0.07
Benzene	0.79	0.35	1.09	0.45	0.70	0.53	0.31
Bromodichloromethane	0.04	n.d.	n.d.	0.02	0.01	0.01	0.01
Bromoform	0.17	n.d.	0.03	0.04	n.d.	n.d.	n.d.
Butanal	0.73	0.70	0.39	1.00	0.43	0.44	0.37
Butyl Acetate	0.39	0.11	0.21	0.16	0.17	0.09	0.07
Butyl formate	0.04	0.05	0.04	0.05	0.05	0.03	0.04
Butyl Propionate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Butyric acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Caproic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Carbon disulfide	0.75	1.88	1.09	4.96	0.29	0.75	0.50
Carbon tetrachloride	0.34	0.21	0.33	0.21	0.27	0.21	0.20
Chlorobenzene	0.02	0.03	0.02	0.04	0.02	0.03	0.02
Chloroform	2.13	6.18	0.05	0.09	0.78	0.05	0.05
cis-1,3-Dichloropropene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
cis-1,4-Dichloro-2-butene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Crotonaldehyde	0.11	0.08	0.05	0.09	0.06	0.06	0.06
Cyclohexanone	0.06	0.06	n.d.	0.06	0.05	0.04	n.d.
Decanal	0.86	0.73	0.86	1.01	1.20	0.92	1.07
Dibromochloromethane	0.08	n.d.	0.02	0.04	n.d.	0.01	n.d.

n.d. not detected

Table 4.19 VOC concentrations (μg m^{-3}) of the Rendering plant samples (cont.)

Compound	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**
Ethylbenzene	0.50	0.23	0.14	0.30	0.37	0.21	0.11
Formic acid	20.04	9.32	n.d.	n.d.	n.d.	n.d.	n.d.
Heptanal	n.d.	0.22	0.52	1.18	n.d.	0.20	0.18
Heptanoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hexanal	1.31	0.76	0.81	4.06	0.98	0.62	0.53
Iodomethane	n.d.	0.01	0.04	0.02	0.02	0.01	n.d.
Isobutyric acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Isocaproic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Isovaleric acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methyl propionate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylene chloride	11.90	8.69	5.86	9.34	15.65	5.41	3.92
Nonanal	2.01	0.79	2.47	2.86	1.93	0.76	0.95
o. m -Xylene	1.27	0.46	0.26	0.33	0.87	0.45	0.19
Octanal	1.66	0.24	0.50	0.60	1.09	0.20	0.24
Pentanal	0.54	0.27	0.23	0.97	0.33	0.19	0.25
Propanal	9.65	6.86	5.99	13.87	4.86	n.d.	2.15
Propionic acid	n.d.	n.d.	n.d.	n.d.	n.d.	0.55	0.45
p-Xylene	0.78	0.34	0.21	0.30	0.58	0.34	0.18
Pyridine	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	n.d.
Styrene	1.66	0.58	0.24	0.56	1.08	0.56	0.14
Tetrachloroethene	0.06	0.06	0.04	0.07	0.07	0.06	0.05
Toluene	19.63	1.37	1.26	4.79	3.39	0.89	0.94
trans-1,2-Dichloroethene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
trans-1,3-Dichloropropene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
trans-1,4-Dichloro-2-butene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroethene	0.34	0.38	0.24	0.31	0.39	0.36	0.22
Valeric acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Vinyl acetate	0.02	0.03	0.03	0.05	0.03	0.02	0.02

n.d. not detected

Table 4.20 Concurrent data set of the odor concentrations (OU m^{-3}) and chemical concentrations (μg m^{-3}) of rendering plant

Sampling point	Odor concentration	TVOC concentration	VFAs	Alde.	Esters	Halo. Comp.	Monoar.	Ketones
1	16619±1528	98±5	20*	17±3	0.46±0.21	17±3	25±8	17±8
2	4001±380	55±3	10±6	12±2	0.20±0.04	16±3	3±0.42	12±7
3	429690±20000	34±2	n.d.	12±2	0.28±0.10	7±2	3±1	9±5
4	683026±25166	78±5	n.d.	28±4	0.26±0.06	12±2	7±2	27±13
5	2819±351	46±3	n.d.	12±1	0.25±0.07	18±4	7±1	9±4
6	4129±231	26±2	1±0.13	4±0	0.14±0.03	7±1	3±0.23	10±5
7	2200±210	19±1	1±0.06	6±1	0.14±0.02	5±1	2±0.32	4±2

* identified only in one sampling point

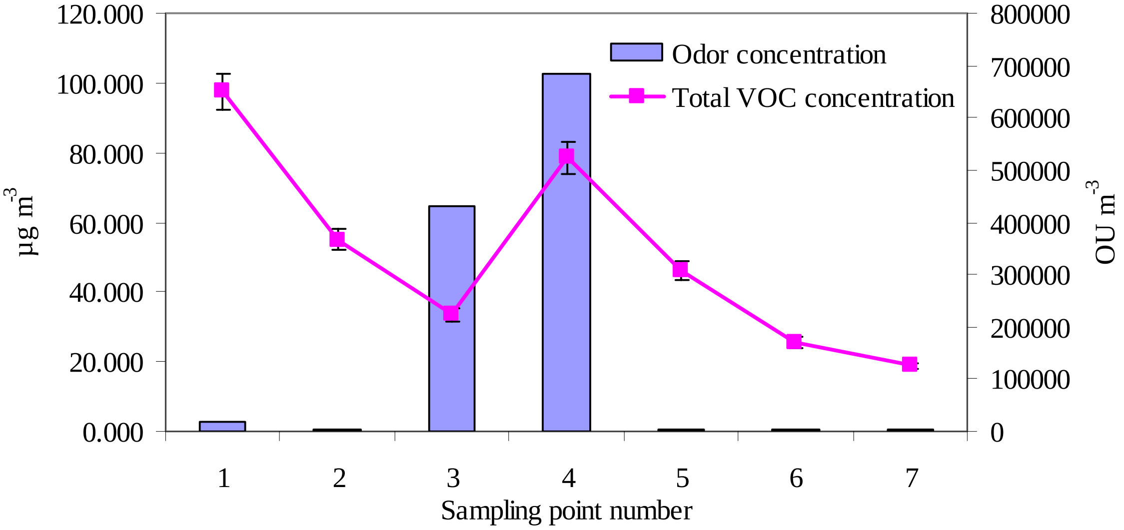

Figure 4.21 Odor and total VOC concentrations of the samples in rendering plant

4.4 Results of campus measurements

The measurement results of the campus site are given in Table 4.21. Thirty-nine VOCs were detected in the campus samples. The measured VOCs were classified as monoaromatics (e.g. benzene, toluene), halogenated compounds (e.g. chloroform, trichloroethene), aldehydes (e.g. hexanal, propanal), ketones (e.g. acetone) and esters (e.g. butyl acetate, butyl formate). VFAs were not found in the samples.

