DOKUZ EYLÜL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

INVENTORY AND MODELING OF ATMOSPHERIC VOC EMISSIONS FROM MAJOR SOURCES IN ALİAĞA, İZMİR

by Sedef ŞİMŞİR

November, 2010 İZMİR

INVENTORY AND MODELING OF ATMOSPHERIC VOC EMISSIONS FROM MAJOR SOURCES IN ALİAĞA, İZMİR

A Thesis Submitted to the

Graduate School of Natural and Applied Sciences of Dokuz Eylül University In Partial Fulfillment of the Requirements for the Degree of Master of Science in Environmental Engineering, Environmental Technology Program

> **by Sedef ŞİMŞİR**

> **November, 2010 İZMİR**

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **INVENTORY AND MODELING OF ATMOSPHERIC VOC EMISSIONS FROM MAJOR SOURCES IN ALĠAĞA, iZMİR** completed by **SEDEF ŞİMŞİR** under supervision of **PROF. DR. ABDURRAHMAN BAYRAM** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Prof.Dr. Abdurrahman BAYRAM

Supervisor

Assoc.Prof.Dr. Tolga ELBİR Assist.Prof.Dr. Eftade GAGA

(Jury Member) (Jury Member)

Prof.Dr. Mustafa SABUNCU **Director** Graduate School of Natural and Applied Sciences

ACKNOWLEDGMENTS

I would like to express my thanks to the precious people who stand by me during the preparation of this study. With this aim, at the beginning I would like to express my gratitude to my supervisor Prof.Dr. Abdurrahman BAYRAM for his invaluable guidance and encouragement during my study.

I would like to thank Assoc.Prof.Dr. Tolga ELBİR, Assist.Prof.Dr. Eftade GAGA and Prof.Dr. Mustafa ODABAŞI for their valuable academic recommendations and contributions. I wish also to thank Specialist Hasan ALTIOK and Research Assistant Yetkin DUMANOĞLU for their academic and moral supports. I am also indebted to Research Assistant Melik KARA and Environmental Engineer Fatih İLEK for their invaluable academic helps.

I would also like to express my special thanks to the personnel of $\overline{\text{z}}$ mir Provincial Environmental Directorate, Environmental Management and Environmental Impact Assessment Departments; the personnel of Aliağa Municipality Environmental Protection Department and a special thanks to Turgay ODABAŞ, the environmental engineer of ALOSBİ.

I want to thank also all of my friends and my dear family for being with me and believing in me. I couldn't have achieved this without their continuous moral support and encouragements.

Sedef ŞİMŞİR

INVENTORY AND MODELING OF ATMOSPHERIC VOC EMISSIONS FROM MAJOR SOURCES IN ALĠAĞA, ĠZMĠR

ABSTRACT

The objective of this study was to calculate the amount of NMVOCs coming from industrial facilities in the Aliağa and to estimate their effects in atmosphere under meteorological and topographical conditions of the region. With this aim, at the beginning, the required information of industrial facilities in Aliağa were collected; then NMVOC emissions were calculated by using these information, with the help of emission factors from literature and a software of USEPA, called TANKS. As a result of these calculations, it was approximately found that nine thousand seven hundred tons per year NMVOC emissions had been emitted to atmosphere from industrial facilities in Aliağa. The highest contributions to these emissions were coming from petrochemical, oil refining and liquid fuel storage and loading activities with thirtynine, thirtyfour and nine percentiles respectively. When the results were assessed according to emission types, it could be seen that the highest NMVOC emissions had come mainly from storage tanks (thirtyfour percentile), equipment leaks (twentyeight percentile), liquid loading (twenty percentile), process (seventeen percentile) and combustion (one percentile). As a second step, contributions of calculated emissions to air quality of the study area was estimated by using ISCST-Three dispersion model of USEPA. According to model results the highest pollution concentrations were found around the petrochemical, oil refinery and fuel loading and storage facilities; maximum values were about six hundred micrograms per cubic meter there. A significant NMVOC concentration dispersion could not be seen around the iron and steel plants because of low emission release from facilities.

Keywords: Aliağa; emission inventory; industrial facilities; non-methane volatile organic compounds (NMVOCs); TANKS; ISCST-Three.

İZMİR'İN ALİAĞA İLÇESİ İÇİN TEMEL KİRLETİCİ **KAYNAKLARDAN ATILAN ATMOSFERĠK UOB EMĠSYONLARININ ENVANTERİ VE MODELLEMESİ**

ÖZ

Bu çalışma ile amaçlanan, Aliağa'daki sanayi tesislerinden kaynaklanan uçucu organik bileĢiklerin (UOB) miktarını hesaplamak ve bölgenin meteorolojik ve topografik koĢulları altında hava kalitesine katkılarını tahmin etmektir. Bu amaçla önce Aliağa'daki sanayi tesislerine ait bilgiler toplanmış; daha sonra bu bilgiler kullanılarak, literatürden emisyon faktörleri ve USEPA'nın TANKS yazılımı yardımı ile UOB emisyonları hesaplanmıştır. Bu hesaplar sonucunda Aliağa'da sanayi tesislerinden yıllık yaklaĢık dokuzbinyediyüz ton UOB emisyonunun atmosfere verildiği bulunmuştur. Bu emisyonlara en yüksek katkılar sırasıyla yüzde otuzdokuz, otuzdört ve dokuzluk oranlar ile petrokimya, rafineri ve sıvı akaryakıt depolama ve dolum aktivitelerinden gelmektedir. Sonuçlar emisyon türlerine göre değerlendirildiğinde ise, en yüksek UOB emisyonlarının sırasıyla depolama tanklarından (yüzde otuzdört), bağlantı ekipmanlarından (yüzde yirmisekiz), dolum kollarından (yüzde yirmi), proseslerden (yüzde onyedi) ve yanmadan (yüzde bir) kaynaklandığı görülmüştür. İkinci aşama olarak, hesaplanan emisyonların çalışma alanının hava kalitesi üzerindeki etkileri, USEPA'nın ISCST-Üç adlı dağılım modeli kullanılarak tahmin edilmiştir. Model sonuçlarına göre en yüksek kirlilik konsantrasyonları petrokimya,rafineri ve akaryakıt dolum ve depolama faaliyetleri çevresinde bulunmuştur ki oradaki maksimum değerler altıyüz mikrogram bölü metreküp mertebelerindedir. Demir-çelik tesislerinden atılan UOB emisyonları çok düĢük seviyelerde olduğundan, buralarda kaydedeğer bir UOB konsantrasyon dağılımı bulunmamıştır.

Anahtar sözcükler : Aliağa; emisyon envanteri; sanayi tesisleri; uçucu organik bileĢikler (UOB); TANKS; ISCST-Üç.

CONTENTS

Page

CHAPTER ONE INTRODUCTION

The hydrocarbon gases and vapours in the air which have a vapour pressure between 0.13 and 101.3 kPa at ambient temperature and pressure are called volatile organic compounds (VOCs) (Derwent, 1995). They are one of the most important air pollutants because of causing undesired ozone formation, promoting the global greenhouse effect and having toxic effects on human health. VOC inventories are useful devices to determine the pollutant concentrations, their sources and effects on earth.

Izmir is one of the most developed cities of Turkey with its industrial activities, besides the commercial, economical, and social facilities. There are several industrial areas in the city which contribute to air quality significantly. Aliağa is one of these areas, even the most important one (Müezzinoğlu et al., 2000), because of having the most important heavy industrial facilities like an oil refinery, a large petrochemical industry, a lot of iron and steel plants, fuel and LPG storage and loading facilities, chemical plants and much more other industrial facilities in its boundaries. Moreover, it is a popular ever-growing area that, much more industries are planned to be established here. So that, air quality management studies are very important and required for this region.

Volatile organic compounds (VOCs) are one of the most important pollutants in Aliağa (Müezzinoğlu et al., 2000), because of being emitted in large quantities mainly from oil refining (crude oil processing), petroleum storage and distribution, solvent usage, chemical processes, metals industries, stationary combustion, landfilled wastes, food manufacture and agriculture (Derwent, 1995; Passant, 1995), and Aliağa has the large part of these industrial sectors.

In the previous years, several studies were carried out to determine the concentration levels of VOCs in Aliağa atmosphere (Eryiğit, 2000; Andiç, 2008; Civan et al., 2008; Doğan et al., 2008; Dumanoğlu et al., 2008; Elbir et al., 2008). However these studies included either a few types of VOCs or a few industrial plants. A detailed study on concentrations of total volatile organic compounds and for the Aliağa region was not achieved by this time. This study was prepared to overcome an important deficiency on emission levels and sources of nonmethane volatile organic compounds (NMVOCs) and their dispersion movements under certain meteorological and topographical conditions in Aliağa region. With this aim, at the beginning, the required information of industrial facilities in Aliağa were collected by the help of the questionnaries and the emissions were calculated. After the emission calculations, the dispersion of emission values were modeled by using the ISCST3 Dispersion Model of United States Environmental Protection Agency (USEPA).

The objectives of this study were;

- 1. to estimate the NMVOC emissions from industrial facilities in Aliağa industrial region,
- 2. to investigate the contribution of these emissions to the air quality under the meteorological and topographical conditions of the study area.

CHAPTER TWO

LITERATURE REVIEW

2.1 Volatile Organic Compounds (VOCs)

Pollutants can be categorized into two as primary and secondary pollutants. Primary pollutants are the pollutants that are emitted directly to atmosphere from a source, while secondary pollutants are the pollutants which come out as a result of some atmospheric reactions of primary pollutants (Müezzinoğlu, 2003). The most important secondary pollutant in the literature is ozone and VOCs (volatile organic compounds) is one of the most important primary pollutants which cause ozone formation as a result of several chemical reactions in the atmosphere.

There are various definitions about volatile organic compounds in the literature. The hydrocarbon gases and vapours in the air are generally called volatile organic compounds in a simple definition. Their vapour pressure at ambient temperature and pressure are between 0.13 and 101.3 kPa (Derwent, 1995).

According to EPA, the term volatile organic compounds (VOC) defines any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions (USEPA, 2010c). There are some compounds that have negligible photochemical reactivity. These compounds are mostly chlorofluorocarbons and also in spite of being important organic compounds, methane and ethane are not considered as VOC because of their properties of low reactivity. For this reason, in this study the emissions of only nonmethane volatile organic compounds were considered and this point forward, the term NMVOC was used to define the volatile organic compounds emissions.

NMVOC formation can be investigated in two different categories. The first one has natural origin, which comes from plants, trees, wild animals, natural forest fires and anaerobic processes in bogs and marshes (Derwent, 1995). The second one is

anthropogenic origin, which includes evaporation of petrol vapours from vehicle exhausts, oil refining (crude oil processing), petroleum storage and distribution, solvent usage, chemical plants, metals industries, stationary combustion, landfilled wastes, food manufacture and agriculture (Derwent, 1995; Passant, 1995).

NMVOC emissions from oil refining, petroleum (liquid and gaseous) storage and distribution facilities, steel making facilities, chemical processes, petrochemical activities and some other various industrial facilities and stationary combustion emissions from all of these facilities are mainly considered in this study.

The term NMVOC defines a large number of pollutants, and all effects of all of them can not be explained here in detail. But there are some common effects of these compounds, which can be found in the literature. These common effects can be discussed under five main headings; "stratospheric ozone depletion", "ground level photochemical ozone formation", "toxic or carcinogenic human health effects", "enhancing the global greenhouse effect", and "accumulation and persistence in the environment" (Derwent, 1995).

