EVALUATION OF BTEX CONCENTRATIONS IN SELECTED INDUSTRIES PRODUCING AND APPLYING PAINT BASED ON HUMAN HEALTH RISKS THROUGH INHALATION

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

GİZEM NAZ DÖLEK

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ENVIRONMENTAL ENGINEERING

JULY 2014

Approval of the thesis:

EVALUATION OF BTEX CONCENTRATIONS IN SELECTED INDUSTRIES PRODUCING AND APPLYING PAINT BASED ON HUMAN HEALTH RISKS THROUGH INHALATION

submitted by **GİZEM NAZ DÖLEK** in partial fulfillment of the requirements for the degree of **Master of Science in Environmental Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen ______________
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. F. Dilek Sanin ______________
Head of Department, **Environmental Engineering**

Assoc. Prof. Dr. Ayşegül Aksoy ______________
Supervisor, **Environmental Engineering Dept., METU**

Assoc. Prof. Dr. Elçin Kentel ______________
Co-supervisor, **Civil Engineering Dept., METU**

Examining Committee Members:

Prof. Dr. F. Dilek Sanin ______________
Environmental Engineering Dept., METU

Assoc. Prof Dr. Ayşegül Aksoy ______________
Environmental Engineering Dept., METU

Assoc. Prof. Dr. Elçin Kentel ______________
Civil Engineering Dept., METU

Assoc. Prof. Dr. Emre Alp ______________
Environmental Engineering Dept., METU

Assist. Prof. Dr. Barış Kaymak ______________
Environmental Engineering Dept., METU

Date: 21.07.2014

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : GİZEM NAZ DÖLEK

Signature :

ABSTRACT

EVALUATION OF BTEX CONCENTRATIONS IN SELECTED INDUSTRIES PRODUCING AND APPLYING PAINT BASED ON HUMAN HEALTH RISKS THROUGH INHALATION

Dölek, Gizem Naz
M.Sc., Department of Environmental Engineering
Supervisor : Assoc. Prof. Dr. Ayşegül Aksoy
Co-Supervisor : Assoc. Prof. Dr. Elçin Kentel

July 2014, 132 pages

In Turkey, ambient air quality control is managed by the Ministry of Environment and Urban Affairs (MoEU) with Air Quality Evaluation and Management Regulation, Industrial Sourced Air Pollution Control Regulation, Large Combustion Plants Regulation and Heating Sourced Air Pollution Control Regulation. These regulations stated that “indoor air of workplaces which are under occupational health and safety legislation are out of the scope” and “regulations are prepared for ambient air pollution prevention sourced by industrial facilities”. This situation indicates that legislation of MoEU is responsible only for ambient air quality. The task of providing a safe and healthy working environment for employees is given to the Ministry of Labor and Social Security (MoLSS). For this purpose, Institute of Occupational Health and Safety (ISGUM) of MoLSS measures chemical exposures of employees at workplaces, compares these concentrations with national legislative limits and stores the results in reports. It is seen that there is not any national legislation evaluating Indoor Air Quality (IAQ) and limiting indoor air pollutants. IAQ is evaluated by the amount of hazardous chemicals in indoor air. Volatile Organic Compounds (VOCs) which are considered in this evaluation are emitted from especially paint, varnish, thinners and adhesives production and usage. In this study, health risks are calculated for employees who are exposed to benzene, toluene, ethylbenzene and xylene (BTEX) during paint production and usage. 195 BTEX concentrations, measured at 57 different workplaces by ISGUM between 2006 and 2013, are used. Data is evaluated with respect to two classifications: type of industries and type of actions. By using the data, health risk assessment of inhalation exposure is conducted via using methodology provided by Environmental Protection Agency, RAGS, Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment) (U.S. EPA, 2009). The results of the study demonstrate that employees of shipyard, automotive and furniture painting are exposed to BTEX more than employees of paint production and other industries. Furthermore, although concentrations are below the legislative limits, when HRA is conducted, it has been seen that health risks of exposure to these concentrations significantly exceed the acceptable cancer risk ($1x10^{-6}$) and Hazard Index (1).

Keywords: BTEX exposure, health risk assessment, occupational safety and health, cancer risk, hazard quotient

ÖZ

BOYA ÜRETİLEN VE KULLANILAN SEÇİLMİŞ ENDÜSTRİLERDE BTEK KONSANTRASYONLARININ SOLUMA YOLUYLA OLUŞAN İNSAN SAĞLIK RİSKLERİ BAZINDA DEĞERLENDİRİLMESİ

Dölek, Gizem Naz
Yüksek Lisans, Çevre Mühendisliği Bölümü
Tez Yöneticisi : Doç. Dr. Ayşegül Aksoy
Ortak Tez Yöneticisi : Doç. Dr. Elçin Kentel

Temmuz 2014, 132 sayfa

Türkiye'de dış ortam hava kalitesi kontrolü Çevre ve Şehircilik Bakanlığı'nca (ÇŞB) Hava Kalitesi Değerlendirme ve Yönetimi Yönetmeliği, Sanayi Kaynaklı Hava Kirliliğinin Kontrolü Yönetmeliği, Büyük Yakma Tesisleri Yönetmeliği ve Isınmadan Kaynaklı Hava Kirliliğinin Kontrolü Yönetmeliği gibi düzenlemelerle sağlanmaktadır. Adı geçen yönetmeliklerde "işçi sağlığı ve güvenliği mevzuatı kapsamına giren iş yerleri iç ortamlarında uygulanmaz" ve "sanayiden kaynaklanan dış ortam hava kirliliğinin önlenmesi amacıyla hazırlanmıştır" hükümleri yer alır. Bu durum göstermektedir ki ÇŞB mevzuatı yalnızca dış ortam hava kalitesinden sorumludur. Çalışanlara sağlıklı ve güvenli bir çalışma ortamı sağlama görevi Çalışma ve Sosyal Güvenlik Bakanlığına (ÇSGB) verilmiştir. Bu amaçla ÇSGB'ye bağlı İş Sağlığı ve Güvenliği Enstitüsü Müdürlüğü (İSGÜM) işyeri ortamında çalışanların kimyasallara maruziyetini konsantrasyon olarak ölçerek ulusal mevzuattaki sınır değerlerle karşılaştırır ve sonuçları rapor halinde saklar. Görülmektedir ki ulusal mevzuatta İç Ortam Hava Kalitesini (İOHK) değerlendiren ve kirleticiler için sınır değerleri belirten bir düzenleme bulunmamaktadır. İOHK ise sağlığa zararlı solunabilir kimyasal maddelerin ortam havasında bulunma miktarıyla değerlendirilir. Bu değerlendirmede göz önünde bulundurulan Uçucu Organik Bileşikler (UOB) özellikle boya, vernik, inceltici ve yapıştırıcı gibi malzemelerin üretim ve kullanımından kaynaklanmaktadır. Bu çalışmada boya üretimi ve boya uygulaması esnasında iç ortama salınan benzen, tolüen, etilbenzen ve ksilene (BTEK) maruz kalan çalışanlar için sağlık riskleri belirlenmiştir. İSGÜM'ün 2006-2013 yılları arasında boya üretimi ve uygulaması yapan 57 farklı işyerinde ölçtüğü 195 BTEK konsantrasyonu kullanılmıştır. Elde edilen veri; sanayi tipi ve işlemin türü olmak üzere iki farklı açıdan değerlendirilmiştir. Bu veriler kullanılarak Çevre Koruma Ajansı, RAGS, Sayı I: İnsan sağlığı Değerlendirme Kılavuzu'nda (U.S. EPA, 2009) soluma maruziyeti sağlık risk değerlendirmesinde kullanılması önerilen metot ile sağlık risk değerlendirmesi yapılmıştır. Çalışmanın sonuçları göstermiştir ki, boya uygulaması yapan tersane, otomotiv, mobilya gibi sektörlerde çalışanlar boya üretimi sektöründe çalışanlara göre daha çok BTEK'e maruz kalmaktadır. Ayrıca, konsantrasyon değerleri mevzuat sınır değerlerinin altında kalsa da sağlık risk değerlendirmesi yapıldığında bu konsantrasyonlara maruziyetin sağlık risklerinin kabul edilebilir kanser riski ($1x10^{-6}$) ve tehlike indeksi (1) değerlerini oldukça aştığı görülmüştür.

Anahtar sözcükler: BTEK maruziyeti, sağlık risk değerlendirmesi, İş Sağlığı ve Güvenliği, kanser riski, tehlike indeksi

To my family

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to the following people for their tremendous help and support. Without their encouragement and guidance, I would never have been able to realize this work.

First and foremost, I would like to express my greatest appreciation to my thesis supervisor Assoc. Prof. Dr. Ayşegül Aksoy for her patience, unlimited support, enthusiasm, and valuable comments. I also sincerely thank to my co-supervisor Assoc. Prof. Dr. Elçin Kentel for her never ending support, continuous understanding, invaluable patience, and guidance throughout this study. It was a pleasure for me to study with them.