The most abundant group was aldehydes (30% of total VOC concentrations) followed by halogenated compounds (40%), ketones (26%), monoaromatics (4%) and esters (0.2%).

Among the 39 compounds identified, some compounds were found at significant levels in the samples. These compounds were acetone, methylene chloride, propanal and toluene, and the average concentrations of these compounds were 17.04, 25.67, 14.20 and 1.06 µg m^{-3}, respectively. As discussed in previous sections, the B:T of the campus site was found 0.36 indicating that the ambient concentrations of these compounds were mainly affected by traffic emissions.

At the noon time, all VOC compounds had the highest concentration value, especially methylene chloride.

The results of olfactometric and chemical analysis are given in Table 4.22. Olfactometric concentrations varied between 10-52 OU m^{-3} with a mean value of 17 OU m^{-3} and the total VOC concentrations varied between 26-145 µg m^{-3} (average, 57 µg m^{-3}).

The relationship between concentrations of odors and total VOCs measured in the present study was statistically analyzed by performing linear regression analysis. A statistically significant relationship was found between odor and TVOC concentrations in campus samples ($r^2 = 0.99$, $n = 3$, $P<0.05$) (Figure 4.22).

Campus site was selected mainly for comparing the findings in odorous compounds from other urban and industrial activity sites. Identified and quantified VOCs in the campus had the lowest concentration values together with the odor concentration levels comparing to other sampling sites.

Table 4.21 VOC concentrations of the campus measurements

Compound	**C1**	**C2**	**C3**	**Compound**	**C1**	**C2**	**C3**
1.1.1-Trichloroethane	0.06	0.03	0.04	Crotonaldehyde	0.1	0.14	0.08
1.1.2.2-Tetrachloroethane	n.d.	n.d.	n.d.	Cyclohexanone	n.d.	n.d.	n.d.
1.1.2-Trichloroethane	n.d.	n.d.	n.d.	Decanal	n.d.	0.63	0.56
1.1-Dichloroethane	n.d.	n.d.	n.d.	Dibromochloromethane	n.d.	n.d.	n.d.
1.1-Dichloroethene	0.03	n.d.	0.02	Ethylbenzene	0.14	0.16	0.16
1.2-Dichlorobenzene	n.d.	0.01	0	Formic acid	n.d.	n.d.	n.d.
1.2-Dichloroethane	0.04	0.03	0.06	Heptanal	0.2	n.d.	n.d.
1.2-Dichloropropane	n.d.	n.d.	n.d.	Heptanoic acid	n.d.	0.22	0.24
1.3-Dichlorobenzene	0	0.03	n.d.	Hexanal	1.09	0.73	0.76
1.4-Dichlorobenzene	0.14	0.38	0.34	Iodomethane	n.d.	0.04	0.01
2-Butanone	n.d.	n.d.	n.d.	Isobutyric acid	n.d.	n.d.	n.d.
2-Hexanone	n.d.	n.d.	n.d.	Isocaproic acid	n.d.	n.d.	n.d.
4-Methyl-2-pentanone	0.06	0.06	0.04	Isovaleric acid	n.d.	n.d.	n.d.
Acetic acid	n.d.	n.d.	n.d.	Methyl propionate	n.d.	n.d.	n.d.
Acetone	13.06	27.21	10.86	Methylene chloride	0.66	76.19	0.17
Acrolein	1.81	2.44	1.2	Nonanal	0.48	0.52	0.71
Acrylonitrile	0.09	0.06	0.08	o. m -Xylene	0.29	0.42	0.48
Benzene	0.13	0.93	0.08	Octanal	0.25	0.85	1.13
Bromodichloromethane	0.01	0.01	0.01	Pentanal	0.46	0.36	0.39
Bromoform	n.d.	n.d.	n.d.	Propanal	7.71	28.45	6.45
Butanal	1.09	0.59	0.55	Propionic acid	n.d.	n.d.	n.d.
Butyl Acetate	0.05	0.11	0.04	p-Xylene	0.22	0.25	0.26
Butyl formate	0.07	0.03	0.05	Pyridine	n.d.	n.d.	n.d.
Butyl Propionate	n.d.	n.d.	n.d.	Styrene	0.37	0.37	0.39
Butyric acid	n.d.	n.d.	n.d.	Tetrachloroethene	0.03	0.1	0.03
Caproic acid	n.d.	n.d.	n.d.	Toluene	0.68	1.83	0.67
Carbon disulfide	0.03	1.22	0.05	trans-1.2-Dichloroethene	n.d.	n.d.	n.d.
Carbon tetrachloride	0.17	0.13	0.15	trans-1.3-Dichloropropene	n.d.	n.d.	n.d.
Chlorobenzene	0.01	0.02	0.01	trans-1.4-Dichloro-2-butene	n.d.	n.d.	n.d.
Chloroform	0.07	0.03	0.03	Trichloroethene	0.14	1.52	0.1
cis-1.3-Dichloropropene	n.d.	0.02	n.d.	Valeric acid	n.d.	n.d.	n.d.
cis-1.4-Dichloro-2-butene	n.d.	n.d.	n.d.	Vinyl acetate	0.02	0.08	n.d.

n.d. not detected

Table 4.22 Concurrent data set of the odor concentrations (OU m^{-3}) and chemical concentrations (μg m^{-3}) of campus