Many organic compounds can reach to stratosphere from atmosphere and as a result of photolysis and hydroxyl radical destruction, stratospheric ozone depletion occurs. This is also known as ozone hole formation and is a serious threat for both humans and natural life balances.

In the ground level, organic compounds take part in photochemical ozone formation by reacting with the hydroxyl radical in the lack of the NO_x compounds. If there are enough NOx compounds in the ground level, the hydroxyl radical prefers to react with NO_x . But if the hydroxyl radical prefers to react with NMVOC as a result of lack of NOx, ozone formation occurs in the atmosphere. This is an undesired case, because ozone has toxic effects in the lower layers of atmosphere (Eryiğit, 2000).

NMVOCs not only effect the humans by ozone formation, but also have dangerous and harmful effects on people. They can cause cancer and genetic problems besides developmental disorders and problems on reproductive functions (Müezzinoğlu, 2003).

Some organic compounds can accumulate in the troposphere and absorb solar or terrestrial infrared radiation. This causes the greenhouse effect (these organic compounds are called radiatively active gases). But many compounds act as secondary greenhouse gases, that means they cause greenhouse effect indirectly. If a compound reacts to produce ozone in the troposphere or the same compound increases or decreases the tropospheric hydroxyl radical distribution, it can be classified as a secondary greenhouse gas (Derwent, 1995).

2.2 Emission Inventories and Preparation Methods

The term *emission* defines the mass flow rate of a pollutant which is released to atmosphere from an identified pollutant source. EPA describes the same term as the gases and particles which are emitted by various sources (USEPA, 2010b). Based on those definitions, EPA defines the term *emission inventory* as the quantities of pollutants measured over a certain period (USEPA, 2010b). It can also be defined as the list of emission estimates for sources of air pollution in a certain area for a specified time period is called emission inventory (BAAQMD, 2010). They are detailed studies which help to identify the main sources of pollutants such as combustion, industrial processes, product use, agricultural facilities, waste control facilities, natural sources, etc. (EEA, 2009).

Emission inventories are useful and required tools for both scientific researches and decision mechanisms of local authorities about air quality management strategies. Emission maps which show the geographic distribution of emissions, can be plotted as a result of emission inventories and these maps help in case of land use planning (Hutchinson, 1997). Hutchinson (1997) also points out that, "Emission inventories can be used in conjuction with an atmospheric dispersion model to assess trends in air quality". According to study, it is also possible to evaluate possible

future scenarios for air quality in the study area, by changing the input data of the model study.

The emission data are required for the following purposes (Obermeier, Seier, Friedrich, & Voβ, 1992):

- identification of main sources of pollutants
- quantification of the objectives of pollution control
- establishment of a basis for evaluation of optimal emission reduction strategies
- creation of input data for models of transport and chemical transformation of air pollutants.

To sum up, the existing pollution levels in an area (e.g., country, city, town or zone) can be determined by using emission inventories. The potential pollutant levels for the years ahead can be estimated by using various mathematical models or computer softwares using emission data in inventories. Then prevention strategies and techniques can be developed by local authorities in association with the researchers to reduce the emission values and reach the desired air quality levels for health.

The USEPA reported that (USEPA, 1980; USEPA, 1997), there are mainly four stages which can be followed to prepare an emission inventory. The first stage is *planning*. The purpose of the inventory study and the planned end use should be explained at the beginning. After this, the pollutants, emission source categories (i.e., point, area, line sources) and geographical boundaries of the study area should be designated. Then a work plan should be prepared to determine the steps for the creation of the intended inventory. Source category coverage, selection of emission estimation methods and data management and reporting strategies should be included in the work plan. A work plan is very important for an emission inventory study to study systematically and solve the possible problems during the study easily.

The second stage of an emission inventory study is *data collection*. After planning the study, the data collection can be started. At this stage, according to type of the emission source (i.e, point, area, line), questionnaries are prepared and distributed or meetings with the relevant institutions (e.g., industrial plants and governmental institutions) are organized to have the required information clearly. The necessary information are mainly composed of nature of facility, production capacity, raw material and fuel consumption data. Furthermore, if there is a control device in the plant to reduce the emissions, it should also be noted in this stage of the study.

The third stage is composed of the *analysis of data collected* and the *development of emission estimates*. In this stage, the collected data should be arranged and evaluated to use in emission estimations. The emission estimations can be done in three different ways; the source test method, material balance method and emission factors method. In source test method, the process conditions and emission concentrations are reported as a result of direct measurements or monitoring service. In material balance method, the emissions from solvent evaporation are estimated; but to achieve this method, the inputs and outputs must be known for each point of the flow diagram of the process. In emission factors method, some coefficients which were created in different previous studies as a result of source test or material balance methods done previously are used to estimate emissions. In fact, in recent years, emission estimation models (computer softwares) and various calculation methods are also used to determine the emissions from point, area or line sources. In this study,emission factors were mainly used to estimate industrial emissions, and besides them a software, which was produced by USEPA, was also used to estimate emissions.

The fourth and the last stage of generating an emission inventory is *reporting*. In this stage, the results of emission inventory should be expressed clearly with the help of tables and graphics also. Emission inventories are the tools which can be used while making researches on air quality of a region, estimating the possible pollution levels in further years and improving pollution prevention strategies for the region. This means, different people from various institutions can make benefit of the results of the mentioned inventory, so that it is very important to present the study results clearly.

2.2.1 Using Emission Factors to Estimate Emissions

One of the most frequently used emission estimation methods is determining emissions using emission factors from literature. Emission factors are the coefficients which are prepared as a conclusion of various emission measurement studies done before, and they define the amount of pollutants given to the atmosphere per an unit of activity by a definite source. A general equation for emission estimation with an emission factor can be seen below (USEPA, 2009).

$$
E = A \times EF \times (1 - \frac{ER}{100}) \tag{2.1}
$$

- E : emissions
- A : activity rate
- EF : emission factor
- ER : overall emission reduction efficiency (%).

In the literature, there are several reliable emission factor databases which were generated by USEPA (United States Environmental Protection Agency), EEA (European Environment Agency), IPPC (European Commission Integrated Pollution Prevention and Control) and IPCC (Intergovernmental Panel on Climate Change). There are a huge number of emission factors for various situations in these databases and they are updated regularly depending on the developments in technology.

2.2.2 Using a Computer Software to Estimate Emissions

Storage tanks are one of the most important constituents of NMVOC emissions in industrial plants. Although the tanks, which are used for storage, are sheltered not to exude the contents out, fugitive emissions can be occured from tanks. This cause a common and important emission problem for industries which have tank farms. So, The United States (US) Environmental Protection Agency's (EPA) Office of Air Quality Planning and Standards (OAQPS) developed a software, called TANKS 4.0, to determine the fugitive emissions arising from tanks. The working principle of this software belongs to the emission factors method (USEPA, 1995c) and it was created to accelerate the emission calculation studies.

According to the software, there are 3 tank types; fixed roof tanks, external floating roof tanks and internal floating roof tanks.

Fixed roof tanks (Figure 2.1) are made up of a cylindrical steel shell and a flat or dome or cone shaped stationary roof. The tank can have a breather (pressure/vacuum) vent or can be freely vented. There can be very small changes in liquid level, temperature or pressure in the tank, and if the system has a breather vent, these changes do not cause the vapor release from the tank. This is an advantage of a tank with a breather vent when compared with a freely vented tank. Fixed roof tanks are also the most economic tank type when compared with the other tank types in the software.

Figure 2.1 Fixed roof tank (USEPA, 1995c)

There are two types of emissions from fixed roof tanks according to the software. They are storage and working losses. When there is a change in temperature and barometric pressure, the vapor in the tank expands or contracts, so that a part of this vapor leaves the tank. This is called *standing storage loss (breathing loss)*. It should be considered that there is not a significant change in liquid level in the tank in case of storage loss. There are also other losses which come into existence during liquid filling and emptying activities and the total of these losses is called *working loss*. There is a liquid level change in the tank in this case, opposite of the storage loss.

Emissions from fixed roof tanks can vary according to vessel capacity, vapor pressure of the stored liquid, utilization rate of the tank and atmospheric conditions at the tank location (USEPA, 1995c).

The total emission value is composed of storage losses and working losses in fixed roof storage tanks and it is calculated in the software as shown below (USEPA, 1995c).

$$
L_T = L_S + L_W \tag{2.2}
$$

 L_T : total losses, lb year⁻¹

 L_S : standing storage losses, lb year⁻¹

 L_W : working losses, lb year⁻¹

$$
L_S = 365 V_V W_V K_E K_S \tag{2.3}
$$

 L_S : standing storage loss, lb year⁻¹

 V_V : vapor space volume, ft³

 W_V : stock vapor density, lb ft⁻³

 K_{E} : vapor space expansion factor, dimensionless

 K_S : vented vapor saturation factor, dimensionless

 365 : constant, the number of daily events in a year, (year)⁻¹

Here, V_V is the function of the tank diameter and effective height of tank; W_V is the function of molecular weight of vapor, pressure of vapor at daily average liquid surface temperature. K_E is the function of vapor temperature, ambient temperature, solar insolation or the function of vapor temperature, vapor pressure, breather vent pressure, atmospheric pressure and average liquid surface temperature; one of these two functions can be selected according to the values of true vapor pressure of the liquid in the tank and the breather vent settings (pressure/vacuum values). Finally, K_S is the function of vapor pressure at liquid surface temperature and heights of tank and liquid.

$$
L_W = 0.0010 \, M_V \, P_{VA} \, Q \, K_N \, K_P \tag{2.4}
$$

- L_W : working loss, lb year⁻¹
- M_V : vapor molecular weight, lb (lb mole)⁻¹
- PVA : vapor pressure at daily average liquid surface temperature, psia
- Q : annual net throughput, bbl year⁻¹
- K_N : working loss turnover factor, dimensionless
- K_P : working loss product factor, dimensionless

Here, K_P is a constant that changes according to the liquid type. K_N is a function of turnovers per year. Q is the annual net throughput and it is calculated by the multiplication of tank capacity and annual turnover rate. P_{VA} times M_V is equal to the multiplication of W_V , the idle gas constant (R) and daily average liquid surface temperature (T_{LA}) .

Floating roof tanks have two different types; external (Figure 2.2) and internal (Figure 2.3) floating roof tanks. Although their construction mechanisms are substantially same, there are some differences between them. Both of them are made up of a cylindrical steel shell and a floating roof on the liquid content. The floating roof goes up and down according to the change of liquid content level in the tank. The tank system also contains a deck, fittings and rim seal system. The deck is in contact with the tank wall with the rim seal system. The purpose of the floating roof and the rim seal system is to reduce the evaporative loss of the stored liquid. The difference is the fixed roof above the floating roof which is available in internal floating roof tanks, while the external one has an open-top. Also, the internal floating roof tanks have a lighter floating deck than the external one; this is also another difference (USEPA, 1995c).

Figure 2.2 External floating roof tank (USEPA, 1995c)

Emissions of external and internal floating roof tanks are composed of withdrawal losses and standing storage losses. When the floating roof goes down depending on the decrease of liquid level in the tank, a part of liquid remains on the inner part of the tank wall (on the upper part) and this liquid remains evaporate. This is called *withdrawal losses*. Rim seal, deck fitting and deck seam losses are the constituents of *standing storage losses*. There is also a little amount of breathing losses which occur during the pressure and temperature changes, that can be considered under the standing storage losses. The total emissions of a floating roof tank are the sum of the withdrawal and standing storage losses and their calculation equations are described below (USEPA, 1995c).