I would also like to thank to my committee members Prof. Dr. Dilek Sanin, Assoc. Prof. Dr. Emre Alp and Assist. Prof. Dr. Barış Kaymak for their insightful comments and valuable suggestions.

I send heartfelt thanks to my parents, Fatma and Hasip Çalışkan and my brother, Ömer Alperen Çalışkan. They put faith in me all through my life and without their support and encouragement nothing would be possible.

Finally, I would thank to my best friend, my husband Emre Dölek who has been my biggest support through this study and my life. The words are not enough to express my appreciation to him for his deepest love, endless support and persistent confidence in me. This study will never be ended without his limitless understanding and support.

TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
ALT	Average Life Time
AT	Average Time
BAT	Best Available Techniques
BLV	Biological Limit Value
BREF	Best Available Techniques Reference Documents
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
BTX	Benzene, Toluene, Xylene
BW	Body Weight
C	Ceiling Concentration
CA	Contaminant Concentration
CAS	Chemical Abstract Service
CCOHS	Canadian Centre for Occupational Health and Safety
CDI	Chronic Daily Intake
CO_2	Carbon dioxide
COPD	Chronic Obstructive Pulmonary Disease
EC	Exposure Concentration
ED	Exposure Duration
EF	Exposure Frequency
EINECS	European Inventory of Existing Commercial Chemical Substances

EPA	Environmental Protection Agency
EPA-IRIS	Integrated Risk Information System
EU	European Union
ET	Exposure Time
FID	Flame Ionization Detector
g	Gram
GC	Gas Chromatography
GDOHS	General Directorate of Occupational Health and Safety
HI	Hazard Index
hr	Hour
HRA	Health Risk Assessment
HSE	Health and Safety Executive
HQ	Hazard Quotient
IAC	Indoor Air Contaminants
IAQ	Indoor Air Quality
IARC	International Agency for Research on Cancer
ILO	International Labor Organization
IOELV	Indicative Occupational Exposure Limit Values
IR	Inhalation Rate
IUR	Inhalation Unit Risk
kg	Kilogram
L	Liter

LE	Length of Exposure
LCR	Life Time Cancer Risk
LOAEL	Lowest Observed Adverse Effect Levels
m	Meter
m^3	Meter cube
Max	Maximum
µg	Mikrogram
Min	Minimum
min	Minute
MoLSS	Ministry of Labor and Social Security
MoEU	Ministry of Environment and Urban Affairs
NA	Not Available
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NIOSH	National Institute for Occupational Safety and Health
NOAEL	No Observed Adverse Effect Levels
NTP	National Toxicology Program
NY	Number of days per Year
OEL	Occupational Exposure Limit
OELV	Occupational Exposure Limit Value
OSH	Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit

PPE	Personal Protective Equipment
ppm	Parts Per Million
RA	Risk Assessment
RAGS	Risk Assessment Guidance for Superfund
REL	Recommended Exposure Limits
RfC	Reference Concentration
RHSMWCS	Regulation on Health and Safety Measures for Works with Chemical Substances
RHSPWCMA	Regulation on Health and Safety Precautions on Works with Carcinogenic or Mutagenic Agents
SCOEL	Scientific Committee on Occupational Exposure Limits
SDS	Safety Data Sheet
SME	Small and Medium Enterprises
STEL	Short Term Exposure Limit
TWA	Time Weight Average
USA	United States of America
VOC	Volatile Organic Carbons
y	Year
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

The inborn right of every human being is to live in a healthy environment and breathe clean air. There are several regulations relevant to air pollution control and management that are enforced by the Ministry of Environment and Urban Affairs (MoEU). These regulations focus on outdoor air quality rather than indoor. Examples are Regulation on Air Quality Assessment and Management (Official Gazette Date: 06.06.2008 No: 26898), Regulation on Industrial Air Pollution Control (Official Gazette Date: 03.07.2009 No: 27277), Regulation on Gasoline and Diesel Quality by Exhaust Emission Control (Official Gazette Date: 30.11.2013 No: 28837), Regulation on Large Combustion Plants (Official Gazette Date: 08.06.2010 No: 27605) and Regulation on Control of Air Pollution from Warming (Official Gazette Date: 13.01.2005 No: 25699).

The word "environment" is understood to comprise all that which is external to the human host, including physical, biological and social aspects, any or all of which can influence the health status of populations. Thus, the environment encompasses not only the general outdoor environment, to which everyone is exposed, but also specific indoor environments, such as the workplaces and the domestic environment, where people spend a considerable amount of their time (Corvalán et al., 2000).

Although lagged behind outdoor air quality, public health awareness has led to consideration and management of indoor air quality (IAQ) as well (Branco et al., 2013). People spend considerable amount of time indoors and therefore exposed to indoor air pollutants. Moreover, indoor concentrations of many air pollutants can be higher compared to outdoor concentrations (Jones, 1999). As a result, exposure to indoor air pollutants cannot be disregarded for human health protection.

Activities of daily living require individuals to spend more than 80% of their time indoors; therefore, the air quality of such spaces may affect the health of their inhabitants. The World Health Organization (WHO) has estimated that there are 2 million annual deaths worldwide attributable to indoor air contaminants (IAC), and has also ranked this phenomenon as the tenth avoidable risk factor in importance for the health of the general population (Fernandez et al., 2012).

Residences and non-industrial workplaces are the focus areas of IAQ management (Jones, 1999). Yet, IAQ should also be taken into consideration in industrial workplaces. In Turkey and around the world, IAQ in industries are evaluated under occupational safety and health (OSH). Provision of healthy and safe environments in workplaces is the responsibility of the Ministry of Labor and Social Security (MoLSS) in Turkey (Law on Organization and Duties of Ministry of Labor and Social Security, Law No: 3146). For this purpose, Directorate of Institute of Occupational Health and Safety (ISGUM) performs air pollutant measurements in workplaces upon request. These measurements are generally conducted via sampling in the direct exposure zone of employees. General indoor air sampling can also be realized and results are assumed as personal exposure. Measurements include: chemical (chemical and dust concentrations in the zones where employees are working and exposed to pollutants through inhalation, ingestion or dermal contact etc.) and physical analyses (ergonomics, noise, vibration, and light limitations in workplaces). However, with a new perspective in the Law on Occupational Health and Safety (2012) (Law No: 6331), ISGUM will only take and analyze samples in their accredited laboratories only in accordance to their own projects and needs. Service based on requests by workplaces will not be practiced by ISGUM anymore.

One of the major group of indoor air pollutants responsible from poor IAQ in several industries is BTEX (benzene, toluene, ethylbenzene and xylene), a subset of Volatile

Organic Compounds (VOCs) (Huang et al., 2013). BTEX is known to have non-carcinogenic effects on human health. Moreover, benzene is regarded as carcinogenic (U.S. EPA, 2009). One of the main sources of BTEX observed in indoors is paint (Güllü, 2013). As a result, one can expect to observe high BTEX concentrations in indoor air at industries where paint is either produced or applied, if precautions are not taken.

Paint manufacturing and application are known as the main BTEX sources of indoor air (MoLSS, 2005). One of the workplace categories for which ISGUM has performed sampling visits is paint manufacturing and application industry as well. During sampling, air samples are taken from the breathing zone of employees while they are performing their work (i.e. paint application or work related with paint production). Through this procedure it is aimed to detect exposure of an employee to pollutants in the air through “inhalation”. It is hard to obtain measurement results for all air pollutants that may exist at different kinds of workplaces in Turkey. However, there are sufficient amount of sampling results for BTEX measured at paint production and application workplaces in the database of the institution. So in this study paint production and application works are selected and health risks due to BTEX exposures through inhalation are evaluated through a health risk assessment (HRA) study.

In this study, BTEX concentrations observed in selected industries producing and/or using paint are evaluated based on human health risks through inhalation. The database of ISGUM is scanned and investigated for this purpose. The BTEX measurements at selected industries between 2006 and 2013 are compiled for HRA. As well as the current approach of comparing the measured concentrations with the legislative limit values in Turkey; evaluations are made in regard to cancer and non-cancer health risks. Health risks of emerging or existing environmental pollutants are subjected to close scrutiny by many regulatory authorities as more evidences on their adverse health effects appear in scientific and public media. Thus, assessment of health risks becomes a crucial step for any further regulatory actions (Cao et al., 2011).

The objective of the study is to evaluate cancer and non-cancer health risks for employees in paint industry and application related works due to BTEX exposure through inhalation. For this reason, safety of the paint industry related workplaces in terms of human health is evaluated with respect to both indoor air BTEX concentrations (mg/m^3) and their associated health risks. BTEX concentrations and related health risks are evaluated with respect to two classifications: type of industries and type of actions. HRA for BTEX exposure due to “inhalation” is determined with the methodology suggested by EPA (U.S. EPA, 2009).