Sampling time	Odor concentration	TVOC concentration	Aldeh.	Esters	Halo. C.	Monoa.	Ketones
C1 (08:00)	10±0	30±3	13±2	0.15±0.03	1±0.28	2±0.20	13±9
C2 (12:00)	52±7.5	145±14	35±9	0.22±0.04	79±20	4±0.63	27±19
C3 (15:00)	10±0	26±2	12±2	0.09±0.004	1±0.10	2±0.22	11±8

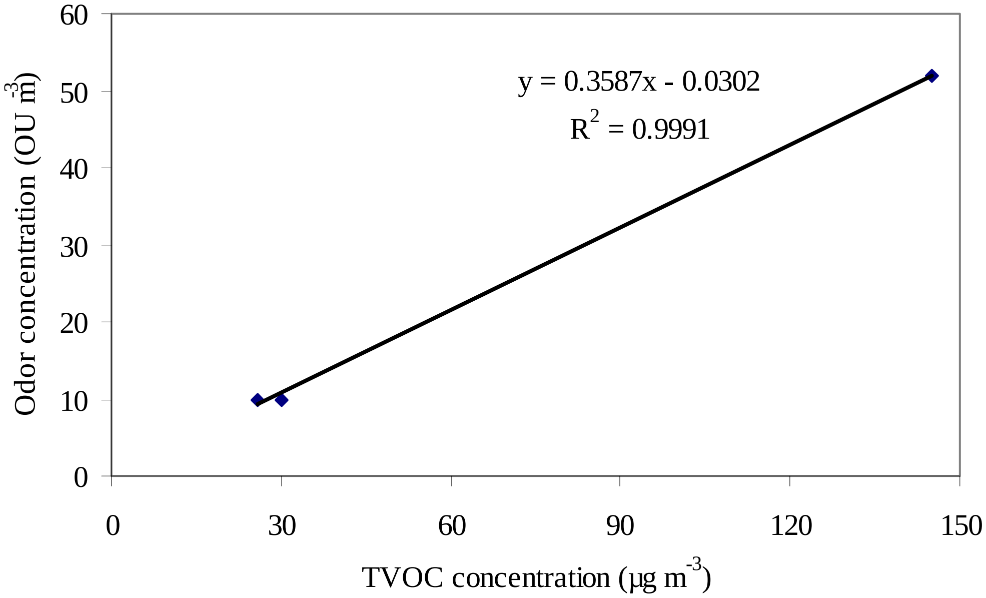

Figure 4.22 The relationship between odor and total VOC concentrations for campus results

CHAPTER FIVE
CONCLUSIONS

The odor levels and the composition of odorous gases emitted from selected facilities around Izmir city were studied. Several VOCs in different classes (mono aromatics, halogenated compounds, aldehydes, ketones, esters, and volatile fatty acids) are identified and quantified in these facilities. Sixty two and 49 VOCs were identified and quantified in landfill and Aliağa samples in three sampling campaigns, respectively. Fourthy-eight and 47 VOCs were detected in WWTP and rendering plant samples, respectively. Detected VOCs in the campus samples were thirthy-nine.

Collected samples were evaluated for odor concentrations by olfactometry. Odor concentrations of the studied facilities are very high indicating a serious potential for annoyance by the public. Especially at the landfill, WWTP and rendering plant, the odor levels are so high that they possibly have adverse effects to the site operators and neighborhood.

Relationships between odor concentrations and the results of analytical measurements were evaluated. According to the statistical evaluations, it is concluded that a relationship exists between odor and total VOC concentrations at the studied facilities except rendering plant. No significant correlation was found between odor and total VOC concentrations in rendering plant. For landfill, Aliağa, and WWTP samples, the odor concentration correlated with the total VOC concentrations.

The relationships of odor concentrations with the different groups of chemicals were also examined and it was found that the concentrations of aldehydes and monoaromatics are the best estimators in odor concentrations of landfill and Aliağa.

When the detection thresholds of the odorous compounds were compared with the analytical results, it is noted that the concentration of propanal in the air was found to exceed the odor threshold. Based on the evaluations of odor contribution analyses propanal and other aldehydes are among the most contributing compounds in the perceived odors at the sites due to their low odor threshold concentrations.

One of the results of this thesis shows that, although it is usually taken for granted that the RSCs (especially the H_2S) are the most responsible components for the odor problems at the WWTPs, there are also other significant contributors. In the first units of the WWTP, H_2S is the most significant component in odor formation. However, among other contributors carbonyls like propanal, decanal, etc. and the monoaromatics are also important. Especially as the treatment operation continues, such as in the sludge units the main contributors turn out to be the carbonyls and toluene.

The benzene-to-toluene (B/T) ratios at the landfill site in the sampling campaigns were found to be significantly lower than the usual value determined in urban areas. This indicates the presence of higher amounts of toluene than benzene in landfills compared to urban areas.

For reasons of validation, it would be useful to extend both data sets by additional measurements. Further studies will decrease the uncertainties and give more dependable correlation coefficients.

According to the results of the study, the measured VOCs are shown to be important in the odor formation and composition in selected activity sites. The character of the odor created by a multi-component organic mixture of gases, however, is different depending on the chemical groups as in the case of landfill, Aliağa and WWTP odors.

In the scope of this study only measurements and investigations of chemical characterization of odors from certain industrial activity sites are covered. In the next step suitable odor abatement processes must be designed and constructed for the urban and industrial facilities that create odor nuisance and complaints by using these information. This thesis is the first step of an overall odor management system which must be backed up with another study investigating an adequate treatment system of odors. Comprehensive studies are necessary to establish a successful odor management system.