Figure 2.3 Internal floating roof tank (USEPA, 1995c)

Floating roof tank emissions are estimated for two different conditions; the first one is *normal operation* and the second one is *roof landing* situation.

For normal operation;

$$
L_T = L_R + L_{WD} + L_F + L_D \tag{2.5}
$$

 L_T : total loss, lb year⁻¹

 L_R : rim seal loss, lb year⁻¹

 L_{WD} : withdrawal loss, lb year⁻¹

 L_F : deck fitting loss, lb year⁻¹

 L_D : deck seam loss, lb year⁻¹

L_D is considered for bolted internal floating roof tanks only. In the study, all of the internal floating roof tanks are acknowledged as welded. So the emissions are always equal to zero in the study.

$$
L_R = (K_{Ra} + K_{Rb} v^n) D P^* M_V K_C
$$
 (2.6)

 L_R : rim seal loss, lb year⁻¹

 K_{Ra} : zero wind speed rim seal loss factor, lb-mole (ft year)⁻¹

 K_{Rb} : wind speed dependent rim seal loss factor, lb-mole $((mph)ⁿft year)⁻¹$

v : average ambient wind speed at tank site, mph

n : seal-related wind speed exponent, dimensionless

 P^* : vapor pressure function, dimensionless

D : tank diameter, ft

 M_V : average vapor molecular weight, lb (lb-mole)⁻¹

 K_C : product factor depending on the stored liquid type

Here, P^* is a function of atmospheric pressure and vapor pressure at liquid surface temperature. K_{Ra} , K_{Rb} and n factors can be taken from a table in which the factors alternate according to the rim-seal system type. Average ambient wind speed (v) and tank diameter (D) are requested directly by the software to be entered by the user. M_V is taken from the related table depending on the stored liquid. Finally, K_C is a constant value which alternates according to the liquid.

$$
L_{WD} = \frac{(0.943) \, Q \, C_S W_L}{D} \tag{2.7}
$$

 L_{WD} : withdrawal loss, lb year⁻¹

- Q : annual throughput, bbl year⁻¹
- C_S : shell clingage factor, bbl $(1,000 \text{ ft}^2)^{-1}$

 W_L : average organic liquid density, lb gal⁻¹

D : tank diameter, ft

 0.943 : constant, 1,000 ft³ gal bbl⁻²

Here, Q is the multiplication value of tank capacity and annual turnover rate. C_S is a factor which can be read from a table, and alternates depending on the stored product (like gasoline or crude oil) and shell condition (light rust, dense rust or gunite lining). W_L is selected from the related tables according to the stored product and finally D is entered to the software by the user.

$$
L_F = F_F P^* M_V K_C \tag{2.8}
$$

 L_F : the deck fitting loss, lb year⁻¹

 F_F : total deck fitting loss factor, lb mole year⁻¹

P^{*} : vapor pressure function, dimensionless

 M_V : vapor molecular weight, lb (lb mole)⁻¹

 K_C : product factor depending on the stored liquid type

Here, K_C , M_V and P^* are known from the previous equations. F_F is a new definition and calculated as below;

$$
F_F = [(N_{F1} K_{F1}) + (N_{F2} K_{F2}) + \dots + (N_{F_{n_f}} K_{F_{n_f}})]
$$
\n(2.9)

 N_{Fi} : number of deck fittings of a particular type (i = 0,1,2,...,nf), dimensionless K_{Fi} : deck fitting loss factor for a particular type fitting (i = 0,1,2,...,nf), lb mole year⁻¹

 n_f : total number of different types of fittings, dimensionless

For roof landings;

$$
L_{TL} = L_{SL} + L_{FL} \tag{2.10}
$$

 L_{TL} : total losses during roof landing, lb per landing episode

LSL : standing idle losses during roof landing, lb per landing episode

LFL : filling losses during roof landing, lb per landing episode

When the storage tank is emptied, the roof no more floats on the surface of the liquid and it lands on deck legs. During the drop of liquid and landing on deck legs (with a little liquid in the tank, this is also called liquid heel), a vacuum condition arises. This is a dangerous situation, because of the vacuum the roof can collapse. To avoid the danger, an equilibrium should be created in pressure; so a breather vent must be used. This vent remains open while the roof is landed. The vapor that occurs in this time period goes out of the tank by using this breather vent and is called standing idle loss (Figure 2.4).

Figure 2.4 Standing idle with a liquid heel in floating tanks (Troxel, 2009).

In external floating roof tanks with a liquid heel, the wind affects the emission releases from the tank. Because the wind causes the liquid vapor to go out of the tank and the liquid produces vapor again to fill the space under the roof (Figure 2.5) (USEPA, 1995c).

$$
L_{\text{slwind}} = 0.57 n_d D P^* M_V \tag{2.11}
$$

Figure 2.5 Wind effect on external floating rood tanks (Troxel, 2009).

$$
L_{FL} = \left(\frac{PV_V}{RT}\right)M_V \left(C_{sf} S\right) \tag{2.12}
$$

 L_{FL} : filling loss during roof landing, lb

P : true vapor pressure of the liquid within the tank, psia

 V_V : volume of the vapor space, ft³

R : ideal gas constant, 10.731 psia ft^3 (lb mole $^\circ \text{R})^{-1}$

T : average temperature of the vapor and liquid below the floating roof, ${}^{\circ}R$

 M_V : stock vapor molecular weight, lb (lb mole)⁻¹

 $C_{\rm sf}$: filling saturation correction factor, dimensionless

S : filling saturation factor, dimensionless (0.60 for a full liquid heel; 0.50 for a partial liquid heel)

Here, S is a dimensionless factor that alternates according to the liquid heel to be full or partial. C_{sf} is calculated as a function of standing idle losses with and without the wind effect.

A group of data should be entered into the software in four main steps. These are identification, physical characteristics, site selection and tank contents. At the beginning, an identification number should be given for the tank that will be defined, and the definitive notes should be added in the identification step. In physical characteristics step, tank dimensions, shell and roof characteristics and breather vent settings should be entered. In the other step, the location of the tank must be defined and the meteorological properties of the location should be described into the software. Finally the liquid in the tank should be selected from the list in tank contents step or if it does not exist in the list, it should be defined in the software with its specific characteristics like density, molecular weight, vapor pressure for different temperatures and etc.

2.2.3 Using an Emission Factor Based Method to Estimate Emissions

Petroleum and petrochemical liquid loading facilities are also an important source of volatile organic compound emissions to the atmosphere. These emissions from loading facilities are called *loading losses*. Loading losses can occur at three stages. While the liquid in the tank is being emptied, it evaporates at the same time; this is the first type of emission. There are always liquid residues in the tank after a liquid is being emptied, and in spite of being empty, an evaporation occurs in the tank; this is the second type emission. Finally, while the new liquid is being loaded within the tank, the third type of evaporation occurs. These three type of evaporations constitute the total loading losses.

There are two types of loading methods; *splash loading* and *submerged loading*. In splash loading (Figure 2.6), a pipe is swung into the tank and the liquid is loaded into the tank from above. A liquid turbulence comes into existence while the liquid is loaded and a vapor-liquid contact occurs in this type of loading; vapor generation and losses are relatively higher.

Figure 2.6 Splash loading method (USEPA, 1995d)

In submerged loading, there are two methods; *submerged fill pipe* (Figure 2.7) and *bottom loading* (Figure 2.8). The pipe is swung into the tank from above again in submerged fill pipe method, but it's different from splash loading because the end of loading pipe is almost at the bottom of the tank and after a short while it is submerged by the liquid. In bottom loading method, there is a fixed pipe under the tank and the liquid is loaded from that pipe. Both submerged loading methods cause less emissions than splash loading method.

Figure 2.7 Submerged fill pipe method (USEPA, 1995d)

Figure 2.8 Bottom loading method (USEPA, 1995d)

Emissions from liquid loading facilities can be estimated as explained below by the reference of USEPA (1995d).

$$
L_L = 12.46 \frac{SPM}{T} \tag{2.13}
$$

 L_L : loading loss, pounds per 1000 gallons (lb $(10^3 \text{ gal})^{-1}$) of liquid loaded

- S : a saturation factor
- P : true vapor pressure of liquid loaded, psia
- M : molecular weight of vapors, lb $(1b \text{ mole})^{-1}$
- T : temperature of bulk liquid loaded, ^oR

Here, T should be known. M and P can be selected from Table 2.1 and Table 2.2 and S should be selected from Table 2.3.

For marine vessels, for products other than gasoline and crude oil, the saturation factor (S) can be selected from Table 2.2. If there is a marine loading of gasoline, emission factors from Table 2.4 should be used to estimate the NMVOC emissions. If the product is crude oil, equations 2.14 and 2.15, and Table 2.5 should be used.

Petrochemical Name	Molecular Weight lb (lb mole) $^{-1}$	Liquid Density lb $(gal)^{-1}$	Vapor Pressure psi
Acrylonitrile	53.06	6.8	5.2
Benzene	78.11	7.4	4.2
Paraxylene	106.20	7.2	6.2
Monoethylene glycol	62.07	9.3	5.2
Diethylene glycol	106.12	9.3	5.2
Ortoxylene	106.20	7.2	6.2
Vinyl chloride	62.5	7.7	5.2
Hexane	86.2	5.9	5.2
Heptane	100.20	5.9	5.2
Acetic Acid	60.05	8.8	9.6
Propylene	42.08	4.4	5.2
Butadiene	54.70	5.1	5.2
Toluene	92.14	7.3	4.2
Ethylene	28.05	4.7	3.4
Ammonia	17.03	5.7	3.4

Table 2.1 Properties of selected petrochemicals.

Table 2.2 Properties of selected petroleum liquids (USEPA, 1995c)

Cargo Carrier	Mode of Operation	S Factor
Tank trucks and rail tank cars	Submerged loading of a clean cargo tank	0.50
	Submerged loading: dedicated normal service	0.60
	Submerged loading: dedicated vapor balance	1.00
	service	
	Splash loading of a clean cargo tank	1.45
	Splash loading: dedicated normal service	1.45
	Splash loading: dedicated vapor balance service	1.00
Marine vessels*	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

Table 2.3 Saturation (S) factors for calculating petroleum liquid loading losses (USEPA, 1995d)

*For products other than gasoline and crude oil.For marine loading of gasoline, factors from Table 2.4 should be used. For marine loading of crude oil, Equations 2.14, 2.15 and Table 2.5 should be used.

$$
C_L = C_A + C_G \tag{2.14}
$$

 C_{L} : total loading loss, lb $(10^{3}$ gal)⁻¹ of crude oil loaded

 C_A : arrival emission factor, contributed by vapors in the empty tank compartment before loading, lb $(10^3 \text{ gal})^1$ loaded

 C_G : generated emission factor, contributed by evaporation during loading, lb $(10^3 \text{ gal})^{-1}$ loaded

$$
C_G = 1.84(0.44 P - 0.42) \frac{M G}{T}
$$
\n(2.15)

 C_G : generated emission factor, contributed by evaporation during loading, lb/10³ gal loaded

P : true vapor pressure of loaded crude oil, psia

M : molecular weight of vapors, lb $(lb \text{ mole})^{-1}$

- G : vapor growth factor = 1.02 (dimensionless)
- T : vapor temperature, ${}^{\circ}R$, (${}^{\circ}F + 460$)

 C_A and C_G factors are for total organic carbons. NMVOC factor can be calculated by multiplication of C_A and C_G factors with 0.85 (USEPA, 1995d).