The organization of this thesis is as follows. In the second chapter, literature review and background information are provided. Within the chapter, information about paint composition, detailed information on nature of BTEX and health risks associated with exposures, relevant previous studies and national and international legislation related to the study are provided. In the third chapter, the methodology used in the study is given. This chapter includes information about data gathering, analysis of data, HRA methodology and applied equations. In the fourth chapter, evaluations of concentrations, associated cancer and non-cancer risks for chronic exposures, corresponding risks calculated for legislative limit values, and also proposed concentration limits based on health risks are discussed. Finally, in the fifth chapter, conclusions and recommendations are suggested.

CHAPTER 2

LITERATURE REVIEW AND THEOROTICAL BACKGROUND

The link between environment and human health operates through the exposure of humans to environmental hazards. These hazards may originate naturally whereas the majority is driven from human activities and interventions. However, in all cases health effects only arise if humans are exposed to the existing hazards at a specific place and time. Emissions may be released into the environment in a variety of ways from industry, agriculture, transportation etc., and may then be dispersed and accumulate in different environmental media (i.e. air, water, soil, food). Exposure occurs when humans are encountered with the contaminants through any one of these media and then the adverse health effects of the exposure are seen (see Figure 2.1) (Corvalán et al., 2000).

Corvalán et al. (2000) stated that *driving forces, pressures, state, exposures, effects and actions* should be defined in order to describe and analyze the global situation in relation to health, environment and development. Development in industry with respect to air pollution is *the driving force* with *the pressure* on the workplaces. *The state* of the workplace exposure levels leads to monitoring *the exposures* in the workplaces or in individual workers. *The effects* of these exposures are occupational diseases and cancer risks. *The actions* to be taken for the exposures are: emission control measures, chemical safety legislation, epidemiologic studies, improved labeling and environmental health impact assessments.

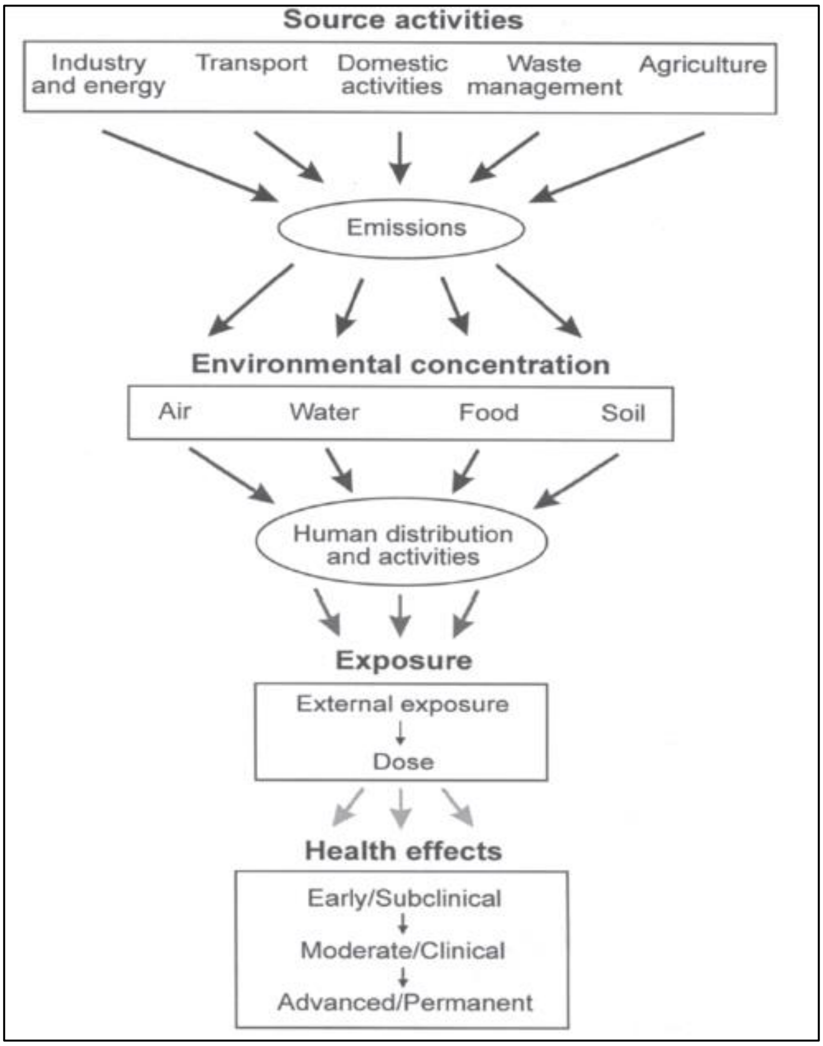


Figure 2.1 Environmental Health and Hazard Pathway (Corvalán et al., 2000)

Industries such as paint manufacturing and application are known as the VOC emission sources (Environment Australia, 1998). Hazardous air pollutants such as VOCs, particulate matter, etc. arising from paint manufacturing and application can contribute to health problems that may affect employees, their families, and the community (URL 1).

Paint is generally known as a pigment which is suspended within a liquid. It is applied to protect and enhance the appearance of a surface (U.S. EPA, 1994). However, although its primary purpose is surface protection, paint also serves as a decoration alternative for users. Thus, paint is applied for interiors and exteriors of houses, boats, automobiles, planes, furniture, and many other places where protection and decoration are desired (URL 2).

Conventional paints that contain high amounts of VOC have been linked to health problems and air pollution as well. Furthermore, producing conventional paints is also resource intensive (Robertson, 2011). However, there are new paint types called "waterborne" paints which contain low amounts of VOC (Conseil Européen de l'Industrie des Peintures, 2011). Therefore, substitution of high amount VOC containing paints with low VOC paints (i.e. waterborne paints, powder coatings, ultra-violet (UV) light, or higher solids paints) is a possible solution to reduce the adverse effects of exposure to VOC namely BTEX originated from painting or paint production activities.

Paint has started to become the main element of almost all sectors with the industrial revolution and after that its importance in market and economies of countries has also started to increase. Many of today's paint and coating materials may be unnoticed by the consumer, but play valuable roles in delivering high-quality foodstuffs, durable goods, housing, furniture and thousands of other products in market (URL 3). Paint industry of Turkey has a total annual production capacity of almost 800,000 tons/year. This corresponds to approximately 2% of the world's paint market. With this production capacity, Turkey has the 6th largest paint industry in Europe (State Planning Organization, 2006).

According to the Paint Production Guidance (MoEU, 2009), which was prepared under the scope of the Project of Improving the Management of Hazardous Waste from Industries in Turkey, there are about 20 large scale facilities producing paint using advanced manufacturing technologies. Moreover, there are almost 600 other small and medium sized enterprises (SME) in the paint industry in Turkey. The operating conditions in these plants may vary significantly compared to their counterparts in Europe. The difference in production approaches and quality of occupational conditions results in variations in indoor concentrations of air pollutants.

As stated in the 9th Development Plan, there are 17,000-20,000 employees who are involved directly in paint production. In addition, approximately 100,000 painters and 25,000 employees in hardware stores are also exposed to paints. The overall number of employees in the paint sector is estimated around 200,000 in Turkey. Total production capacity of Turkey is composed of 61% waterborne paints whereas 39% of solvent based paints. Since the importance given to the environment and human health has increased, more environment and human health friendly paint types (i.e. low VOC containing paints, powder coatings etc.) has started to be used in painting activities. However, there are still solvent based paints in the market and these are applied during painting (State Planning Organization, 2006).

Employee profiles of the industry can be obtained from the project evaluation report of OSH inspection for paint production workplaces (MoLSS, 2005). A total of 427 site visits were conducted by inspectors to workplaces where paint is produced in 30 provinces during the project. It was declared that about 15% of the employees were females which indicate that males are dominant in the sector. As the case for all chemical industries, paint industry leads to emissions as well which affect air quality and human health adversely. For instance, Yin et al. (1987) presented a study in China in which almost 280,000 (53%) workers among 528,729 who were exposed to benzene or benzene mixtures were paint workers.

According to an interview conducted with a member of MoLSS (2014), who is authorized to take sample from workplaces and analyze them in laboratory, paint is generally applied via paint spray. Painting with brush is not generally practiced at paint houses. However, although painting in a cabinet with ventilation or water curtain is a crucial precaution to decrease the amount of exposure, employees generally paint pieces with sprays generally at wide ateliers where other duties relevant to the workplace (i.e. maintenance, repair or welding etc.) also continue.

2.1 Paint Production and Composition

The paint production flow chart is given in Figure 2.2. Paint production process generally starts with alkid production. Then, resins and solvents are added to the produced alkid which is then followed by pre-mixing step. After that, pigments are homogenously spread on the paint film through dispersion. To adjust the usage properties, formulation phase is conducted preceding color adjustment. Produced paint goes through quality control at the last stage of production. Then filling and handling are realized for marketing (Şengül et al., 2003).