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APPENDIX-A

Names, odor characteristics and odor threshold concentrations of the studied compounds

Table A.1 The names, odor characteristics and odor threshold concentrations of the studied compounds

Compound	*Formula*	*MW*	*Odor characteristics*	*Odor threshold concentration ($\mu g/m^3$)*	*Reference*
Aldehydes					
Acrolein	C_3H_4O	56	Pungent, choking	250	Amoore and Hautala, 1983
Butanal	C_4H_8O	72.11	acrid smell	12.55	Devos et al., 1990
Crotonaldehyde	C_4H_6O	70.09	strong odor	344	AIHA, 1989
Decanal	$C_{10}H_{20}O$	156.27	soap, orange peel	5.81	Lornage et al., 2005
Heptanal	$C_7H_{14}O$	114.19	fatty, citrus, rancid	22.8	Lornage et al., 2005
Hexanal	$C_6H_{12}O$	100.16	grass, tallow, fat	57.5	Lornage et al., 2005
Nonanal	$C_9H_{18}O$	142.24	fatty, citrus, green	13.3	Lornage et al., 2005
Octanal	$C_8H_{16}O$	128.21	fatty, soap, lemon, green	7.21	Lornage et al., 2005
Pentanal	$C_5H_{10}O$	86.13	strawberry, fruity, tomato	21.6	Lornage et al., 2005
Propanal	C_3H_6O	58.08	Pungent, suffocating, unpleasant	3.6	EPA, 1992
Esters					
Butyl Acetate	$C_6H_{12}O_2$	116.16	fruity odor, pear	1600	AIHA, 1989
Butyl formate	$C_5H_{10}O_2$	102.13		NA	
Butyl Propionate	$C_7H_{14}O_2$	130.18		NA	
Methyl propionate	$C_4H_8O_2$	88.11		NA	
Vinyl acetate	$C_4H_6O_2$	86.09	Sour sharp	400	EPA, 1992

NA: not available

Table A.1 The names, odor characteristics and odor threshold concentrations of the studied compounds (cont.)

Compound	*Formula*	*MW*	*Odor characteristics*	*Odor threshold concnetration ($\mu g/m^3$)*	*Reference*
Sulfur compounds					
Carbon disulfide	CS_2	76.1	Sweet, ethereal, sulfidy	303	Lornage et al., 2005
Dimethyl disulfide	$C_2H_6S_2$	94.2	Vegetal, cabbage, onion-like	48.3	Lornage et al., 2005
Dimethyl sulfide	C_2H_6S	62.12	Canned corn, cooked cabbage	5.8	Lornage et al., 2005
Ethyl mercaptan	C_2H_6S	62.14	Decayed cabbage	2.11	Amoore and Hautala, 1983
Hydrogen sulfide	H_2S	34.08	Rotten egg, sewage-like	12.30	Amoore and Hautala, 1983
Methyl mercaptan	CH_4S	48.11	Decayed cabbage	3.44	Amoore and Hautala, 1983
n-propyl mercaptan	C_3H_8S	76.16	offensive, cabbage-like	NA	
Tetrahydrothiophene	C_4H_8S	88.17		NA	
2-methyl-2-propanethiol	$C_4H_{10}S$	90.19	Sulfurous	NA	
Monoaromatics					
Benzene	C_6H_6	78.11	Aromatic/sweet/solvent	11800	Lornage et al., 2005
Ethylbenzene	C8H10	106.2	Oily/solvent, aromatic	400	EPA, 1992
o, m –Xylene	C8H10	106.2	Sweet	850	EPA, 1992
p-Xylene	C_8H_{10}	106.17	Sweet	570	EPA, 1992
Styrene	C8H8	104.15	Solvent, rubbery, plasticy	140	EPA, 1992
Toluene	C_7H_8	92.14	Mothballs, rubbery	80	EPA, 1992

NA: not available

Table A.1 The names, odor characteristics and odor threshold concentrations of the studied compounds (cont.)

Compound	*Formula*	*MW*	*Odor characteristics*	*Odor threshold concentration ($\mu g/m^3$)*	*Reference*
Volatile fatty acids					
Acetic acid	$C_2H_4O_2$	60.05	Sour, vinegar	198.34	AIHA, 1989
Butyric acid	$C_4H_8O_2$	88.11	unpleasant, rancid	2.71	Minnesota EQB, 1999
Caproic acid	$C_6H_{12}O_2$	116.16	Sour, vinegar	108.9	Minnesota EQB, 1999
Formic acid	CH_2O_2	46.03	pungent, irritating	49.32	Minnesota EQB, 1999
Heptanoic acid	$C_7H_{14}O_2$	130.18	pungent, irritating	29.06	Minnesota EQB, 1999
Isobutyric acid	$C_4H_8O_2$	88.11	unpleasant, rancid	43.27	Minnesota EQB, 1999
Isocaproic acid	$C_6H_{12}O_2$	116.16	Sour, vinegar	39.93	Minnesota EQB, 1999
Isovaleric acid	$C_5H_{10}O_2$	102.13	Unpleasant	21.89	Minnesota EQB, 1999
Propionic acid	$C_3H_6O_2$	74.08	pungent, disagreeable, rancid	66.14	AIHA, 1989
Valeric acid	$C_5H_{10}O_2$	102.13	Unpleasant	1.28	Minnesota EQB, 1999
Ketones					
2-Butanone	C_4H_8O	72.1	Sweet/sharp, acetone like	17400	Amoore and Hautala, 1983
2-Hexanone	$C_6H_{12}O$	100.16	acetone-like odor	700	Lornage et al., 2005
4-Methyl-2-pentanone	$C_6H_{12}O$	100.2	Sweet/ sharp, pleasant	2240	Lornage et al., 2005
Acetone	C_3H_6O	58	fragrant, mint-like	33660	Amoore and Hautala, 1983
Cyclohexanone	$C_6H_{10}O$	98.14	Sweet sharp	3860	Amoore and Hautala, 1983

Table A.1 The names, odor characteristics and odor threshold concentrations of the studied compounds (cont.)