Vessel Tank	Previous	Ships/Ocean Barges		Barges	
Condition	Cargo	$mg1^{-1}$	lb $(10^3 \text{ gal})^{-1}$	$mg1^{-1}$	lb $(10^3 \text{ gal})^{-1}$
		Transferred	Transferred	Transferred	Transferred
Uncleaned	Volatile	315	2.6	465	3.9
Ballasted	Volatile	205	1.7		
Cleaned	Volatile	180	1.5		
Gas-freed	Volatile	85	0.7		
Any condition	Nonvolatile	85	0.7		
Gas-freed	Any Condition			245	2.0
Typical overall situation	Any Condition	215	1.8	410	3.4

Table 2.4 Volatile organic compound (VOC) emission factors for gasoline loading operations at marine terminals (USEPA, 1995d)

Table 2.5 Average arrival emission factors (C_A) , for crude oil loading emission equation (USEPA, 1995d)

Ship/Ocean Barge Tank	Previous Cargo	Arrival Emission Factor,
Condition		lb $(10^3 \text{ gal})^{-1}$
Uncleaned	Volatile	0.86
Ballasted	Volatile	0.46
Cleaned or gas-freed	Volatile	0.33
Any condition	Nonvolatile	0.33

2.3 Dispersion Modeling

Creating an emission inventory is the first step of an air quality assessment. The emission inventory can give an idea about the amount of a pollutant; but its dispersion with meteorological conditions on air, corresponding pollutant concentrations and effects on air quality can be estimated by using special dispersion models. Activating a mathematical simulation which is used to simulate the behaviour of air pollutants in the ambient atmosphere under certain meteorological conditions is defined as *dispersion modeling*. The dispersion models achieve the estimation of downwind concentrations of air pollutants emitted from various sources (e.g., industrial, domestic or traffic based). There are many special computer programs, achieving dispersion modeling (i.e., BLP, CALINE3, CDM2, ISCST3,

MPTER, PTPLU, etc.) created by various organizations. In this study the Industrial Source Complex Short Term Model (ISCST3) of USEPA was used to estimate the dispersion of industrial based NMVOCs on Aliağa; because it was a widely-used program in similar previous studies.

Modeling is a cheap and easy way to comment on air quality of an area when compared with air quality monitoring activities. Monitoring activities require special and long periods of time, special devices and money correspondingly. But modeling can be realized any time in anywhere in which a computer exists.

Dispersion modeling is an easy way of estimating the concentrations of a pollutant under various meteorological and geographical conditions. The most widely used models are based on Gaussian distribution (Godish, 1997). ISCST3 is also a steady-state Gaussian plume model that can be used to estimate pollutant concentrations from various sources (e.g., stacks, storage tanks, liquid loading pipelines and pipeline equipments in this study) of an industrial facility. The model calculates the concentrations according to the following equation of Gaussian distribution given below with equation number 2.16 (Cooper, & Alley, 1994; USEPA, 1995b). The coordinate systems, used in Eq. 2.16, are applied as shown in Figure 2.9.

$$
C_{(x,y,z,h)} = \frac{Q}{2\pi u \sigma_y \sigma_z} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \left\{ \exp\left[-\frac{(z-H)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+H)^2}{2\sigma_z^2}\right] \right\} \tag{2.16}
$$

C : steady-state concentration at a point (x,y,z) , $\mu g m^{-3}$

Q : emissions rate, μ g s⁻¹

σy, σ^z : horizontal and vertical spread parameters, m (the functions of distance, x, and atmospheric stability)

u : average wind speed at stack height, $(m s⁻¹)$

- y : horizontal distance from plume centerline, m
- z : vertical distance from ground level, m
- H : effective stack height (the sum of physical stack height and plume rise), m

The assumptions about Eq. 2.16 are given below;

- the turbulence is the same for anywhere,
- σ_y and σ_z are the functions of distance, x,
- the wind speed and wind direction are constant at the plume layer,
- the plume dispersion is a Gaussian distribution. σ_y and σ_z are the standard, deviation values of plume concentration distribution in lateral and vertical directions,
- the total reflection occurs in the ground surface; a storage in this surface or a reaction with this surface are not possible.

Figure 2.9 Coordinate systems for Gaussian plume model.

2.4 Previous Studies

Emission inventories have been prepared for different areas all over the world for many years. Elbir (1997) treated the emission inventories for different scales of important organizations and project teams those had been carried out till the year 1997 in his study. Generation methods, similarities and differences of different emission inventories were investigated by exploring the important inventories of OECD-MAP, CEC-CORINAIR, ECE-EMEP and much more in this study. Elbir mentioned a local scale emission inventory study in his work. The aim of that study which was achieved by Müezzinoğlu, Elbir, Bayram, & Seyfioğlu (1997), was to identify the major air pollution sources and emission levels of Izmir for the year 1996. In the study, emissions from industrial facilities, domestic heating and traffic were considered. The emissions were estimated by the use of emission factors together with the fuel consumption values for each source. The emission factors were taken from Corinair and USEPA's databases. At the end of the study, it was found that, in Turkey, 9% of SO_x , 6% of NO_x , 3.5% of NMVOC and 3.5% of CO emissions were originated from Izmir. When these values were evaluated according to only industrial pollution, 30% of SO_x , 18% of NO_x and 52% of CO were originated from Izmir. It was specified in the study results that, this was because of the use of poor quality fuels and inappropriate technology use in industrial facilities. According to the study, industries were the main pollutant sector for SO_X and NMVOC, while for NO_X and CO traffic was the main pollutant sector in İzmir in 1996.

The same project group (Müezzinoğlu et al., 2000) created a regional emission inventory for the Aegean Region in Turkey then, as a follow up study. In that study, the same approach was used to estimate industrial, domestic and traffic emissions; the fuel consumptions and emission factors were used together for seven cities in the region. At the end of the study, Izmir was found to have the highest emissions for both industrial and domestic heating sectors. Specialized result for Aliağa in that study was $10,645$ tons year⁻¹ NMVOC emissions.

In 2004, again Elbir & Müezzinoğlu (2004) published an article which reports the emission values of Izmir , for the year 2000; coming from point (industrial), line (vehicular) and area (domestic) sources. In that article, it was specified that SO_2 was the major pollutant with $84,271$ ton year⁻¹ total emission value in Izmir and the most pollutant sector for this pollutant was the industry with $74,443$ ton year⁻¹. For PM, the most polluting sector was domestic heating with $14,697$ ton year⁻¹ and for NOX, the most polluting sector was the traffic with $29,711$ ton year⁻¹. According to the study results, the petroleum refinery and the petrochemical industry were found as the largest sources of air pollution.

When looked at national scale, the study of Ağaçayak (2007) can be viewed. In this study, an emission inventory was prepared for Turkey by considering the emissions coming from mobile sources, small combustion processes, large combustion plants and the most important industrial processes. Study results showed that, Istanbul, Ankara and Izmir had the highest pollution levels. NO_X was the most emitted pollutant from mobile sources. PM_{10} emissions came from industrial combustion processes and cement production at first. Power plants were the main contributories of SO_2 emissions with a percentage of 67% of all pollutant sectors.

Another country based emission inventory was prepared for Thailand by Pham, Manomaiphiboon, & Vongmahadlek (2008). In this study, emissions from power plants and industrial facilities were estimated using fuel consumptions. In the inventory, the examined pollutants were nitrogen oxides (NO_X) , sulfur dioxide $(SO₂)$, carbon monoxide (CO), non-methane volatile organic compounds (NMVOC), ammonia (NH_3) , organic carbon (OC) and black carbon (BC) . Emissions were calculated by the multiplication of activity rates (i.e., fuel consumption values) and emission factors. The emission factors were selected from different sources; from USEPA, IPPC, and different previous studies of other scientists. At the end of the study, the total annual NMVOC emissions of power plants due to fuel consumption were found as $6.1x10^3$ tons. For industrial facilities this number was found as $33.4x10³$ tons NMVOC emissions (due to fuel consumption), and $76.0x10³$ tons NMVOC emissions due to industrial processes. It was reported that the Central and Eastern regions of the country emitted the 70%-80% of the national emissions from industrial facilities and the largest emissions came from Food and Beverage, Chemical and Non-Metal industries. Large NMVOC emissions were seen in Food and Beverage industry and large CO emissions were seen in Paper industry. Petroleum facilities also emitted large amount of NMVOC, i.e., it was approximately equal to half of NMVOC emissions from total industrial processes.

In another study, Srivastava & Majumdar (2010) prepared an inventory of evaporative non-methane hydrocarbons for four metro cities (Delhi, Mumbai, Chennai and Kolkata) in India for the time period of April 2003 to March 2004. The

evaporative emissions from activities of dry cleaning, architectural surface coating, automobile refinishing, newspaper printing, petrol loading, petrol refuelling, computer printers, commercial consumer product, graphic art applications, and also emissions from transit losses and fuel evaporation losses from vehicles during different conditions were considered in the study. Various emission factors were accepted for these activities by making assumptions in line with related information taken from the relevant institutions. Finally, it was found that, evaporative emissions existed highest to lowest in Delhi, Chennai, Mumbai and Kolkata respectively. The total evaporative emissions of hydrocarbons were calculated as 3.7683 Gg year⁻¹ at these four metros. The highest emission values in these cities were from vehicular activities; with a value of approximately 96% of the total evaporative emissions. Also surface coating, consumer products, graphic art printing, petrol refuelling, loading/unloading and dry cleaning activities were the major responsible of these emissions.

When the literature is examined, a detailed emission inventory of total NMVOCs for Aliağa can not been found; although there are several measurement studies of different organic compounds for the town. The first study about NMVOC concentrations in Aliağa (Eryiğit, 2000) includes the measurements of benzene, toluene, xylenes with gas chromotography, using the sampling method of activated carbon adsorption, and formaldehyde with two different colorimetric methods. The results were found as 101-180 μ g m⁻³ for formaldehyde while 0.8-35.5, 0.4-100.7, 7.3-25.6, 5.6-97.1 and 5.6-28.8 μ g m⁻³ were detected for benzene, toluene, p-xylene, m-xylene and o-xylene respectively. The second study (Andiç, 2008) is a passive sampling study of twenty-three different volatile organic carbons. Four of them, called BTEX (i.e., benzene, toluene, ethyl benzene and xylene) were also examined in detail because of having harmful effects on human health. As a result, it was found that styrene, 2-methylhexane and toluene were respectively the most abundant compounds in Aliağa and the highest NMVOC concentrations were detected around the refinery and petrochemical industry. In other studies (Civan et al., 2008; Doğan et al., 2008; Dumanoğlu et al., 2008) passive and active sampling methods were applicated to determine the NMVOC concentrations in Aliağa. These studies indicate
that, highway traffic and domestic heating are effective on NMVOC pollution, but the highest concentrations come from industrial facilities in the region, and mainly from refinery and petrochemical industry. From this point of view, Elbir and colleagues (2008) examined the NMVOC emissions from storage tanks and liquid loading facilities of petroleum refinery in Aliağa. The NMVOC emissions from storage tanks were found as 85 tons year⁻¹, while the emissions from liquid loading were $1,162$ tons year⁻¹. In the study, NMVOC concentrations were measured also near five different tanks and the values changed between 229 to 3577 μ g m⁻³.