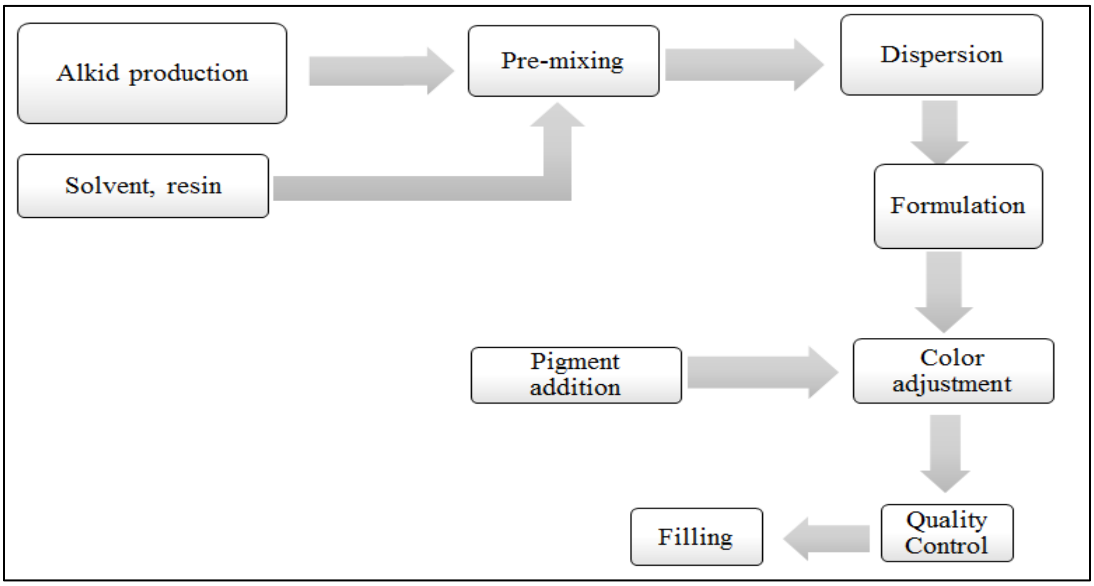


Figure 2.2 Flow Chart of Paint Production (Şengül et al., 2003)

Paint application is quite common in almost all kinds of industrial sectors. Especially in automotive sector, shipyards, furniture manufacturing, etc., several operations or manufacturing stages include paint application. Paint consists of 4 major components which are:

1. Pigments,
2. Binders,
3. Chemical additives and,
4. Solvents.

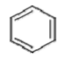
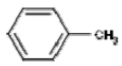
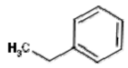
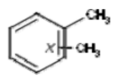
Pigment is a solid substance which can be organic or inorganic dispersed throughout the coating to impart a color and protect it. The binder is used to aid the pigment to hold on the surface and connect the grains tightly. It is the liquid portion of the paint and there are three varieties according to surface type and usage purpose: aqueous, oily and natural/plastic resin. On the other hand, additives are generally used for modifying the existing paint properties. Finally, solvents are volatiles, which are used to solve or distribute the binder or to facilitate the production process and to improve application conditions (Erkmen, 2012). During paint application and drying, solvents are emitted to air mainly as mixtures of organic hydrocarbons, alcohols, esters and ketones (Rentz et al., 2002).

BTEX is one of the group of compounds emitted during paint production and application. Paint is a combination of many substances and chemical such as pigments, solvents, additives, and binding elements. Furthermore, there are about 3,400 substances used in the paint production according to use purpose or different properties of paint. Thus, there is not a general formula for paint since there are many types of it (MoLSS, 2005).

2.2 BTEX

Chemical Abstract Service (CAS) and chemical structure of BTEX compounds are given in Table 2.1. In general, the primary sources of the BTEX compounds in ambient air are known as emissions from motor vehicles and aircraft exhaust, spills of petroleum and cigarette smoke. Also, refined petroleum products, some chemical intermediates and consumer products like paints, thinners, rubber products, inks, cosmetics and pharmaceutical products can cause BTEX emissions as well. Once released into the environment, BTEX evaporates quickly into the air (Leusch and Bartkow, 2010).

Table 2.1 Name, Chemical Abstract Service (CAS) and Chemical Structure of BTEX Compounds

CAS	Compound	Formula	Chemical Structure
71-43-2	Benzene	C_6H_6	
108-88-3	Toluene	$C_6H_5CH_3$	
100-41-4	Ethylbenzene	CH_3-CH_2-C_6H_5	
1330-20-7	Xylene	$C_6H_4(CH_3)_2$	

2.2.1. Benzene

According to WHO (2000); benzene is a colorless, flammable liquid at room temperature with relatively low boiling point and a high vapor pressure. As a result, it evaporates quickly at room temperature. It is slightly soluble in water and miscible with most organic solvents. Benzene in ambient air exists predominately in the vapor phase, with residence times varying between a few hours and a few days, depending on the environmental conditions, climate and concentrations of other pollutants.

Benzene is a natural component of crude oil, and petroleum. It is produced in large quantities from petroleum sources and used for the chemical synthesis of ethylbenzene, phenol and other substituted aromatic hydrocarbons. In 1988, about 20 million tons and 5 million tons benzene were produced worldwide and within the countries of the European Economic Community, respectively. Benzene production in the United States of America (USA) in 1990 was estimated nearly 5.4 million tons (WHO, 2000). In 2010, estimation of benzene production was 6.8 million tons in USA (URL 4). The increase in benzene production may result due to increase in gasoline use in all around the world.

The major sources of benzene in ambient air are exhaust emissions and evaporation losses from motor vehicles as well as evaporation losses during handling, distribution and storage of petroleum. Benzene has also been detected at high levels in indoor air. Although some of the exposure to benzene might arise due to building materials (paints, adhesives, etc.), mostly cigarette smoke at homes and public areas is the source. Benzene can also be found in products such as synthetic rubber, plastics, nylon, insecticides, paints, dyes, resins-glues, furniture wax, detergents and cosmetics (WHO, 2000).

According to WHO (2000), inhalation is the dominant pathway for benzene exposure for humans; whereas intakes through food and water consumptions are minimal. Smoking is a significant source of personal exposure as mentioned above. Also short-term exposures may be due to refueling of motor vehicles. In the USA, the daily exposures to benzene from ambient and indoor air have been calculated to range between 180 μg/day and 1,300 μg/day, respectively. The intake concentration from food and water is up to 1.4 μg/day. There are negative health effects due to exposure to benzene and several types of blood dyscrasia have been noted.

Benzene may be one of the risk factors in the incidence of chronic diseases such as diabetes, and lung and breast cancers in the developing countries based on the toxicity mechanism of benzene. Epidemiologic and experimental studies suggest that benzene exposure can lead to numerous non-cancer health effects associated with functional aberration of vital systems in the body like reproductive, immune, nervous, endocrine, cardiovascular, and respiratory. Moreover chronic benzene exposure should be a matter of concern for societies (Bahadar et al., 2014).

Most of the observed disease cases reported several years ago were due to exposure to benzene while using solvents in different workplaces. An increased frequency of anemia (decrease in number of red blood cells or having less than the normal quantity of hemoglobin in the blood) was detected among shoe factory workers, rotogravure printing workers and rubber factory workers with prolonged exposure to high benzene concentrations (hundreds of milligrams of benzene per m^3). One of the first epidemiological studies in Turkey demonstrated an increased incidence of leukemia among shoe factory workers in Istanbul. Shoe factory workers in Florence, Italy, were subject to an increased risk of leukemia before 1963 (WHO, 2000). These situations could have occurred due to the use of adhesives and paint in shoe production industry.

Under the light of the given information, the most significant adverse health effects due to prolonged exposure to benzene are being toxic to genes and carcinogenicity. It should be noted that benzene is carcinogenic to human and safe level of exposure of benzene cannot be recommended. Besides, acute occupational exposure to benzene is known to be the reason of headache, dizziness, drowsiness, confusion, tremors and loss of consciousness and eye and skin irritations (WHO, 2000). The increase in the lifetime cancer risk of an individual who is exposed to 1 $\mu g/m^3$ benzene in air for a lifetime is in the range of $2.2x10^{-6}$ to $7.8x10^{-6}$ (U.S. EPA-IRIS, 2003).

2.2.2. Toluene

Toluene is a noncorrosive and volatile liquid with an aromatic odor. It is generally used as a solvent for paint or a thinner for paint, coatings, gums, printing, rubber, cosmetics, oils and resins. It is estimated that 10 million tons of toluene has been produced worldwide. The bulk of production is in the form of a benzene-toluene-xylene (BTX) mixture used in the back blending of petroleum for enhancing octane rates. Moreover, sources of emissions of toluene result from production, marketing and storage of petroleum. Due to the high volatility in air and low solubility in water, toluene present in natural waters may be expected to be released to the atmosphere (WHO, 2000).

Non-occupational uses of paints and thinners, together with tobacco smoke, represent the principal sources of toluene in indoor environments. It is expected that toluene levels in indoor environments are significantly higher than outdoor levels involving non-occupational use of paint and thinners, and also tobacco smoke existence. Inhalation is the predominant route of exposure to toluene. In rural areas average ambient air concentrations of toluene are almost lower than 5 $\mu g/m^3$, while in urban air the mentioned concentrations are in the range 5–150 $\mu g/m^3$. This is because concentrations could be higher via getting closer to industrial emission sources (WHO, 2000).