Compound	*Formula*	*MW*	*Odor characteristics*	*Odor threshold concentrations ($\mu g/m^3$)*	*Reference*
Halogenated compounds					
1,1,1-Trichloroethane	$C_2H_3Cl_3$	133.4	Sweet, etherish	88000	EPA, 1992
1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$	167.85	Sweet	50000	EPA, 1992
1,1,2-Trichloroethane	$C_2H_3Cl_3$	133.4	Chloroform like, sweet	3000	Haz-Map
1,1-Dichloroethane	$C_2H_4Cl_2$	98.96	Chloroform like, sweet	216000	Haz-Map
1,1-Dichloroethene	$C_2H_2Cl_2$	96.97	sweet, sharp	25000	EPA, 1992
1,2-Dichlorobenzene	$C_6H_4Cl_2$	147	Aromatic/sweet/solvent	4600	AIHA, 1989
1,2-Dichloroethane	$C_2H_4Cl_2$	99	Chloroform like/pleasant	25000	EPA, 1992
1,2-Dichloropropane	$C_3H_6Cl_2$	112.99	Sweet/ethereal	1300	AIHA, 1989
1,3-Dichlorobenzene	$C_6H_4Cl_2$	147	Aromatic/sweet/solvent	730	EPA, 1992
1,4-Dichlorobenzene	$C_6H_4Cl_2$	147	Camphor/mothballs, penetrating	730	EPA, 1992
Bromodichloromethane	$CHBrCl_2$	163.8		NA	
Bromoform	CHBr3	252.75	Chloroform/sweet/ suffocating	2100	Haz-Map
Carbon tetrachloride	CCl_4	153.82	Sweet/dry/cleaner, distinctive	11500	EPA, 1992
Chlorobenzene	C_6H_5Cl	112.56	Almond like/ shoe polish	6500	AIHA, 1989
Chloroform	$CHCl_3$	119.38	Sweet/suffocating, characteristic	3000	EPA, 1992
cis-1,3-Dichloropropene	$C_3H_4Cl_2$	110.97	sharp, sweet, irritating, chloroform-like odor	NA	
cis-1,4-Dichloro-2-butene	$C_4H_6Cl_2$	125	sweet, pungent	NA	

NA: not available

Table A.1 The names, odor characteristics and odor threshold concentrations of the studied compounds (cont.)

Compound	*Formula*	*MW*	*Odor characteristics*	*Odor threshold concentration ($\mu g/m^3$)*	*Reference*
Dibromochloromethane	$CHBr_2Cl$	208.28		NA	
Iodomethane	CH_3I	141.94	pungent, ether-like	NA	
Methylene chloride	CH_2Cl_2	84.93	Sweet/ethereal, penetrating	4100	EPA, 1992
Tetrachloroethene	C2Cl4	165.83	Etherish	12000	EPA, 1992
trans-1,2-Dichloroethene	$C_2H_2Cl_2$	96.94	slightly acrid, chloroform-like	350	Haz-Map
trans-1,3-Dichloropropene	$C_3H_4Cl_2$	110.97	sharp, sweet, irritating, chloroform-like odor	NA	
trans-1,4-Dichloro-2-butene	$C_4H_6Cl_2$	125	sweet, pungent	NA	
Trichloroethene	C_2HCl_3	131.39	Ether/solvent,chloroform	115000	EPA, 1992
N-compounds					
Acrylonitrile	C_3H_3N	53	Onion-garlic pungency	3800	AIHA, 1989
Pyridine	C_5H_5N	79.1	Burnt, pungent, diamine	80	EPA, 1992

NA: not available

APPENDIX-B

Example result of the Olfactometer TO7

TO7 by ECOMA GmbH Software (0.9c) by Consult Smyth

Olfactometric measurement according to VDI-RL 3881, 3882 and prEN13725

Measurement	: tansas (user defined)
Date	: 05.05.2005, 14:27:50
Sample	: nokta7 (user defined)
Blanks	: 0%

Results of the Panelists

Measuring	Start step	Pre-dilution	Pre-dilution	Panelist 1	Panelist 2	Panelist 3	Panelist 4
1	4000	1	100	2000	2000	1000	1000
2	4000	1	100	2000	2000	4000	1000
3	4000	1	100	2000	1000	1000	2000

Z50 = 2200 GE/m^3 33.5 dB ± 1.3 dB

Z16 = 3500 GE/m^3 Zll = 3000 GE/m^3

Z84 = 1400 GE/m^3 Zul = 1700 GE/m^3

Error report of the panelists

Reference air errors

Measuring squence	Panelist 1	Panelist 2	Panelist 3	Panelist 4
1	0	1	0	0
2	0	0	0	0
3	0	0	0	0

Errors on blanks

Measuring squence	Panelist 1	Panelist 2	Panelist 3	Panelist 4
1	0	0	0	0
2	0	0	0	0
3	0	0	0	0

Comments:

Die Vorderdünnung und der Vormischer sind bereits im Ergebnis verrechnet

TO7 by ECOMA GmbH Software (0.9c) by Consult Smyth

Olfactometric measurement according to VDI-RL 3881, 3882 and prEN13725

Measurement : aliağa (user defined)

Date : 12.05.2005, 15:27:42

Sample : nokta1 (user defined)

Blanks : 0%

Results of the Panelists

Measuring	Start step	Pre-dilution	Pre-dilution	Panelist 1	Panelist 2	Panelist 3	Panelist 4
1	640	1	1	10	10	20	20
2	640	1	1	20	20	20	20
3	640	1	1	20	10	20	20

Z50 = 25 GE/m^3 14.0 dB ± 0.8 dB

Z16 = 33 GE/m^3 Zll = 30 GE/m^3

Z84 = 19 GE/m^3 Zul = 21 GE/m^3

Error report of the panelists

Reference air errors

Measuring squence	Panelist 1	Panelist 2	Panelist 3	Panelist 4
1	0	0	0	0
2	1	0	0	0
3	0	0	0	0

Errors on blanks

Measuring squence	Panelist 1	Panelist 2	Panelist 3	Panelist 4
1	0	0	0	0
2	0	0	0	0
3	0	0	0	0

Comments:

Die Vorderdünnung und der Vormischer sind bereits im Ergebnis verrechnet

TO7 by ECOMA GmbH Software (0.9c) by Consult Smyth

Olfactometric measurement according to VDI-RL 3881, 3882 and prEN13725

Measurement : harmandali (user defined)

Date : 12.05.2005, 14:42:47

Sample : evsel3 (user defined)

Blanks : 0%

Results of the Panelists

Measuring	Start step	Pre-dilution	Pre-dilution	Panelist 1	Panelist 2	Panelist 3	Panelist 4
1	256000	4	100	64000	64000	64000	128000
2	256000	4	100	64000	32000	32000	128000
3	256000	4	100	32000	32000	64000	64000