CHAPTER THREE MATERIALS AND METHODS

3.1 Study Area

Aliağa is a town of İzmir which is located in the northern part of the city with its surface area of 412.5 km^2 . It is surrounded by Manisa on the East, Bergama and Dikili on the North, Menemen on the South and Foça on the Southwest directions. The West border is Aegean Sea. There are Dumanlı and Yunt (~1000 m) Mountains around the town. Güzelhisar is the only watercourse within the town boundaries with an average flowrate about 3.71 $m^3 s^{-1}$ (Aliağa Municipality, 2009). There is also a dam on this brook, called Güzelhisar Dam, which was constructed by Petkim Petrochemical Company and managed by DSI (General Directorate of State Hydraulic Works) to supply the water demand of Petkim and other industrial plants in the zone besides drinking and other usage demands. The dam has a volume capacity of 158 million m^3 .

The dominant climate type is the mild Mediterranean climate in Aliağa. This means that winters are mild and rainy, and the summers are hot and arid. In winter, northerly winds are dominant in the town but in summer, the breeze comes from West and refreshes the environment. The average temperature in Aliağa in winter is about 10°C and the coldest month is January while the average temperature is between $24 - 27$ °C in summer. The dominant vegetation is compatible with the climate type; so it has very few forests but lots of maquis shrublands.

Aliağa has a human population of 63,503 according to 2009 population census (TUİK, 2010). 51,108 people of this value live in the centre of the town and $12,395$ people live in the surrounding villages (TUİK, 2010). The ratio of men population to women is approximately 1.02 in the town (TUİK, 2010).

Aliağa is one of the most developed towns of İzmir in terms of industrial facilities. The first industrialisation activities started at seventies with establishments

of the refinery and the petrochemical industry. Several liquified gas filling and storage facilities, arc furnaces and rolling industries were established later. In the town, private sector investments are established in eighties, and especially in the second half of the nineties, they became accelerated. Today, there are a lot of iron and steel industries, gas and liquid fuel filling, storage and sale facilities, ship breaking facilities, paper and fertiliser industries, rolling mills and other various industries in Aliağa besides the refinery and the petrochemical industry (Figure 3.1). There are also 3 power plants, using natural gas, which have installed powers of 250 MW, 180 MW and 1532 MW (Aliağa Municipality, 2009) in the town.

Figure 3.1 Study area and the industries in Aliağa town.

In Aliağa, there are 15 iron and steel plants; 10 of them have only rolling mills, and the others have both steel mills and rolling mills. In steel mills, the scrap iron is melted in electric arc furnaces with the help of carbon electrodes and NMVOC emissions come out during this process. In rolling mills, hot rolling technology is used to produce billets and various steel profiles from steel ingots. The ingots are heated in reheating furnaces and then passed through the cylinders. The lubricating oil between the cylinders become evaporated while the steel ingots are passing and this cause NMVOC emissions during the process.

There is an important oil refinery in Aliağa which was established in 1972 and now have a crude oil processing capacity of 11 million tons per year. The main NMVOC sources in the refinery are storage, product loading and handling facilities, fugitive emissions from pipeline equipment (e.g., valves, flanges, etc.) and flare systems.

Aliağa is an inviting place for liquid fuel loading and LPG loading facilities because of the refinery in the region. There are 5 liquid fuel loading and 7 LPG loading plants in the town. Liquid fuel loading plants emit NMVOC from storage tanks, liquid loading activities and leaks from equipment like valves, flanges and etc. Also, LPG loading facilities cause NMVOC emissions from equipment leaks and bottle painting; but there is not any emissions from storage tanks, because of being pressurized and not having breathers.

The petrochemical industry is also an important NMVOC emissions source in the region. The volatile organic emissions come from almost every product's manufacture (i.e, aromatics, ethylene, propylene, polyethylene, polypropylene, terephtalic acid, acrylonitrile, vinyl chloride monomer and ethylene dichloride).

There are also 5 plants in the region which emit NMVOC emissions in remarkable levels as a result of chemical processes. They work generally about paint or other chemicals manufacture.

In addition, there is a solvent reclamation plant in the region. A reclamation plant have several steps, which causes volatile organics, like solvent storage and condensation. Also fugitive emissions from loading and spillage are available. Additively, equipment leaks are available in spite of not having a special emission factor in the literature.

There are also 8 coal screening plants in Aliağa. In 4 of them, coal drying which is one of the processes that causes NMVOC emissions, is applied besides the breaking and screening processes.

Besides these plants, there are also other various industrial activities in Aliağa like ship breaking, mineral oil, paper production, etc. which are also considered in the study. It was assumed that, there was no evaporation in mineral oil facilities because of using heavy oils, so there were no NMVOC emissions. Emission factors for ship breaking facilities could not be found in the literature, so this industry type was neglected in the study. The literature (EEA, 2009; IPPC, 2009; USEPA, 2009) points out that paper industries had the considerable VOC emissions from pulp production. But the paper factory in Aliağa does not produce pulp, they buy the pulp from an other company; so these emissions were neglected in the study. The NMVOC emissions from printing units were also neglected in the study.

3.2 Emission Estimations

Eight different industrial sectors were mainly considered as NMVOC sources in the town. These were oil refinery, petrochemical, chemical, iron and steel, liquid fuel storage and loading, LPG storage and loading, coal drying, and electricity production sectors. Besides these, there were also other various facilities in Aliağa like ship breaking, mineral oil, paper, and etc. production subjects which were also considered in the study. They were counted under "others" title as a ninth sector in the study.

NMVOC emissions were calculated in five different classes. These were emissions from process, combustion, storage tanks, liquid loading facilities and equipment leaks (Table 3.2). Process emissions referred to NMVOC emissions those came into being during the main process of the facility. As an example those could be the NMVOC emissions while the scrap iron was melted in the arc furnace in iron and steel industries. Combustion emissions referred to the emissions from boilers in plants. There was an exception for electricity production plants that their emissions were considered as process emissions although they came from combustion; because it was the main process of these plants. On the other hand, combustion emissions referred to the emissions from small boilers generally for heating. Both of these emissions (i.e., process and combustion) originated from almost every plant. But emissions from storage tanks, liquid loading and equipment leaks came only from oil refinery, petrochemical industry, liquid fuel storage and loading facilities and a few chemical plants. LPG storage and loading facilities had only equipment leak emissions besides the bottle painting emissions. There was not a different emission class for bottle painting emissions; they were considered as process emissions for LPG storage and loading facilities in this study.

In the study, process, combustion and equipment leak emissions were calculated by using emission factors from the literature (EEA, 2009; IPPC, 2009; USEPA, 2009). Emissions from storage tanks were calculated by using a software, called TANKS 4.0, which was produced by USEPA and liquid loading emissions were calculated by using a special method (USEPA, 1995d) from USEPA again (Table 3.1).

	Emission Factors Method	Computer Software (TANKS 4.0)	Emission Factors Based Liquid Loading Method
Process Emissions	X		
Combustion Emissions	X		
Storage Tanks Emissions		X	
Liquid Loading Emissions			X
Equipment Leaks Emissions	X		

Table 3.1 Methods used in emission estimations.

	Sources of Emissions				
Sectors	Combustion Process		Storage	Liquid	Equipment
		Tanks	Loading	Leaks	
Chemical Processes	X	X			
Coal Drying	X				
Electricity Production	X				
Iron and Steel Production	X				
Liquid Fuel Storage and		X	X	X	X
Loading					
LPG Storage and Loading	X				X
Petrochemical Production		X	X	X	X
Oil Refinery		X	X	X	X
Other		X			

Table 3.2 Classification of emissions according to industrial sectors.

3.2.1 Combustion Emissions of an Oil Refinery and a Petrochemical Plant

There were 2 major plants in Aliağa; an oil refinery and a petrochemical plant which promoted the town to be an important industrial zone. Both of them had large amount of working capacities with a vast number of process flows. Upon their requests, stack emissions coming from combustion activities in the facilities were measured by Air Pollution Laboratory staff of Dokuz Eylül University Environmental Engineering Department in the past. The emission measurement methods, used in those studies, based on the Turkish standard called TS EN 13649 (TSE, 2003). According to this standard, the sample was taken from the stack by using a sorbent tube which had activated carbon as an adsorbent in itself. Then in the laboratory, the sample was desorbed and analyzed in the gas chromograph. Both studies were very detailed and reliable studies; so that their emission results were considered as combustion emissions of those industries instead of new calculations in this study.

3.2.2 Emission Estimations Using Emission Factors

In the study, related documents of IPPC (European Commission Integrated Pollution Prevention and Control), USEPA (United States Environmental Protection Agency), EEA (European Environment Agency) and IPCC (Intergovernmental Panel on Climate Change) were examined. The emission factors were taken mainly from EEA EMEP/Corinair and USEPA AP-42 databases and Industrial Air Pollution Control Turkish Regulation.

Emission factors were used in the study to estimate emissions from process, combustion and pipeline equipment leaks. All of these factors, used in the study, were tabled below in Tables 3.3 to 3.8.

Industrial Sector	Process Name	NMVOC Emission Factor	Source
Iron and Steel	Electric Arc Furnace	0.046 $kg \text{ ton}^{-1}$ steel produced	EEA, 2009
Production	Hot Rolling Mills	0.007 $kg \text{ ton}^{-1}$ steel produced	EEA, 2009
Coal Drying	Coal Drying	0.196 $kg \text{ ton}^{-1} \text{ coal}$	USEPA, 2009
Chemistry	Paint, ink production	11.00 $kg \text{ ton}^{-1}$ product	EEA, 2009
	Chemicals production	10.00 $kg \text{ ton}^{-1}$ product	EEA, 2009
Solvent Reclamation	Storage tank vent	0.010 kg ton $^{-1}$ reclaimed solvent	EEA, 2009
	Condenser vent	1.650 $kg \text{ ton}^{-1}$ reclaimed solvent	EEA, 2009
	Fugitives-spillage	0.100 $kg \text{ ton}^{-1}$ reclaimed solvent	EEA, 2009
	Fugitives-loading	0.360 kg ton $^{-1}$ reclaimed solvent	EEA, 2009
Electricity and Heat Production	Gas turbines	0.001 $kg \text{ GJ}^{-1}$ natural gas	EEA, 2009
	Reciprocating engines	0.046 $kg \text{ GJ}^{-1}$ natural gas	EEA, 2009
Painting Applications	Industrial paint application	400 kg ton ⁻¹ paint applied	EEA, 2009

Table 3.3 Process emission factors for the industries in Aliağa.

Fuel Name	NMVOC Emission Factor
Coal	$88.80 \text{ g } \text{GI}^{-1}$
Fuel Oil	10.00 g GI^{-1}
Diesel	$10.00 \text{ g } \text{GI}^{-1}$
LPG	$10.00 \text{ g } \text{GI}^{-1}$
Natural Gas	$2.50 \text{ g } \text{GI}^{-1}$

Table 3.4 Combustion emission factors for the industries in Aliağa (EEA, 2009).

Table 3.5 Some properties of fuel types used in the study (USEPA, 2009).

*Unit of coal heating value is kcal ton $^{-1}$, the other fuels' are kcal m⁻³.

Equipment Type	Emission Factor (kg (hour source) ⁻¹)
Valves	0.00560
Safety Valves	0.10400
Open-Ended Lines	0.00170
Connectors	0.00083

Table 3.7 Equipment leak emission factors for LPG loading facilities (USEPA, 1996; SKHKKY, 2009).

Table 3.8 Equipment leak emission factors for petrochemical industry (USEPA, 1996; SKHKKY, 2009).