1,020 toluene exposed workers who had been employed for a minimum period of three months during the period of 1925–1985 were examined in a study. No significant increases in tumors and no cumulative dose–response relationship in workers were observed in an exposure period of at least five years and a latency period of 10 years. Moreover, there was no quantitative estimate of carcinogenic risk from inhalation exposure to toluene (WHO, 2000). Thus, there is inadequate evidence in humans for the carcinogenicity of toluene and it cannot be classified as carcinogenic to humans (HPA, 2007).

Acute and chronic health effects are observed mostly on central nervous system as a result of toluene exposure. Acute inhalation or ingestion can cause systemic effects such as euphoria, excitation, hallucinations, dizziness, drowsiness, ataxia, slurred speech, tremors, respiratory depression, arrhythmias and convulsions. Furthermore, coma and death can occur following substantial exposures (HPA, 2007). Canadian Centre for Occupational Health and Safety (CCOHS, 2013) states that toluene may irritate nose and throat. Also due to inhalation of toluene; headache, nausea, dizziness, drowsiness, confusion and unconsciousness can be observed as adverse health effects (CCOHS, 2013).

2.2.3. Ethylbenzene

Ethylbenzene is generally emitted from consumer products of paint, ink, plastics, and pesticides. It is highly flammable and colorless liquidized compound primarily used for the production of styrene. It is also known that in 1975, 98% of all ethylbenzene produced in the USA was used as the raw material for styrene manufacture (WHO, 2000).

U.S. EPA declares that short term ethylbenzene exposure causes adverse effects on respiratory system, such as throat irritation and chest constriction and also irritation of the eyes, and neurological effects such as dizziness. On the other hand, long-term exposure via inhalation has shown conflicting results regarding its effects on the blood in human. Animal studies have reported effects on the blood, liver, and kidneys from chronic inhalation exposure to ethylbenzene. However, there is limited information on the carcinogenicity of ethylbenzene for human; in other words, the information of quantitative estimate of carcinogenic risk from inhalation exposure to ethylbenzene is not available (URL 5).

2.2.4 Xylene

Xylene is an aromatic hydrocarbon consisting of a benzene ring with two methyl substituent. It is a colorless liquid which is insoluble in water. It has three isomers of dimethylbenzene which are distinguished by the designations of ortho- (o-), meta- (m-), and para- (p-), which specify to which carbon atoms of the benzene ring the two methyl groups, are attached (WHO, 2000).

Xylene is generally used in gasoline and as a solvent in printing, rubber and leather industry. It is released into the atmosphere via emissions mainly from industrial sources, automobile exhaust, and through volatilization during their usage as solvents. It has also been detected at low levels in indoor as xylene has been widely used in house products such as synthetic fragrances and paints (Oregon Department of Human Services, 1994).

Irritation of eyes, nose, and throat, gastrointestinal effects and neurological effects are seen in short term (term of "acute" can also be used) due to exposure through inhalation of mixed xylenes. Long term (term of "chronic" can also be used) inhalation exposure of humans results primarily in central nervous system effects, such as headache, dizziness, fatigue, and incoordination. Respiratory, cardiovascular, and kidney effects have also been investigated. On the other hand, quantitative estimate of carcinogenic risk from inhalation exposure to xylene is not available (WHO, 2000).

2.3. Major Health Problems Associated with Paint Production and Application

Workers in paint production and application industries are potentially exposed to the chemicals found in paint products during production and application. These exposures may result in some obvious and non-obvious health problems. In other words, chronic or acute health effects due to exposure to the chemicals in paint could be observed.

As stated before, a solvent is a substance used to dilute or dissolve another substance to produce a solution. There are mainly two types of solvents: organic and inorganic. Ammonia, carbondioxide, phosphorus tribromide and water are the inorganic solvents while carbon containing solvents are called as the organic solvents. Examples for organic solvents are; hydrocarbon solvents, alcohols, esters, ethers, and volatile organics (Arslan Tatar, 2012).

There are three ways that solvents or other volatile paint components can penetrate into a human body (Figure 2.3) (URL 6):

1. Inhalation
2. Ingestion
3. Skin contact

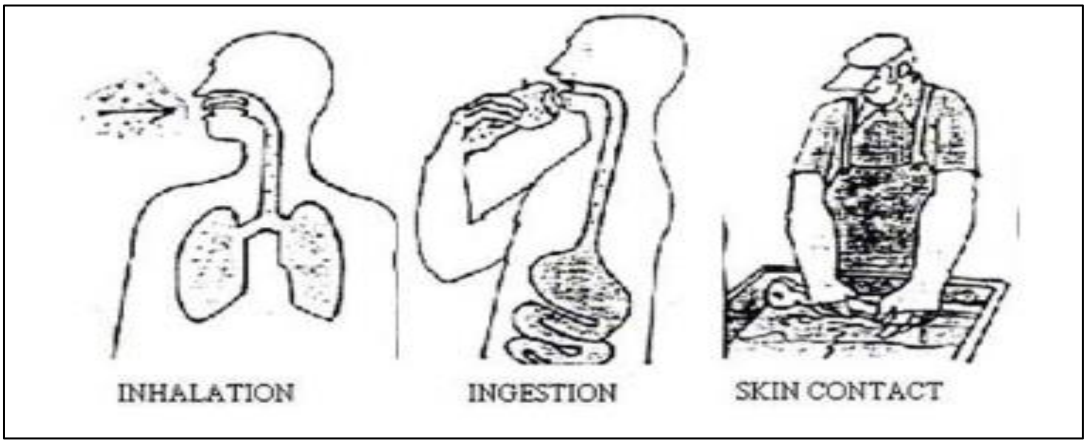


Figure 2.3 Chemical Exposure Routes (URL 6)

1. Inhalation: Breathing in solvent vapors is a common route of exposure. Vapors can directly irritate the eyes and/or nose, and if inhaled, they may cause drowsiness, fatigue, loss of coordination, irregular heartbeats, and slowed and labored breathing. In extreme cases, exposures can be lethal. Excessive, repeated, and prolonged exposure to some types of solvent vapors has been known to result in permanent nerve or brain damage. It is also known that some solvents, such as benzene, can cause cancer due to inhalation under rare conditions (U.S. Department of Defense, 2007).

2. Ingestion: Although not commonly seen, directly swallowing of solvents or consuming food or drink contaminated with solvents can cause negative health effects on human (U.S. Department of Defense, 2007).

3. Skin Absorption: Many solvents can easily pass through the skin. Some also can pass through gloves or other protective clothing if they are not designed for the specific solvent. Skin contact with solvents can result in loss of the protective fats and oils in the skin, resulting in dryness and irritation, rashes, or chemical burns. Simple skin irritation may take about a week to clear up, but in severe cases, it may take longer. Excessive skin exposure to some solvents can result in many of the same health effects seen after breathing in solvent vapors (U.S. Department of Defense, 2007).

Indoor ambient monitoring revealed that high levels of VOCs are associated with places where solvents are frequently used such as paint dilution (Lerner et al., 2012). VOCs from painting solvents are one of the most important sources of pollutants for the paint industry. They include a large group of air pollutants such as benzene, toluene, xylene, hexane, heptane, trichloroethane, perchloroethane and cyclohexane. Additionally, exposure to VOCs is associated with allergies and adverse respiratory effects, frequently expressed as asthma or Chronic Obstructive Pulmonary Disease (COPD). On the other hand, lung, stomach, colon, bladder, esophagus, kidney cancer risks are higher for painters and, if paint contains benzene, due to solvent effect, early dementia, endocrine disorders, COPD, mixed dust pneumoconiosis and kidney diseases are also known as the high risked illnesses related with the job (Lerner et al., 2012).

Common reasons for occurrence of poor IAQ in closed environments are listed as follows (URL 7):

- Improper or inadequately maintained heating and ventilation systems,
- High or low humidity,
- Contamination by construction materials, glues, fiberglass, and particle boards, paints, chemicals, etc.
- Increase in number of building occupants and time spent indoors.