Z50 = 81000 GE/m^3 49.1 dB ± 1.4 dB

Z16 = 130000 GE/m^3 Zll = 110000 GE/m^3

Z84 = 49000 GE/m^3 Zul = 58000 GE/m^3

Error report of the panelists

Reference air errors

Measuring squence	Panelist 1	Panelist 2	Panelist 3	Panelist 4
1	0	0	0	0
2	0	0	0	0
3	0	0	1	0

Errors on blanks

Measuring squence	Panelist 1	Panelist 2	Panelist 3	Panelist 4
1	0	0	0	0
2	0	0	0	0
3	0	0	0	0

Comments:

Die Vorderdünnung und der Vormischer sind bereits im Ergebnis verrechnet

APPENDIX-C

Sample calculation for odor and analytical measurement results and odor activity values (OAVs)

(n.d., not detected)

As mentioned in Section 3.3.2.1, two or three liters of sample volumes were obtained from Nalophan® bags for every adsorbent tube. For a 2 liter sample volume, the result of GC-MS and concentration calculation of each ompound are presented in Table C-1. The results obtained from chromatograph are in pg, concentration values are in µg m^{-3}. Concentration values are found by dividing the “sample-blank amount” (in pg) to sample volume (in l). Concentration values are expressed as µg m^{-3} after conversions.

Sample calculation for acrolein:

Sample amount from chromatogram = 1255.78 pg
Blank amount = 289.79 pg
Sample-Blank amount=1255.78 pg - 289.79 pg = 965.99 pg
Sample volume = 2 liters
Concentration of acrolein = 965.99 pg / 2 liters = 482.99 pg/l

Concentration of acrolein = $482.99\frac{pg}{l} x10^{-3}\frac{ng}{pg} x10^{-3}\frac{\mu\mathrm{g}}{\mathrm{ng}} x10^{3}\frac{l}{m^{-3}} = 0.48\frac{\mu\mathrm{g}}{\mathrm{m}^{-3}}$

Table C.1 Example of sample calculation for analytical measurement (Sample volume was 2 liters)

	Sample amount (pg)	Blank Amount (pg)	Sample-blank Amount (pg)	Concentration (µg m^{-3})
Acrolein	1255.78	289.79	965.99	0.48
Acetone	42508.84	5106.44	37402.40	18.70
Propanal	22754.21	2965.48	19788.73	9.89
1,1-Dichloroethene	666.55	n.d.	666.55	0.33
Acrylonitrile	219.25	n.d.	219.25	0.11
Iodomethane	n.d.	n.d.	n.d.	n.d.
Methylene chloride	17115.40	1215.39	15900.01	7.95
Carbon disulfide	2673.68	517.17	2156.51	1.08
trans-1,2-Dichloroethene	n.d.	n.d.	n.d.	n.d.
1,2-Dichloropropane	n.d.	n.d.	n.d.	n.d.
1,1-Dichloroethane	17.90	n.d.	17.90	0.01
Vinyl acetate	183.56	n.d.	183.56	0.09
Butanal	868.23	n.d.	868.23	0.43
Chloroform	158.90	n.d.	158.90	0.08
Methyl propionate	n.d.	n.d.	n.d.	n.d.
2-Butanone	n.d.	n.d.	n.d.	n.d.
1,1,1-Trichloroethane	91.77	n.d.	91.77	0.05
1,2-Dichloroethane	84.53	n.d.	84.53	0.04
Crotonaldehyde	119.94	n.d.	119.94	0.06
Benzene	505.82	93.01	412.81	0.21
Carbon tetrachloride	317.08	n.d.	317.08	0.16
Pentanal	977.94	n.d.	977.94	0.49
Trichloroethene	125848.25	38.19	125810.06	62.91
Bromodichloromethane	n.d.	n.d.	n.d.	n.d.
Butyl formate	110.27	n.d.	110.27	0.06
cis-1,3-Dichloropropene	79.92	n.d.	79.92	0.04
4-Methyl-2-pentanone(MIBK)	180.40	n.d.	180.40	0.09
Pyridine	n.d.	n.d.	n.d.	n.d.
trans-1,3-Dichloropropene	188.55	n.d.	188.55	0.09
Toluene	4077.43	951.04	3126.39	1.56
1,1,2-Trichloroethane	154.09	n.d.	154.09	0.08
2-Hexanone	199.04	n.d.	199.04	0.10
Dibromochloromethane	n.d.	n.d.	n.d.	n.d.
Hexanal	3452.53	143.46	3309.07	1.65

Table C.1 Example of sample calculation for analytical measurement (Sample volume was 2 liters) (cont.)

	Sample amount (pg)	Blank Amount (pg)	Sample-blank Amount (pg)	Concentration ($\mu g\ m^{-3}$)
Tetrachloroethene	2190.47	n.d.	2190.47	1.10
Butyl Acetate	940.27	n.d.	940.27	0.47
Chlorobenzene	25.64	n.d.	25.64	0.01
Ethylbenzene	901.48	12.81	888.67	0.44
p-Xylene	2684.70	20.69	2664.01	1.33
Bromoform	n.d.	n.d.	n.d.	n.d.
Styrene	2338.13	19.55	2318.58	1.16
o, m -Xylene	2149.77	27.45	2122.32	1.06
Cyclohexanone	n.d.	n.d.	n.d.	n.d.
Heptanal	1098.27	n.d.	1098.27	0.55
cis-1,4-Dichloro-2-butene	n.d.	n.d.	n.d.	n.d.
Butyl Propionate	n.d.	n.d.	n.d.	n.d.
1,1,2,2-Tetrachloroethane	n.d.	n.d.	n.d.	n.d.
trans-1,4-Dichloro-2-butene	n.d.	n.d.	n.d.	n.d.
1,3-Dichlorobenzene	13.37	n.d.	13.37	0.01
Octanal	3194.89	n.d.	3194.89	1.60
1,4-Dichlorobenzene	434.61	61.01	373.60	0.19
1,2-Dichlorobenzene	28.24	n.d.	28.24	0.01
Nonanal	3552.33	1117.80	2434.53	1.22
Decanal	1314.28	n.d.	1314.28	0.66
Formic acid	n.d.	n.d.	n.d.	n.d.
Acetic acid	n.d.	n.d.	n.d.	n.d.
Propionic acid	n.d.	n.d.	n.d.	n.d.
Isobutyric acid	n.d.	n.d.	n.d.	n.d.
Butyric acid	0.11	n.d.	0.11	0.06
Isovaleric acid	0.10	n.d.	0.10	0.05
Valeric acid	n.d.	n.d.	n.d.	n.d.
Isocaproic acid	n.d.	n.d.	n.d.	n.d.
Caproic acid	n.d.	n.d.	n.d.	n.d.
Heptanoic acid	n.d.	n.d.	n.d.	n.d.
Total VOC concentration				116.66