		Emission Factor	
Equipment Type	Service	$(kg (hour source)-1)$	
	Gas	0.00597	
Valves	Light Liquid	0.00403	
	Heavy Liquid	0.00023	
Pump Seals	Light Liquid	0.01990	
	Heavy Liquid	0.00862	
Compressor Seals	Gas	0.22800	
Pressure Relief Valves	Gas	0.10400	
Connectors	All	0.00183	
Open-Ended Lines	All	0.00170	
Sampling Connections	All	0.01500	

3.2.3 Emission Estimations Using TANKS 4.0 Software

In this study, Version 4.0 of TANKS Software (TANKS 4.0) was used to calculate the NMVOC emissions for tank farms and single tanks of liquid fuel storage and loading facilities, petrochemical industry and oil refinery. The software is installed from TANKS Software Web Site (USEPA, 2010a) and the working principle is studied from both the User's Manual of the software and "Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources" (AP-42), Section 7.1, Organic Liquid Storage Tanks (USEPA, 1995c).

The meteorological data of Aliağa which were obtained from Turkish Meteorological Data Archive System (TÜMAS, 2010) were presented in Table 3.9. These data were required to run TANKS 4.0 and calculate the emissions from storage tanks. Table 3.10 showed the same data converted to the units used in the software. Other required data like dimensions, shell and roof characteristics and breather vent settings of the tank, and the properties of the tank liquid were obtained from questionnaires for mentioned plants. Default values of the software were used instead of the missing data.

The NMVOC emissions from storage tanks were estimated for an annual period using the software. The results were in lbs year⁻¹ unit; then converted to tons year⁻¹.

	Average	Minimum	Maximum	Average	Average	Solar
	monthly	monthly	monthly	wind	pressure	Insolation
Months	temperature	temperature	temperatures	speed	(mBar)	Value*
	$({}^{\circ}C)$	$(^{\circ}C)$	(°C)	$(m s^{-1})$		(hour day ⁻¹)
January	9.2	3.0	14.9	3.3	1013.4	4.2
February	9.0	4.3	16.8	3.7	1008.3	3.8
March	10.7	5.6	17.9	2.9	1010.1	6.0
April	14.7	11.0	17.8	2.4	1010.9	7.4
May	19.9	15.5	24.0	2.7	1011.3	11.3
June	24.7	19.7	28.4	3.2	1008.3	12.7
July	27.3	25.2	29.5	3.5	1006.6	12.8
August	26.2	23.2	28.6	3.9	1007.8	12.2
September	21.8	18.5	25.4	2.9	1010.8	9.1
October	19.7	13.5	23.4	2.8	1010.9	7.2
November	13.8	9.2	18.9	2.5	1014.1	6.3
December	12.2	6.5	17.8	3.2	1008.6	2.6

Table 3.9 Meteorological parameters of Aliağa according to the months of year 2009. (TÜMAS, 2010)

*These values belong to Dikili station, because DMİ (Turkish State Meteorological Service) does not measure this parameter in Aliağa station.

	Average monthly	Minimum monthly	Maximum monthly	Average wind	Average	Solar Insolation
Months	temperature	temperature	temperatures	speed	pressure (psi)	Value* (Btu (ft ² day) ⁻¹)
	(F)	(F)	(F)	(mph)		
January	48.6	37.4	58.8	7.4	14.7	1332.3
February	48.2	39.7	62.2	8.3	14.6	1205.4
March	51.3	42.1	64.2	6.5	14.7	1903.3
April	58.5	51.8	64.0	5.4	14.7	2347.3
May	67.8	59.9	75.2	6.0	14.7	3584.5
June	76.5	67.5	83.1	7.2	14.6	4028.6
July	81.1	77.4	85.1	7.8	14.6	4060.3
August	79.2	73.8	83.5	8.7	14.6	3869.9
September	71.2	65.3	77.7	6.5	14.7	2886.6
October	67.5	56.3	74.1	6.3	14.7	2283.9
November	56.8	48.6	66.0	5.6	14.7	1998.4
December	54.0	43.7	64.0	7.2	14.6	824.7

Table 3.10 Meteorological parameters of Aliağa according to the months of year 2009 in British unit system.

* These values belong to Dikili station, because DMI (Turkish State Meteorological Service) does not measure this parameter in Aliağa station.

3.2.4 Emission Estimations Using Liquid Loading Method

The emission calculation method in the document of "Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources, (AP-42), Section 5.2, Transportation and Marketing of Petroleum Liquids (USEPA, 1995d)" was used in the study to estimate the NMVOC emissions from liquid loading facilities of oil refinery, petrochemical industry and liquid fuel storage and loading plants. The information about amounts of loaded liquids and the types of loading were obtained from questionnaires for some plants; and the others were taken from previous studies achieved by Dokuz Eylül University Environmental Engineering Department.

3.3 Dispersion Modeling

The second part of this study contained the dispersion modeling of the emissions calculated in this study. One of the objectives of this study was to investigate the contribution of the calculated emissions to the air quality under the meteorological and topographical conditions of the study area. With this objective, the Industrial Source Complex Short Term Model (ISCST3) of USEPA was used to estimate the dispersion of industrial based VOCs on Aliağa in this study. The required input data were obtained from questionnaires again. The geographical coordinates of the plants and the lengths of area source borders were identified by using Google Earth and previous studies of DEÜ Environmental Engineering Department. The topographical data were prepared from a digital map of Aliağa town. As the meteorological data for the model, data of Aliağa Horozgediği meteorological station which had been used before in previous studies of DEÜ, was used.

The model was run for an area of 30 km x 30 km with a spatial resolution of 1 km. The hourly emissions were estimated for a whole year.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results of Emission Inventory

At the beginning of the study, several lists from different corporations (i.e. Aliağa Municipality, İzmir Provincial Environmental Directorate and Chamber of Commerce of Aliağa) which included the industrial facilities in Aliağa were compared. Some facilities in the town, not emitting NMVOC emissions according to literature (Derwent, 1995; Passant, 1995) were ignored in the study. The required information of others were obtained by using questionnaries. Some missing information of the considered facilities after having the questionnaries back, were estimated by comparing the related information of similar plants. Besides this, for a few plants no information could be obtained; these plants were also ignored in the study.

The number of considered facilities was 50 in this study. Their calculated NMVOC emissions were given in Table 4.1 without specifying the names of the companies. As a result of calculations, the value of total NMVOC emissions from industrial facilities in Aliağa was 9,700 tons year⁻¹. In a previous study (Müezzinoğlu et al., 2000) NMVOC emissions were found as $10,650$ tons year⁻¹ in Aliaga from 18 industrial plants. When that study was achieved, industrial plants in Aliağa were using heavy fossil fuels instead of natural gas; so that the value is greater than our value, although the considered plant number is higher in our study.

According to Table 4.1, the highest value of NMVOC which come from only one plant was $3,741.41$ tons year⁻¹ from Petrochemical Plant. Second highest value belonged to Oil Refinery with $3,254.34$ tons year⁻¹, and the third one is Chemical Plant-1 with 540.44 tons year⁻¹. Similarly, the lowest value belongs to Other Plant-8 with $4.4E-5$ tons year⁻¹. This plant has a very small boiler and no emissions from process, so that the emission values are so small.

	NMVOC Emissions			
Plant Name	$(tons year-1)$			
Chemical-1	540.44			
Chemical-2	0.59			
Chemical-3	23.07			
Chemical-4	63.06			
Chemical-5	141.40			
Coal drying-1	1.88			
Coal drying-2	16.93			
Coal drying-3	7.84			
Coal drying-4	36.29			
Iron and Steel-1	1.40			
Iron and Steel-2	1.63			
Iron and Steel-3	0.12			
Iron and Steel-4	34.61			
Iron and Steel-5	1.27			
Iron and Steel-6	95.37			
Iron and Steel-7	1.75			
Iron and Steel-8	117.73			
Iron and Steel-9	67.24			
Iron and Steel-10	1.16			
Iron and Steel-11	0.65			
Iron and Steel-12	2.23			
Iron and Steel-13	1.97			
Iron and Steel-14	34.94			
Iron and Steel-15	0.51			
Liquid loading-1	184.27			
Liquid loading-2	79.01			
Liquid loading-3	85.49			
Liquid loading-4	355.30			
Liquid loading-5	217.28			
LPG loading-1	4.26			
LPG loading-2	102.59			
LPG loading-3	18.56			
LPG loading-4	79.58			
LPG loading-5	33.21			

Table 4.1 Calculated NMVOC emissions of industrial facilities in Aliağa.

	NMVOC Emissions				
Plant Name	$(tons year-1)$				
LPG loading-6	49.55				
LPG loading-7	21.55				
Oil Refinery	3,254.34				
Petrochemical	3,741.41				
Power plant-1	126.29				
Power plant-2	5.61				
Power plant-3	86.59				
Other-1	0.09				
Other-2	3.28				
Other-3	0.11				
Other-4	0.21				
Other-5	0.03				
Other-6	0.02				
Other-7	14.08				
Other-8	$4.4E - 5$				
Other-9	1.14				
TOTAL	9,657.91				

Table 4.1 Calculated NMVOC emissions of industrial facilities in Aliağa (continue).

The results can be assessed by distributing the emissions according to industrial sectors as shown in Figure 4.1. According to this chart, the highest NMVOC emissions come from petrochemical industry with 39% $(3,741.41 \text{ tons year}^{-1})$. Oil refinery follows it with a percentage of 34% (3,254.34 tons year⁻¹). The third highest value belongs to the liquid fuel storage and loading sector with 9% (921.34 tons year-¹) and plants with chemical processes followed them with 8% (768.56 tons year⁻¹). Others had very small percentiles compared with these four sectors (Figure 4.1).

As mentioned in Chapter 3, there is a solvent reclamation plant in Aliağa. But its NMVOC emissions were too small to be categorized separately so that it was added to "other" sector.

Figure 4.1 Percentage distribution of NMVOC emissions according to different industrial sectors in Aliağa.

During the calculations, NMVOC emissions were divided into 5 parts according to their sources. These were emissions from process, combustion, storage tanks, liquid loading and equipment leaks. At the end of the calculations, storage tanks were found to be the most important NMVOC emitters with $3,250$ tons year⁻¹. Equipment leaks $(2,750 \text{ tons year}^{-1})$, liquid loading $(1,925 \text{ tons year}^{-1})$, process $(1,650 \text{ tons year}^{-1})$ ¹) and combustion (95 tons year⁻¹) emissions followed storage tanks respectively (Figure 4.2).

The main contributor of storage tanks emissions was the petrochemical industry with 2,600 tons year⁻¹ and oil refinery followed it with 350 tons year⁻¹ (Figure 4.3). There was a big difference between these two large industries, because organic chemicals released much more VOC than the petroleum distillates according to the TANKS Software. The main storage liquids were organic liquids in petrochemical industry, while in refinery they were petroleum distillates. So, the emissions from storage tanks were higher in petrochemical industry than the oil refinery.

Figure 4.2 Distribution of NMVOC emissions in tons year⁻¹, according to pollution sources considered in the study.

When the equipment leaks emissions, which was the second highest category, was examined, the oil refinery was the main contributor with 2,000 tons/year that equalled to 70 percentile (Figure 4.4). Petrochemical industry followed it with 700 tons/year. The difference was because of the high equipment (i.e, valves, flanges and etc.) numbers in oil refinery.

Figure 4.3 Distribution of storage tanks emissions

Figure 4.4 Distribution of equipment leaks emissions

The third highest emission class was liquid loading with an approximate total value of $2,000$ tons year⁻¹. 51 percent of this value belonged to oil refinery; 32 percent belonged to liquid fuel loading and storage facilities, and the remainder came from petrochemical industry (Figure 4.5). The sequence was directly proportional to loaded liquid volumes.