The concentrations of indoor and outdoor air pollutants have been increased due to human activities especially in China (Liu et al., 2014). This has pushed stricter air quality standards to be legislated. However, the guideline limits for indoor air pollutants namely formaldehyde, acetaldehyde and benzene can be different in different countries. For example, the limiting concentrations in terms of health risks in Chinese legislation imply 2 to 3 magnitude higher cancer risks compared to the acceptable risk of $1x10^{-6}$ commonly required by EPA (U.S. EPA, 2009). Liu et al. (2014) evaluated personal exposure limit levels of air pollutants in public scale in China. In the scope of the study, indoor concentrations of BTX and carbonyl compounds were measured at 128 homes in Beijing with decoration ages longer than 5 years. The concentrations of BTX and carbonyls were only gathered at living rooms and cooking areas. The aim of the study was to identify the profile of poor IAQ in houses originating from the paint used in buildings. The concentrations of toluene and xylene were detected as 1.3 to 75.6 $\mu g/m^3$, 0.2 to 75.6 $\mu g/m^3$, respectively, in the living rooms and 1.4 to 86.0 $\mu g/m^3$, 0.2 to 78.7 $\mu g/m^3$, respectively in cooking areas. Toluene was the most abundant component among BTX, followed by xylenes. Benzene exhibited lower concentration ranging from 1.0 to 37.5 $\mu g/m^3$ in living rooms and 1.0 to 45.9 $\mu g/m^3$ in cooking areas. As benzene has been widely used as an industrial solvent in paints, varnishes, thinners and gasoline, it could be easily detected in almost all indoor environments (Liu et al., 2014). Toluene has also been used as a solvent in a variety of household products such as paints, rubbers and adhesives. Toluene concentrations, ranged from 0.3 $\mu g/m^3$ to 358 $\mu g/m^3$ in indoor air. The highest values were observed due to usage of cleaning products, in general. In residential houses typical concentrations of toluene ranged from 4 $\mu g/m^3$ to 50 $\mu g/m^3$ xylenes (o,m,p-xylenes). Xylenes are used as solvents for paints, rubbers or adhesive materials and the emission of xylene can also be observed due to cigarette smoking. Liu et al. (2014) calculated the mean cancer risk due to exposure to indoor benzene as 0.9×10^{-4} which was higher than the commonly acceptable risk of $1x10^{-6}$ (U.S. EPA, 2009). Building material, paint solvents, particle board and plywood flooring were the crucial sources contributing to personal exposure to benzene in indoor air.

United States-Occupational Safety and Health Administration (OSHA, 2011) has compiled information on poor IAQ. Headaches, fatigue, trouble concentrating, and irritation of the eyes, nose, throat and lungs are mentioned as the main symptoms of poor IAQ. Additionally, according to U.S. OSHA (2011) exposure to VOCs can result in both acute and chronic health effects, depending on factors like the level of exposure and the length of exposure. A few VOCs, such as benzene, have been directly linked to cancer in humans (and occurs after many years), and others are suspected of causing cancer. U.S. EPA states that health effects from indoor air pollutants may be experienced soon after exposure or, possibly years later than exposure (URL 8).

Chen et al. (2012) declared that “VOCs are commonly used for industrial purposes in vast quantities, but can also be found in any home, in items such as paint.” The adverse effects of exposure to such chemicals can be observed both on personal health and on environment. The authors added that many of these compounds are known as carcinogens (i.e. benzene) or central nervous system toxicants (i.e. toluene). Fernández et al. (2012) mentioned in the study that the estimation of WHO on annual deaths worldwide attributable to IAC was 2,000,000 people and additionally, WHO has also ranked this phenomenon as the tenth avoidable risk with respect to importance for the health of the general population.

BTEX compounds are also known as IAC. Long and short term health effects of these chemicals together with the classifications according to EPA-IRIS, International Agency for Research on Cancer (IARC), and National Toxicology Program (NTP) are given in Table 2.2. Results obtained from a number of studies related with BTEX, IAQ and human exposure studies carried out in different years are given in Table 2.3.

Table 2.2 Short Term and Long Term Effects and Classifications of the Compounds according to EPA-Integrated Risk Information System (EPA-IRIS), International Agency for Research on Cancer (IARC) and National Toxicology Program (NTP)

Compound	Short-term Health Effect*	Long-term Health Effect*	EPA-IRIS*	IARC**	NTP***
Benzene	Drowsiness, dizziness, headache, eye and skin irritation unconsciousness	Leukemia and cancer of the blood-forming organs	Group A, Known human carcinogen	Group 1, Carcinogenic to humans	Known to be a human carcinogen
Toluene	Eye irritation, fatigue, anxiety, sleepiness, headaches, and nausea, even death at higher levels of exposure	Drowsiness, involuntary eye movements, and impaired speech, hearing, and vision, liver or kidney damage	Group D, Not classifiable as to human carcinogenicity	Group 3, Not classifiable as to human carcinogenicity	No evidence of carcinogenicity
Ethylbenzene	Respiratory effects, throat irritation and chest constriction, eye irritation, dizziness	Limited information is available on long term effects	Group D, Not classifiable as to human carcinogenicity	Group 2B, Possibly carcinogenic to humans	No evidence of carcinogenicity
Xylene	Dyspnea and irritation of the nose and throat and eye; impaired short-term memory, impaired body balance	Headache, dizziness, fatigue, incoordination, anxiety, impaired short-term memory, and inability to concentrate, severe chest pain and possible effects on the kidneys	Group D, Not classifiable as to human carcinogenicity	Group 3, Not classifiable as to human carcinogenicity	No evidence of carcinogenicity

** URL 9 http://www.epa.gov*

*** URL 10 http://monographs.iarc.fr/ENG/Classification*

**** URL 11 http://ntpsearch.niehs.nih.gov*

Table 2.3 BTEX Concentrations (μg/m^3-Mean) Detected in Different Residential, Workplace and Outdoor Environment from Literature

Reference	City, Country	Sampling	Benzene	Toluene	Ethylbenzene	Xylene
Bono et al. (2003)	Biella and Torino, Italy	Personal-Passive*	10.3	41.9	-	59.4
Gunatilaka M. (2003)	Christchurch, New Zeland	Air-Passive (Vehicle emissions)	12.1	31.08	5.4	28.1
Vitali et al. (2006)	Rieti, Italy	Personal-Passive (Car painting)	53,100	93,800	23,800	72,500
		Air-Passive (Car painting)	29,400	21,200	4,900	18,400
Parra et al. (2008)	Pamplona, Spain	Indoor air-Passive (Smoking)	2.02	6.41	1.03	1.24
		Indoor air-Passive (Non-smoking)	1.20	4.53	0.80	1.09
		Indoor air-Passive (Pubs and cafes)	2.25	8.96	1.58	1.91
Çökelek (2008)	Kocaeli, Turkey	Air-Active (Point 1)	4.6	6.1	1.5	2.3
		Air-Active (Point 2)	3.0	4.9	1.0	1.4
		Air-Active (Point 3)	2.3	6.4	0.5	1.4
		Air-Active (Point 4)	2.8	4.0	0.8	1.4
		Air-Active (Point 5)	2.9	3.7	0.8	1.4
Liu H. et al. (2009)	China	Personal-Active (Poor vent.)**	192,530	-	-	-
		Personal-Active (Good vent.)**	113,910	-	-	-
Soldatos et al. (2010)	Athens, Greece	Personal-Active (Car parking worker)	366	374	102	279
		Personal-Active (Gasoline station)	1,731	1,995	272	994

** Personal: Workers' breathing zone.*
*** Poor ventilation: Simple electric fans (i.e. floor fans) or natural ventilation; Good ventilation: mechanical ventilation system (i.e. air exhaust hood and mechanical fan).*

Table 2.3 (Continued)

Zhou et al (2011)	Thanjin, China	Air-Passive- Personal	6.65	13.07	2.27	1.07
		Air-Passive- Indoor	6.13	7.47	1.32	0.47
		Air-Passive- Outdoor	3.89	1.89	2.23	0.30
		Air-Passive- Office	1.38	1.46	0.30	0.07
Manuela et al. (2012)	Rome, Italy	Personal-Passive	16.7	65.2	-	107.8
Lerner et al. (2012)	Buenos Aires, Argentina	Air-Passive (Repair and car painting)	59.2	601.5	384.9	959.7
		Air-Passive (Sewing work rooms)	-	6.3	3.3	5.0
		Air-Passive (Chemical analysis laboratories)	6.9	7.7	6.3	15.7
		Air-Passive (Take away food shops)	-	1.9	-	-
		Air-Passive (Photocopy center	-	3.3	-	-
Lan et al. (2013)	Ho Chi Minh, Vietnam	Personal-Passive (Bus driver)	30	~ 46	~ 9	~ 18
		Personal-Passive (Taxi driver)	39	~ 32	~ 13	~ 30
		Personal-Passive(Motorcycle driver)	116	~ 250	~ 50	~ 170
		Personal-Active (Petrol filling workers)	52	~ 73	~ 30	~ 15
		Personal-Active (Street vendors)	32	~ 82	~ 15	~ 30
Du et al. (2013)	Guangzhou, China	Air-Passive	18.5	173.2	-	58.1
Liu et al. (2014)	Beijing, China	Air-Passive (Living room)	10.2	17.7	-	10.8
		Air-Passive(Cooking room)	9.2	16.9	-	11.2

** Personal: Workers' breathing zone.*
*** Poor ventilation: Simple electric fans (i.e. floor fans) or natural ventilation; Good ventilation: mechanical ventilation system (i.e. air exhaust hood and mechanical fan).*

2.4. Literature Review on IAQ and HRA of BTEX Exposure

There are several studies in literature which investigated the details of exposures through several exposure routes and human health effects especially carcinogenicity of the indoor air pollutants and also introduced HRA of these exposures.