According to VDI 3881 (VDI, 1987), three samples had to be collected from one odor source in order to find the mean odor concentration of the source. After sample collection, odor concentration of each sampling bag was measured in the olfactometer. The mean odor concentration of that odor source was then calculated as the geometric mean of the individual odor concentration of sampling bags. An example of the calculation is given in Table C.2.

Table C.2 Example calculation of odor concentration of an odor source

Odor concentration of individual sampling bag (OU m^{-3})	Log value of odor concentrations	Arithmethic mean of Log values	=>	Odor concentration of the source (OU m^{-3})
100000	5	5.06456	10^5.06456	116027
142000	5.15228			
110000	5.04139			

Example calculation for propanal’s OAV:

Concentration of propanal = 9.894 μg m^{-3}

odor threshold of propanal = 3.6 μg m^{-3}

odor activity of propanal = 9.894 μg m^{-3} / 3.6 μg m^{-3} = 2.75

Table C.3 Example calculation of propanal’s and toluene’s OAVs in the landfill results

	Sampling point number	Propanal concentrations (μg m^{-3})	Toluene concentrations (μg m^{-3})	OAVs of propanal	OAVs of toluene
May 2005	1	9.894	1.563	2.75	0.02
	2	4.163	2.310	1.16	0.03
	3	38.545	36.500	10.71	0.46
	4	22.416	47.423	6.23	0.59
	5	30.664	7.046	8.52	0.09
September 2005	1	11.861	4.401	3.29	0.06
	2	5.468	1.907	1.52	0.02
	3	13.448	11.180	3.74	0.14
	4	5.152	4.781	1.43	0.06
	5	6.510	1.507	1.81	0.02
May 2006	2	48.8	12.5	13.55	0.16
	3	139.8	400.8	38.83	5.01
	4	445.8	1975.4	123.83	24.69
	6	126.4	25.8	35.10	0.32
Odor threshold concentrations (μg m^{-3})		3.6	80.0		

APPENDIX-D

Odor activity values of Landfill and Aliaga samples

(n.d., not detected; n.s., not studied)

Table D.1 Odor activity values of Landfill samples (cont.)

	May 2005					**September 2005**					**May 2006**			
Compounds	**1**	**2**	**3**	**4**	**5**	**1**	**2**	**3**	**4**	**5**	**2**	**3**	**4**	**6**
Decanal	0.113	0.256	0.121	0.196	0.146	0.216	0.422	**1.621**	0.719	0.419	0.503	**1.663**	**1.608**	**2.812**
Dimethyl disulfide	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.044	0.106	0.363	0.012
Dimethyl sulfide	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.018	**1.489**	**7.133**	0.541
Ethylbenzene	0.001	0.001	0.012	0.009	0.003	0.001	0.002	0.002	0.001	0.000	0.027	0.074	0.342	0.003
Formic acid	n.d.	0.070	0.517	0.886	n.d.	n.d.	n.d.	0.225	n.d.	n.d.	n.s.	n.s.	n.s.	n.s.
Heptanal	0.024	0.007	0.030	n.d.	0.066	0.011	0.010	0.028	0.013	0.008	0.074	0.234	0.813	0.188
Heptanoic acid	n.d.	0.304	0.137	0.018	0.008	n.d.	0.023	0.023	0.045	0.010	n.s.	n.s.	n.s.	n.s.
Hexanal	0.029	0.008	0.046	0.039	0.103	0.015	0.011	0.062	0.019	0.008	0.077	0.465	**5.015**	0.140
Hydrogen sulfide	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	**7.236**	**3.577**	**8.130**	n.d.
Isobutyric acid	n.d.	0.153	0.012	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.s.	n.s.	n.s.	n.s.
Isocaproic acid	n.d.	0.071	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.s.	n.s.	n.s.	n.s.
Isovaleric acid	0.002	0.276	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	0.009	n.d.	n.s.	n.s.	n.s.	n.s.
Methylene chloride	0.002	0.000	0.001	0.000	0.001	0.000	0.000	0.001	0.000	0.000	0.005	0.008	0.017	0.008
Nonanal	0.134	0.048	0.095	0.153	0.162	0.125	0.219	0.377	0.174	0.096	0.704	**1.151**	**3.361**	0.633
o, m -Xylene	0.001	0.000	0.012	0.009	0.003	0.001	0.001	0.001	0.001	0.000	0.015	0.062	0.360	0.002
Octanal	0.222	0.037	0.196	0.295	0.317	0.085	0.091	0.197	0.120	0.074	0.226	0.000	**3.715**	0.366
Pentanal	0.023	0.007	0.028	0.027	0.089	0.017	0.015	0.040	0.018	0.012	0.058	0.350	2.047	0.557
Propanal	**2.748**	**1.156**	**10.707**	**6.227**	**8.518**	**3.295**	**1.519**	**3.736**	**1.431**	**1.808**	**13.548**	**38.826**	**123.832**	**35.103**
Propionic acid	n.d.	0.053	n.d.	n.d.	0.003	n.d.	n.d.	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000
p-Xylene	0.002	0.001	0.017	0.009	0.002	0.001	0.002	0.002	0.001	0.000	0.032	0.084	0.563	0.003
Styrene	0.008	0.005	0.103	0.014	0.009	0.002	0.002	0.003	0.001	0.001	0.028	0.071	0.554	0.007
Tetrachloroethene	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.102	0.000
Toluene	0.020	0.029	0.456	0.593	0.088	0.055	0.024	0.140	0.060	0.019	0.156	**5.010**	**24.693**	0.322
Trichloroethene	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Valeric acid	n.d.	**3.898**	0.414	0.055	n.d.	n.d.	n.d.	n.d.	0.289	n.d.	n.s.	n.s.	n.s.	n.s.
Vinyl acetate	0.000	0.000	0.006	0.000	0.000	n.d.	n.d.	0.000	0.000	0.004	0.001	n.d.	n.d.	n.d.