Figure 4.5 Distribution of liquid loading emissions

An emission map (Figure 4.6) was also created with the estimated emissions by using a geographical information system (GIS) software, called ArcGIS. In that map, the total emissions were presented in a spatial resolution of 250 m. According to Figure 4.6, the maximum emissions per grids were seen in a few points in ALOSBİ, but mainly in the peninsula of oil refinery, petrochemical industry and fuel loading facilities. The maximum value per a grid was 541 tons year⁻¹.

Figure 4.6 Map of estimated emissions coming from grids of 250 m to 250 m.

4.2 Results of Dispersion Modeling

As the second part of the study, after the calculations, the emission values were put into the ISCST3 Model, and under the certain meteorological and topographical conditions, the dispersion of the emissions in the atmosphere, and the effects on air quality of Aliağa were estimated.

When the data were evaluated in annual period, the highest concentration was found as 859.7 μ g m⁻³ in the X, Y coordinates of (495000, 4292000) and according to the Figure 4.7, the maximum concentrations were around that point, as a result of the presence of oil refinery, petrochemical industry, liquid and LPG fuel storage and loading facilities there. The smaller polluted area, on the right side of the map, pointed at Aliağa Organized Industrial Site (ALOSBİ). There were several important chemical processes which were available there. The NMVOC concentrations there were also significant and about 200 μ g m⁻³.

When the national regulation (SKHKKY, 2009) was examined, two different types of limit values could be seen; those were short-term limit values (KVS) and long-term limit values (UVS). There short-term limit values referred to the hourly and daily values, while long-term limit values referred to the annual values. When the SKHKKY (2009) was examined, there were two important UVS values for NMVOC concentrations in our study. One of them was the value of 500 μ g m⁻³ which was determined for the inside area of oil refineries, petrochemical industries and fuel storage facilities; and the other one was the value of 90 μ g m⁻³ which indicated the NMVOC concentrations in the influence area of the same industrial sectors.

When Figure 4.7 was evaluated according to SKHKKY, it could be seen that the limit value of 500 μ g m⁻³ was exceeded in some areas. When the influence area was considered as a 2 km distance from the plants, the concentration values were again exceeded the limit value of 90 μ g m⁻³. There, the values were about 200 μ g m⁻³ according to the Figure 4.7.

Figure 4.7 Map of model results, annual average NMVOC concentrations in Aliağa atmosphere.

In Figure 4.8, the emissions and their dispersions could be seen. The emissions of the refinery and petrochemical industry were the highest, so the concentrations were very high in that peninsula. The dominant wind directions were southeast and eastsoutheast (Figure 4.9); so a large part of emissions dispersed in those directions. But also there were winds in north directions, so a smaller part of emissions also dispersed in those directions. For ALOSBI also the same comments could be made. In the same figure, it could also be seen that there were emissions from iron and steel plants. But their emissions were in low values compared with the emissions in the peninsula; so their dispersion concentrations were about $10-20 \mu g \cdot m^{-3}$; so they could not be seen on the figure.

Figure 4.8 Emissions and their dispersions in the study area

Figure 4.9 Wind rose of Horozgediği meteorological data

In an ongoing study, passive sampling measurements were achieved to determine the NMVOC emissions in a similar study area in Aliağa (DEÜ, 2010). When those results (Figure 4.10) were compared with Figure 4.6, it could be seen that the highest NMVOC concentrations were measured around the petrochemical industry and oil refinery as they were found in our study, as a result of modeling study. The concentration values in both studies were found similar. That means the emission calculations and modeling studies in our study were reliable.

Figure 4.10 Results of passive sampling measurements of an ongoing study (DEÜ, 2010)

CHAPTER FIVE

CONCLUSIONS

This was an emission inventory preparation study for nonmethane volatile organic compounds (NMVOCs) which were emitted from industrial facilities in Aliağa. With this scope, three calculation methods (i.e., emission factors, TANKS software and petroleum products loading method of USEPA) were used to calculate NMVOC emissions from various types of industrial facilities. After the generation of the inventory, a simple dispersion modeling study was also achieved by using ISCST3 model of USEPA.

In the study area there were 50 industrial plants which emitted NMVOC emissions in significant amounts. These plants were grouped under 9 industrial sectors; chemical processes, coal drying, electricity production, liquid fuel storage and loading, iron and steel production, LPG storage and loading, petrochemical production, oil refinery and others.

The total NMVOC emissions from this 50 plants were calculated as 9,700 tons year⁻¹. The highest NMVOC emissions were coming from petrochemical production, oil refining and liquid fuel storage and loading sectors. The model results also pointed that conclusion by exceeding the limits in national regulation around those industrial facilities. Petrochemical production and oil refining industries generated 73% of total NMVOC emissions together with their emissions from stacks, storage tanks, liquid loading facilities and equipment leaks.

The highest NMVOC emissions were coming from storage tanks with a value above $3,000$ tons year⁻¹. The main sectors in charge were petrochemical production and oil refining here. Then the equipment leaks and liquid loading emissions followed them respectively with emission values approximately 2,750 and 2,000 tons year⁻¹. Fuel storage and loading sectors (i.e., both liquid and gaseous fuels) contributed to these emissions besides the petrochemical and oil refining industries.

In the study the emission factors were selected with an assumption that the industries did not have any emission control systems; so that the real emission values could be lower than the calculated values.

According to ISCST3 model results, the highest pollution concentrations occured around the petrochemical and oil refining facilities. The liquid and gaseous fuel storage and loading facilities were also around that area. Also the facilities which had chemical processes like various chemicals and paints production, located in the organized industrial region (ALOSBI), contributed negative impact on air quality. The effects of iron and steel plants were so small compared with the other sectors that their concentrations were not seen in the dispersion map.

For possible further studies, the advices which are given below can be considered.

- The emissions coming from ship breaking activities can be added.
- The recent process and emission information of industries can be available in governmental agencies.
- National emission factors for various industrial processes for "controlled" situations can be created.
- A more comprehensive inventory can be prepared to see the change of emissions in shorter time periods (e.g., monthly or seasonal changes in emissions).

REFERENCES

- Ağaçayak, T. (2007). *Investigation of an emission inventory for Turkey*. MSc Thesis. İstanbul Technical University, Institute of Science and Technology.
- Aliağa Municipality. (2009). *Aliağa*. Retrieved November 20, 2009, from http://www.aliaga.bel.tr/cografyasi-32.html .
- Andiç, Ö. (2008). *Determination of volatile organic compounds around Aliaga by passive sampling methods*. MSc. Thesis. Graduate School of Natural and Applied Sciences of Dokuz Eylül University.
- BAAQMD, Bay Area Air Quality Management District. (2010). *Emission Inventory*. Retrieved January 10, 2010, from [http://www.baaqmd.gov/Divisions/Planning-and-](http://www.baaqmd.gov/Divisions/Planning-and-Research/Emission-Inventory-and-Air-Quality-Related/Emission-Inventory.aspx)[Research/Emission-Inventory-and-Air-Quality-Related/Emission-Inventory.aspx.](http://www.baaqmd.gov/Divisions/Planning-and-Research/Emission-Inventory-and-Air-Quality-Related/Emission-Inventory.aspx)
- Civan, M., Elbir, T., Seyfioğlu, R., Sofuoğlu, S., Bayram, A., Müezzinoğlu, A., OdabaĢı, M., Kuntasal, Ö., Bozlaker, A., Pekey, H., Andiç, Ö., Yorulmaz, S. Y., & Tuncel, G. (2008). Aliağa bölgesindeki inorganik ve uçucu organik bileşiklerin pasif örnekleme metoduyla belirlenmesi. *Hava Kirliliği ve Kontrolü Ulusal Sempozyumu, Bildiriler Kitabı*, 178-193. 22-25 Ekim 2008, Hatay.
- Cooper, C. D., & Alley, F. C. (1994). An overview. In *Air pollution contr*ol (2nd ed.) (1-70). Illinois: Waveland Press, Inc.
- Derwent, R. G. (1995). Sources, distributions, and fates of VOCs in the atmosphere. In R. E. Hester & R. M. Harrison, (Eds.), *Volatile organic compounds in the atmosphere* (1-15). Cambridge: The Royal Society of Chemistry.
- DEÜ. (2010). *Aliağa Çevre Durum Tespiti ve Taşıma Kapasitesinin Belirlenmesi Projesi*. Dokuz Eylül University, Environmental Engineering Department, İzmir. Unpublished report.
- Doğan, G., Oğuz, Ö., Yılmaz, M. C., Bozlaker, A., Elbir, T., Seyfioğlu, R., Sofuoğlu, S., Bayram, A., Müezzinoğlu, A., OdabaĢı, M., Yorulmaz, S. Y., Pekey, B., & Tuncel, G. (2008). İzmir-Aliağa'da aktif yolla ölçülen uçucu organik bileşik konsantrasyonlarının kısa süreli, 24 saatlik, ve mevsimsel değişimlerinin değerlendirilmesi. *Hava Kirliliği ve Kontrolü Ulusal Sempozyumu, Bildiriler Kitabı*, 265-273. 22-25 Ekim 2008, Hatay.
- Dumanoğlu, Y., Elbir, T., Bayram, A., Seyfioğlu, R., Demircioğlu, H., Altıok, H., Yatkın, S., Bozlaker, A., & Odabası, M. (2008). Bir petrokimya endüstrisi ve petrol rafinerisi çevresindeki halojenli uçucu organik bileşikler. *Hava Kirliliği ve Kontrolü Ulusal Sempozyumu, Bildiriler Kitabı*, 286-297. 22-25 Ekim 2008, Hatay.
- EEA, European Environment Agency. (2009). *EMEP/CORINAIR Air Pollutant Emission Inventory Guidebook-2009*. Retrieved January 10, 2010, from [http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-](http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-2009)[2009.](http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-2009)
- Elbir, T. (1997). *Preparation of emission inventories for use in determination of air quality at different scales.* MSc Thesis. Graduate School of Natural and Applied Sciences of Dokuz Eylül University.
- Elbir, T., & Muezzinoglu, A. (2004). Estimation of emission strengths of primary air pollutants in the city of Izmir, Turkey. *Atmospheric Environment, 38*, 1851–1857.
- Elbir, T., Bayram, A., Dumanoğlu, Y., OdabaĢı, M., Seyfioğlu, R., Demircioğlu, H., Altıok, H., & Yatkın, S. (2008). Petrol rafinerisi depolama tanklarından kaynaklanan uçucu organik bileşik emisyonları. *Hava Kirliliği ve Kontrolü Ulusal Sempozyumu*, *Bildiriler Kitabı*, 312-325. 22-25 Ekim 2008, Hatay.
- Eryiğit, Ö. (2000). *Assessment of volatile organic compounds in ambient air in Aliağa*. MSc. Thesis. Graduate School of Natural and Applied Sciences of Dokuz Eylül University.

Godish, T. (1997). *Air Quality*. Boca Raton: CRC Press LLC.