Sofuoğlu et al. (2010) conducted an HRA on chemical exposure of school children. Children are more sensitive to environmental pollutants than adults due to their higher breathing rates relative to their body size, and continuing growth. Additionally, poor IAQ and poor ventilation in classrooms where children spend a significant time of their daily life results in higher health risk levels. The authors used EPA-IRIS methodology for calculation of cancer risks. Sampling period continued for three seasons (winter, spring and fall). Both indoor (classrooms and the kindergartens) and outdoor (playgrounds) air qualities were measured. They founded that benzene, toluene, and formaldehyde were the most abundant compounds with 95th percentile indoor air concentrations of 29 g/m^3, 87 g/m^3 and 106 g/m^3 for benzene, toluene, and formaldehyde, respectively. Naphthalene and xylenes followed them with an order of magnitude lower concentration for each. Two isomers of dichlorobenzene (1,3 and 1,4) were the other notable compounds. The results were used to group the indoor air pollutants according to potential health effects. The most concerning pollutant with high chronic toxic and carcinogenic risk level seemed to be formaldehyde according to the health assessment which was followed by naphthalene, benzene, and toluene in sequence based on chronic effects. Benzene was also concern as the accepted carcinogenic risk estimates were above the acceptable level of $1x10^{-6}$.

In a study performed in Sweden in 1980, exposure to organic solvents was measured in the breathing zone of 17 Swedish male painters who were presumed to have the highest exposure among 47 workers employed in seven factories in Sweden (WHO, 1989). Air samples were collected and analyzed with two portable gas chromatographs. The median exposure concentrations were: xylene, 111 mg/m^3 (for

16 people); toluene, 11 mg/m^3 (for 16 people); isobutanol, 5 mg/m^3 (for 15 people); ethylacetate, 20 mg/m^3 (for 14 people); ethanol, 13 mg/m^3 (for 13 people); n-butanol, 7 mg/m^3 (for 13 people); methylacetate, 12 mg/m^3 (for 8 people); 719 mg/m^3 dichloromethane (for 3 people), and 129 mg/m^3 isopropanol (for 1 person). Although dichloromethane had the highest concentration, it cannot be said that it is the most crucial compound emitted during painting as sample size (3) was not sufficient compared to the ones used for xylene and toluene (16 samples).

Paint manufacturing employees who were known to be exposed to solvents were monitored at seven different companies in New Zealand in 1986. Toluene, xylene and ethylbenzene were found in indoor air of all of these seven workplaces. Hepane, n-hexane, pentane and methylethylketone were found in few of them (WHO, 1989).

Several studies have focused on car painters because employees usually suffer from chronic exposure to high levels of several different solvents in these workplaces. Vitali et al. (2005) conducted a study in Italy at 8 handicraft car painting shops. The solvents which were analyzed in the content of the study were toluene, ethylbenzene, 1, 2-dichloropropane, n-butylacetate, n-amylacetate, xylene isomers, ethylacetate, and benzene. Exposure of car painters to these VOCs was mainly due to use of varnishes. A simple regression analysis was performed to evaluate the relationships between data obtained through environmental sampling with charcoal tubes, personal sampling with diffusive charcoal samplers, and urinary determination. Regression analyses for toluene and xylene showed positive correlations for urine levels both with stationary and personal air monitoring (which means exposure due to "inhalation"). The correlation was stronger for toluene ($r = 0.85$ and $r = 0.95$ as stationary sampling vs urine level and personal sampling vs urine level, respectively) compared to xylene ($r= 0.14$ and $r=0.37$ as stationary sampling vs urine level and personal sampling vs urine level, respectively). Benzene levels found in post-shift urine were positively correlated with workplace air concentrations measured by stationary ($r = 0.97$) and personal ($r = 0.67$) sampling. The results of high correlation between personal sampling and urinary level concentrations support the idea of exposure to toluene and benzene via inhalation at painting workplaces is a crucial issue which needs attention.

Zhou et al. (2011) stated that personal exposure to VOCs often exceed outdoor exposure. Indoor residential exposure and additionally high VOC concentrations were the dominant contributors to personal exposure as people spend over 80% of their daily time indoors. Moreover, specific activities such as washing dishes and clothes or smoking were the main sources for exposure to certain compounds which may lead to human health problems such as sensory irritation, nervous system impairment, asthma and cancer. For instance, ethylbenzene and xylenes originate from paints, cleaning products and building materials; whereas, benzene, styrene, and other hydrocarbons are associated with smoking.

Zhou et al. (2011) measured the personal exposures of 12 people as well as residential indoors/outdoors, workplace and in vehicle VOC concentrations in Tianjin, China. For the personal exposure measurement, participants wear the passive samplers, and put the sampler beside their bed at night. Passive samplers were placed in the living room of each home as well as workplace, and away from open windows and local sources of VOCs. Samplers in vehicles (i.e. buses and cars) where time for commuting was spent were also placed. A sampler was also placed outside the houses. The inhalation cancer health risks were calculated via EPA-IRIS's Inhalation Unit Risks (IUR). According to the cancer risk analysis relevant to personal exposure, cancer risks were associated with benzene, chloroform, carbon tetrachloride, and 1,3-butadiene with exceedance of the U.S. EPA's benchmark of 10^{-6}. Benzene exhibited the highest risks at about 22 per one million population (with median and mean cancer risks at 21.77 and 32.89 parts per million, respectively), followed by 1,3-butadiene (median and mean cancer risks of 8.85 and 13.16 parts per million, respectively) and chloroform (median and mean cancer risks of 5.58 and 6.47 parts per million, respectively). The cumulative cancer risk of personal exposure to VOCs was the highest and it was followed by indoor exposure and then vehicle originated exposure. Yet, Authors also highlighted the possible uncertainties in risk assessment (RA) due to measured exposure concentrations, IUR values, measurement uncertainties, and short-term monitoring which ignored potential daily variations.

In another study, VOCs in indoor air of SMEs in La Plata city in Argentina and surrounding areas were monitored and analyzed by Lerner et al. (2012) to estimate the health impacts of altering levels of VOC based on Life Time Cancer Risk (LCR) and Hazard Quotient (HQ). VOC samples were gathered from electromechanical repair and car painting center, sewing work rooms, take away food shops, chemical analysis laboratories, and a photo copy center. None of the monitored small enterprises used technological means to reduce chemicals. After 30 days of sampling, cancer risks were calculated. LCR associated to benzene, chloroform and trichloroethylene were calculated via multiplying the result of Chronic Daily Intake (CDI) equation (see Equation 2.1) by potency factors given by EPA-IRIS (Lerner et al., 2012).

$$\mathrm{CDI} = \frac{\mathrm{CC} \times \mathrm{IR} \times \mathrm{ED} \times \mathrm{EF} \times \mathrm{LE}}{\mathrm{BW} \times \mathrm{ALT} \times \mathrm{NY}} \tag{2.1}$$

where CC is the contaminant concentration (mg/m^3), IR is the inhalation rate (m^3/h), ED is the exposure duration (h/week), EF is the exposure frequency (weeks/y), LE is the length of exposure, BW is the body weight (kg), ALT is the average lifetime (period over which exposure is averaged, being used as 47 years), NY is the number of days per year. For calculations, authors assumed an average BW of 70 kg and an average IR of 8.5 m^3/day of air per day, ED of 8 h/d in indoor environments and EF of 48 weeks/y and 5-day work/week, so NY is the number of days per year is calculated as 240 days. The potency factor for benzene, chloroform and trichloroethylene were accepted as 0.029, 0.013 and 0.081 mg/kg-day, respectively.

Via the inhalation reference concentrations (RfC) non-cancer risks were calculated in the study. The exposure rates in each SME were calculated to find a hazard quotient "HQ" as given Equation 2.2 (Lerner et al., 2012):

$$\mathrm{HQ} = \frac{\mathrm{CC}}{RfC} \tag{2.2}$$

where RfC values used in the study for toluene, xylene and hexane were 400, 300 and 200 μg/m3, respectively. It is underlined in the article that HQs >1 means that there could be a health problem which should be thought as a public health concern. However, HQ ≤ 1 means there would be no adverse effects because the exposure was below the threshold level for an adverse effect occurrence. LCR for benzene and trichloroethylene were one and two order of magnitude higher for the electromechanical repair and car painting center, respectively. Moreover, for chloroform, LCR was an order of magnitude higher than electromechanical repair and car painting center and two orders of magnitude higher than other indoor environments analyzed (Lerner et al., 2012).

Repairmen and painters were exposed to health risks originated from benzene. Benzene and chloroform were detected only at the electromechanical repair and car painting center compared to other premises. As a proposal, authors specially stated that the results obtained in the study should be compared with the worker protection legislations. The problematic workplaces were electromechanical repair and car painting center where benzene, toluene and xylene concentrations are close to the limits advised by OSHA (Lerner et al., 2012).