Table D.2 Odor activity values of Aliaga samples

	May 2005			**September 2005**								**June 2006**					
Compound	**1**	**2**	**3**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**1**	**2**	**3**	**5**	**9**	**10**
1,1,1-Trichloroethane	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1,1-Dichloroethane	n.d.	n.d.	n.d.	n.d.	n.d.	0.000	n.d.	0.000	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000
1,1-Dichloroethene	n.d.	n.d.	n.d.	n.d.	n.d.	0.000	n.d.	n.d.	n.d.	n.d.	0.000	0.000	n.d.	n.d.	0.000	0.000	0.000
1,2-Dichlorobenzene	n.d.	n.d.	n.d.	n.d.	n.d.	0.000	n.d.	n.d.	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000
1,2-Dichloroethane	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1,4-Dichlorobenzene	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.007	0.007	0.008	0.006	0.001
2-Hexanone	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	n.d.	n.d.	n.d.	n.d.	0.000	n.d.
4-Methyl-2-pentanone	n.d.	n.d.	n.d.	0.000	n.d.	n.d.	0.000	n.d.	0.000	n.d.	0.000	n.d.	n.d.	n.d.	0.000	n.d.	n.d.
Acetone	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000
Acrolein	0.004	0.003	0.012	0.010	0.009	0.022	0.004	0.015	0.002	0.004	0.004	0.037	0.004	0.023	0.014	0.032	0.003
Acrylonitrile	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	n.d.	0.000	n.d.	n.d.	n.d.	n.d.
Benzene	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.000	0.000
Bromoform	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000
Butanal	n.d.	n.d.	n.d.	0.054	0.050	0.055	0.024	0.079	0.038	0.037	0.025	0.057	0.033	0.068	0.051	0.044	0.016
Butyl Acetate	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.002	0.000	0.000
Carbon disulfide	n.d.	n.d.	0.002	0.002	0.003	0.003	0.005	0.003	0.004	0.001	0.004	0.069	0.004	0.028	0.025	0.015	0.022
Carbon tetrachloride	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Chlorobenzene	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Chloroform	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table D.2 Odor activity values of Aliaga samples (cont.)

	May 2005			**September 2005**								**June 2006**					
Compound	**1**	**2**	**3**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**1**	**2**	**3**	**5**	**9**	**10**
Crotonaldehyde	n.d.	n.d.	n.d.	0.000	0.000	n.d.	0.000	0.000	0.001	0.000	n.d.	0.000	0.008	0.001	0.017	0.010	0.000
Cyclohexanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.000	n.d.	0.000	n.d.	n.d.
Decanal	0.057	0.134	0.111	0.202	0.191	0.208	0.352	0.263	0.175	0.263	0.090	0.953	0.477	0.442	0.938	0.346	0.482
Dimethyl disulfide	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.001	0.002	0.005	0.015	0.008	0.001
Dimethyl sulfide	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.034	0.041	0.008	0.111	0.038	0.008
Ethylbenzene	0.002	0.004	0.002	0.002	0.001	0.001	0.001	0.002	0.001	0.001	0.000	0.003	0.002	0.042	0.027	0.004	0.001
Heptanal	n.d.	n.d.	n.d.	0.015	0.009	0.011	0.010	0.013	0.010	0.012	0.005	0.016	0.013	0.024	0.019	0.018	0.008
Hexanal	0.012	0.011	0.025	0.027	0.018	0.023	0.022	0.027	0.020	0.020	0.013	0.047	0.029	0.039	0.030	0.039	0.012
Hydrogen sulfide	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.244	0.894	**1.138**	0.488	0.813	0.569
Methylene chloride	0.002	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.005	0.009	0.004	0.006	0.009
Nonanal	0.031	0.051	0.066	0.146	0.136	0.116	0.112	0.201	0.106	0.103	0.038	0.292	0.251	0.257	0.269	0.181	0.093
o, m -Xylene	0.002	0.007	0.002	0.002	0.001	0.001	0.000	0.002	0.000	0.001	0.000	0.004	0.003	0.088	0.062	0.005	0.001
Octanal	0.064	0.021	0.082	0.074	0.057	0.062	0.062	0.081	0.054	0.058	0.026	0.159	0.128	0.242	0.154	0.107	0.057
Pentanal	n.d.	n.d.	n.d.	0.025	0.016	0.026	0.014	0.023	0.017	0.020	0.011	0.022	0.014	0.035	0.020	0.037	0.011
Propanal	**1.442**	**2.061**	**1.451**	**1.602**	**1.266**	**1.313**	**1.177**	**2.027**	**1.043**	**1.112**	**0.457**	**4.610**	**1.996**	**3.879**	**2.548**	**2.025**	**3.088**
p-Xylene	0.002	0.024	0.002	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.000	0.005	0.004	0.093	0.066	0.005	0.001
Styrene	0.004	0.007	0.003	0.003	0.002	0.002	0.001	0.003	0.002	0.002	0.001	0.001	0.000	0.002	0.018	0.000	0.000
Tetrachloroethene	n.d.	n.d.	n.d.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Toluene	0.043	0.953	0.047	0.047	0.027	0.034	0.013	0.175	0.014	0.019	0.009	0.064	0.032	0.260	0.720	0.096	0.018
Trichloroethene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Vinyl acetate	n.d.	n.d.	n.d.	0.001	0.000	0.002	0.000	0.001	0.001	0.001	0.000	0.004	0.000	0.003	0.000	0.004	0.000