- Hutchinson, D. (1997). Emission Inventories. In R. E. Hester & R. M. Harrison, (Eds.), *Air Quality Management* (19-39). Cambridge: The Royal Society of Chemistry.
- IPPC, European IPPC Bureau. (2009). *European Commission, Joint Research Centre, Institute for Prospective Technological Studies. Reference Documents*. Retrieved September 12, 2009, from [http://eippcb.jrc.es/reference/.](http://eippcb.jrc.es/reference/)
- Müezzinoğlu, A., Elbir, T., Bayram, A., & Seyfioğlu, R. (1997). *Hava kirletici emisyon envanteri (EUROTRAC/GENEMIS-2)*. TUBITAK Project No: YDABCAG-469/EURO. İzmir.
- Müezzinoğlu, A., Bayram, A., Elbir, T., Seyfioğlu, R., Demircioğlu, H., Dinçer, F., & Sönmez, Y. (2000). *Ege Bölgesi emisyon envanteri*. TUBITAK Project No: YDABÇAG-198Y094. İzmir.
- Müezzinoğlu, A. (2003). *Atmosfer Kimyası*. İzmir: Dokuz Eylül Üniversitesi Mühendislik Fakültesi Yayınları.
- Obermeier, A., Seier, J., Friedrich, R., Voϐ, A. (1992). Generation of emission inventories and evaluation of reduction strategies. In A. Muezzinoglu and M. L. Williams, (Ed.), Industrial air pollution assessment and control (59-80). Germany: Springer-Verlag.
- Passant, N. R. (1995). Source inventories and control strategies for VOCs. In R. E. Hester & R. M. Harrison, (Eds.), *Volatile organic compounds in the atmosphere* (51- 64). Cambridge: The Royal Society of Chemistry.
- Pham, T. B. T., Manomaiphiboon, K., & Vongmahadlek, C. (2008). Development of an inventory and temporal allocation profiles of emissions from power plants and industrial facilities in Thailand. *Science Of The Total Environment, 397*, 103–118.
- SKHKKY, Industrial Based Air Pollution Control Turkish Regulation. (2009). Official Newspaper, Number 27277, Appendix 12.
- Srivastava, A., & Majumdar, D. (2010). Emission inventory of evaporative emissions of VOCs in four metro cities in India. *Environmental Monitoring Assessment,160*, 315– 322.
- Troxel, B.R.. (2009). *Floating Roof Landing Issues*. Retrieved December 13, 2009, from [http://www.api.org/meetings/proceedings/upload/Troxel_FloatingRoofLandingIssues](http://www.api.org/meetings/proceedings/upload/Troxel_FloatingRoofLandingIssues.pdf) [.pdf](http://www.api.org/meetings/proceedings/upload/Troxel_FloatingRoofLandingIssues.pdf) .
- TSE, Institute of Turkish Standards . (2003). TS EN 13649, Stationary source emissions - determination of the mass concentration of individual gaseous organic compounds activated carbon and solvent desorption method.
- TUİK, Turkish Statistical Institute. (2010). *Nüfus İstatistikleri*. Retrieved February 16, 2010, from http://www.tuik.gov.tr/jsp/duyuru/upload/vt/vt.htm.
- TÜMAS, Turkish State Meteorological Service, Turkish Meteorological Data Archive System. (2010). *Meteorolojik İstatistikler*. Retrieved February 20, 2010, from [http://tumas.dmi.gov.tr/wps/portal.](http://tumas.dmi.gov.tr/wps/portal)
- USEPA, United States Environmental Protection Agency. (1980). *Procedures for the emission inventories for volatile organic compounds, Volume I* (2nd Ed.), EPA-450/2-77-028. North Carolina: Research Triangle Park.
- USEPA, United States Environmental Protection Agency. (1995a). User's guide for the industrial source complex (ISC3) dispersion models, volume I – user instructions. EPA-454/B-95-003a. North Carolina.
- USEPA, United States Environmental Protection Agency. (1995b). User's guide for the industrial source complex (ISC3) dispersion models, volume II – description of model algorithms. EPA-454/B-95-003b. North Carolina.
- USEPA, United States Environmental Protection Agency. (1995c). *Compilation of air pollutant emission factors, volume I: stationary point and area sources, (AP-42), Section 7.1, Organic liquid storage tanks.* Retrieved December 13, 2009, from <http://www.epa.gov/ttnchie1/ap42/> .
- USEPA, United States Environmental Protection Agency. (1995d). *Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources, (AP-42), Section 5.2, Transportation and Marketing of Petroleum Liquids*. Retrieved December 20, 2009, from <http://www.epa.gov/ttnchie1/ap42/> .
- USEPA, United States Environmental Protection Agency. (1996). *Preferred and Alternative Methods for Estimating Fugitive Emissions from Equipment Leaks, Emission Inventory Improvement Program, Technical Report Series, Volume 2, Chapter 4*, North Carolina: Morrisville. Retrieved January 10, 2010, from http://www.epa.gov/ttn/chief/eiip/techreport/.
- USEPA, United States Environmental Protection Agency. (1997*). Introduction to the emission inventory improvement program*, Emission Inventory Improvement Program, Technical Report Series, Volume 1, North Carolina: Morrisville. Retrieved January 10, 2010, from http://www.epa.gov/ttn/chief/eiip/techreport/.
- USEPA, United States Environmental Protection Agency. (2009). Emission Factors & AP-42, Compilation of Air Pollutant Emission Factors. Retrieved November 10, 2009, from http://www.epa.gov/ttn/chief/ap42/index.html.
- USEPA, United States Environmental Protection Agency. (2010a). *TANKS emissions estimation software, version 4.09D*. Retrieved January 20, 2010 from http://www.epa.gov/ttnchie1/software/tanks/index.html.
- USEPA, United States Environmental Protection Agency. (2010b). *Air Quality Planning and Standards, Air Pollution Emissions Overview*. Retrieved August 23, 2010, from http://www.epa.gov/air/oaqps/emissns.html.
- USEPA, United States Environmental Protection Agency. (2010c). *Technology Transfer Network, Emission Measurement Center, Frequent Questions*. Retrieved August 23, 2010, from http://www.epa.gov/ttn/emc/facts.html#voc.

APPENDIX-A

The questionnaries used in the study

ALİAĞA ÇEVRE DURUM TESPİTİ PROJESİ SANAYİCİ ANKETİ

ENVIRONMENTAL ASSESSMENT PROJECT OF ALİAĞA INDUSTRIALIST QUESTIONNAIRE

1. Genel Bilgiler/*General Information*

2. Üretim Bilgileri / *Production Information*

TESĠSTE ÇALIġAN PERSONEL SAYISI / *PERSONNEL NUMBER OF THE PLANT*

Vardiyasız personel sayısı / *Number of shiftless personnel* :

ÜRETİM MİKTARLARI / *AMOUNTS OF PRODUCTION*

KULLANILAN HAMMADDELER VE TÜKETİM MİKTARLARI / *RAW MATERIALS AND CONSUMPTION AMOUNTS*

KULLANILAN ENERJĠ MĠKTARLARI / *ENERGY CONSUMPTIONS*

PROSES AKIM ġEMASI / *PROCESS FLOW DIAGRAM*

(lütfen tesisin proses akım Ģemasını ankete ekleyiniz/ *please attach the process flow diagram of the plant to the questionnaire***)**

Tesisin "Sanayi Kaynaklı Hava Kirliliğinin Kontrolü Yönetmeliği" ile ilgili Bilgileri / *Information About "Industrial Based Air Pollution Control Regulation"*

Yönetmelik kapsamında "İzne Tabi Tesis" ise Yönetmelik Ek-8 listesindeki yeri / *Location in the list of Appendix-8 of the regulation, if the plant "subjects to permission" according to the regulation* : ………….………….………….……….………….………….………….…

Tesisin yönetmelikte yer alan Ek-5 listesindeki yeri/yerleri / *Location of the plant in the list of Appendix-5 of the regulation*: .……………….……….………….………….………….…

Emisyon İzni varsa tarihi / *The date of Emission Permission if it is available*: …...............

KULLANILAN YAKMA TESİSİNE AİT BİLGİLER / *INFORMATION ABOUT COMBUSTION SYSTEM*

Yakma tesisi tipleri / Types of combustion system:

1: Kalorifer / *Central heating*; 2: Buhar kazanı / *Steam boiler*; 3: Kızgın yağ kazanı / *Hot oil boiler*, 4: Kojenerasyon / *Cogeneration*

Yakıt türleri / Types of fuel:

1: Kömür / *Coal*; 2: Fuel oil / *Fuel oil*; 3: Motorin / *Diesel*; 4: LPG / *LPG* ; 5: Doğal gaz / *Natural gas*; 6: Pirina / *Olive pomace*; 7: Diğer / *Other*

Not: Varsa yakıt analiz belgesini ankete ekleyebilirsiniz. *Note: If it is available, you can attach your certificate of fuel analysis to the questionnaire.*
BACA ÖZELLİKLERİ / STACK PROPERTIES

1: Siklon / *Cyclone* 2: Islak tutucu / *Wet collector* 3: Torba filtre / *Bag filter*

4: Elektrostatik filtre / *Electrostatic filter*

EMİSYONLARLA İLGİLİ BİLGİLER / *INFORMATION ABOUT EMISSIONS*

Not: Daha fazla sayıda bacanız varsa ekleme yapabilirsiniz. *Note: You can attach if there are more stacks.*

DEPOLAMA TANKLARI ANKETİ *STORAGE TANKS QUESTIONNAIRE*

Tesis Adı / *Plant Name* **:**

1. **Tesisteki Depolama Tanklarına Ait Bilgiler /** *Information About Storage Tanks in the Plant*

Tesisteki Tank Sayısı / *Number of Tanks in the Plant* :

2. Dolum Kolları İle İlgili Bilgiler / *Information About Liquid Loading*

Tesis içinde KARA DOLUM yapılıyorsa / In case of LAND LOADING in the facility;

Tesis içinde LİMANLARDA dolum yapılıyorsa / *In case of loading in MARINE*

TERMINALS in the facility;

3. Ürün İletim Hatları ile İlgili Bilgiler / Information About Liquid *Pipelines*

Not: Hafif Sıvı, 68 F sıcaklıkta 0,044 psia'dan daha büyük buhar basıncına sahip olan sıvıları tanımlamaktadır. Aynı sıcaklıkta 0,044 psia veya daha küçük buhar basıncına sahip olan sıvılar ise Ağır Sıvılar olarak kabul edilmektedirler.

Note: Light Liquid defines the liquids which have a vapor pressure greater than 0.044 psia at 68 °F. The liquids having an 0.044 psia or smaller vapor pressure at the same temperature are accepted as Heavy Liquids.

APPENDIX-B

TANKS Model Outputs

1. OUTPUTS FOR LIQUID LOADING-1 PLANT

TANKS 4.0.9d Emissions Report - Brief Format Total Emissions Summaries - All Tanks in Report

2. OUTPUTS FOR CHEMICAL-3 PLANT

TANKS 4.0.9d Emissions Report - Brief Format Total Emissions Summaries - All Tanks in Report

3. OUTPUTS FOR LIQUID LOADING-3 PLANT

TANKS 4.0.9d Emissions Report - Brief Format Total Emissions Summaries - All Tanks in Report

4. OUTPUTS FOR PETROCHEMICAL PLANT

TANKS 4.0.9d Emissions Report - Brief Format Total Emissions Summaries - All Tanks in Report

5. OUTPUTS FOR LIQUID LOADING-4 PLANT

TANKS 4.0.9d Emissions Report - Brief Format Total Emissions Summaries - All Tanks in Report

6. OUTPUTS FOR LIQUID LOADING-5 PLANT

TANKS 4.0.9d Emissions Report - Brief Format Total Emissions Summaries - All Tanks in Report

7. OUTPUTS FOR OIL REFINERY

TANKS 4.0.9d Emissions Report - Brief Format Total Emissions Summaries - All Tanks in Report