Daengthongdee and Soralump (2013) investigated VOC management during painting activities in automotive industry in a paint shop and a resin shop in Thailand. The general objective of the work was to assess health risks of occupational exposure through inhalation of xylene and toluene particularly from painting in automobile industry. Data were collected for xylene, toluene, and styrene two times between

2005 and 2011. Samples were gathered from 18 spots in paint shops and 5 spots in resin shops. Totally 23 painting workplaces were monitored. Measured concentrations were under the enforced OSH standard of Thailand which is stated as 100 ppm (434 mg/m^3), 200 ppm (753 mg/m^3), 100 ppm (425 mg/m^3) for xylene, toluene, and styrene, respectively, on the basis of 8 hour time weighted average (TWA) values as, respectively. Hazard Index (HI) of exposure within the paint spraying booth, pointed out the highest health risk. In the paint shop and mixing room for resin shop, the average HI values were 20.5 (range of 0 to 83.7) and 79.8 (range of 0 and 173.3), respectively, which were too high compared to the acceptable index of 1 for non-cancer health risks. Each cabinet had different paint spraying methodologies (i.e. spraying portion, solvent flushing method) resulting in different paint and solvent consumption. As a result, the volume of VOCs emitted and thus exposure amounts varied. To reduce health risks of exposure, use of robots to substitute for manual spray guns and auto spray machines were suggested. Furthermore, a ventilation system was suggested in mixing room in order to improve the air quality of workplace.

Liu H. et al. (2009) systematically reviewed the exposure database between 1956 and 2005 in China in order to form a trend of benzene exposure in paint using and manufacturing industries. The data was compiled from 204 papers and 51 journals for different years of occurrence, type of paint/coatings products, and type of industries. The collected data represented 77% of the 31 administrative regions in China. Benzene exposure data was analyzed according to work activities which were brush painting, spray painting, paint mixing, immersion painting, and work processes in paint manufacturing.

The overall median benzene exposure levels were 215 mg/m^3, 82 mg/m^3, 31 mg/m^3, and 6 mg/m^3 during the periods 1956–1978, 1979–1989, 1990– 2001, and 2002–2005, respectively. Mean benzene exposure was significantly lower for paint production than paint spraying. As benzene emission is higher during paint application compared to paint production since closed system (i.e. tanks and mixers) is used at paint production. However, no significant evidence supported the possibility of different benzene exposures due to painting for different paint types. Benzene exposure was significantly higher in poor ventilated workplaces as expected. Ventilation is one of the most crucial factors affecting both IAQ and pollutant exposure. No significant differences were gathered in benzene exposure as a function of industry type (Liu H. et al., 2009). More recent benzene exposure measurements suggested that many facilities in the paint industries in China still had benzene concentrations that were above the Chinese Occupational Exposure Limit (OEL) of 6 mg/m^3 TWA. Yet, concentrations were lower than the ones in previous years (Liu H. et al., 2009).

There are other studies in literature which clarify the dose-response relationships for paint manufacturing and painting activities like outdoor ship painting (Seeber et al., 1996; Malherbe and Mandin, 2007) as well as organic solvent emissions in indoor and outdoor painting (Çelebi and Vardar, 2008). These and occupational exposure assessment studies (Uang et al., 2006; Qian et al., 2006; Charretton and Vincent, 1997) set out the negative effects of BTEX concentrations in indoor and outdoor air, occupational exposures to BTEX compounds especially emitted through painting activities.

2.5. Legislation

There are regulatory restrictions in order to control outdoor air quality and personal exposures which can be assumed as indoor air quality limits. These regulations are present in both national and international legislations and given in detail in the following.

2.5.1 National Legislation

In Turkey, outdoor air quality is under the control of MoEU with regulations named as the Regulation on Air Quality Assessment and Management, Regulation on Industrial Air Pollution Control, Regulation on Gasoline and Diesel Quality by Exhaust Emission Control, Regulation on Large Combustion Plants and Regulation on Control of Air Pollution from Warming. In these regulations the general phrases of *"the objective of this regulation to protect outdoor air quality from adverse effects of air emissions originated from the enterprises"* and *"the workplaces included within the occupational health and safety legislation except outdoor environment is not under the scope of this regulation"* are included. This means that only outdoor air quality is controlled by MoEU and there is no legislation enforced by MoEU on IAQ management.

Personal exposure in indoor environments (especially workplaces); on the other hand, is considered under the scope of OSH field. MoLSS is responsible from the enforcement of this regulation and it provides new policies and approaches in order to protect employees from adverse health effects of workplace air conditions and exposures to pollutants.

The former approach of the MoLSS which was committed in Statute of Employee Health and Occupational Safety (1978) was reactive. This means that, it was a guide only for actions that should be adopted following accidents or occurrence of occupational diseases rather than prevention approaches. However, with the Law of Occupational Health and Safety, Law No: 6331 (2012), the proactive approach has been adopted in work life. In this point of view, all means of technology, engineering and new approaches adopted by developed countries have been internalized both for employees and employers in order to protect health and safety of employees. It should be highlighted that the new statue has been prepared and published in order to create a parallelism with the European Union (EU) Workplace Health and Safety

Directive (89/391/EEC), which is crucial for the EU harmonization process of Turkey. Related regulations to the Directive have been published as well.

Occupational chemical exposures in Turkey are handled and managed through the Regulation on Health and Safety Measures for Works with Chemical Substances (RHSMWCS, 2013) and the Regulation on Health and Safety Precautions on Works with Carcinogenic or Mutagenic Agents (RHSPWCMA, 2013). These regulations are quite important because Turkey's economy is significantly based on chemical industry. In order to protect employees from occupational diseases or illnesses resulting from exposures as well as protect environment from hazardous effects of high amounts of chemical emissions or spills, RA should be performed. For this reason, article 6 of the Regulation on Occupational Health and Safety Risk Assessment (2012) should be reviewed. The article particularly indicates the key points of RA for works that involve chemical substances in order to prevent not only the health and safety of employees but also workplace and neighbor workplaces. Due to the EU harmonization, all limit values of BTEX are taken directly from EU OSHA standards and adopted into national legislation (URL 12). Points which should be taken into account in particular in RA for activities involving usage of chemical substances are:

a) Hazards and damages of chemical substance with respect to OSH,
b) Safety Data Sheet (SDS) provided by manufacturers, importers or sellers,
c) Exposure type, level and duration,
d) Amount of chemical substance, condition of usage, and frequency of usage,
e) Occupational Exposure Limit Values (OELV) and Biological Limit Values (BLV) given in the Appendix of the Regulation,
f) The effects of already taken or potential prevention measures,
g) If exists, the results of past health surveillances,
h) Interactions of substance with each other in works including more than two chemical substances.

Table 2.4 gives the OELV of toluene, ethylbenzene and xylene as given in the Appendix 1 of RHSMWCS. In Table 2.4, the average exposure to a contaminant to which employees may be exposed to without adverse health effects over a period of 8 hr/day or 40 hr/ week is stated as TWA and STEL (Short Term Exposure Limit), respectively. STEL represents the limit value above which exposure should not occur in a reference period of 15 minutes. The aim of a STEL is to prevent adverse effects due to maximum exposure that could not be controlled by the use of an 8 hour TWA limit. In addition to this Regulation, RHSPWCMA includes OELV for benzene, which is carcinogenic (see Table 2.5).

As it is mentioned above, exposure limits given in Turkish legislation are the same as the EU Directive values, which are also valid for all EU Member States. It is stated in the "*Methodology for the Derivation of Occupational Exposure Limits: Key Document"* of European Commission that Scientific Committee on Occupational Exposure Limits (SCOEL) was established in 1995 by a European Commission Decision to provide the toxicological examination of chemicals for the purpose of detecting their effects on the health of employees. In the purposes of this document, it is stated that "the objective in establishing OELVs is to set limits for exposure via the airborne route such that inhalation, even when repeated on a regular basis throughout a work life, will not lead to adverse effects on the health of exposed persons and/or their progeny at any time" (European Commission, 2013).

While defining the exposure limits (i.e. TWA), Scientific Committee on Occupational Exposure Limits adopt a 'case-by-case' approach, considering each substance individually. It is stated that wherever possible the Committee attempt to establish health based limits. The steps of the general procedure of SCOEL are: integration of all relevant data on the hazards of the substance (i.e. relevant human, animal and other laboratory base experimental information, as well as background data like physical properties), identification of the adverse effects of exposure, to detect and review of the quality of the relevant scientific studies (in humans or animals) which characterize the key effects carefully, assessment of the dose-response data for each key effect and establish ‘no observed adverse effect levels’ (NOAELs) wherever possible, or if otherwise establishment of ‘lowest observed adverse effect levels’ (LOAELs), making the decision on whether a short-term exposure limit (STEL) is required in addition to an 8-hour TWA limit, and finally establishment of a numerical value for an 8-hour TWA limit at or below the NOAEL (or, if this is not possible, below the LOAEL) (European Commission, SCOEL, 2013).

Table 2.4 Occupational Exposure Limit Values of Toluene, Ethylbenzene and Xylene (in RHSMWCS)

EINECS	**CAS**	**Substance**	**Limit Value**			
			TWA (8 hr)		**STEL (15 min.)**	
			mg/m^3	**ppm**	**mg/m^3**	**ppm**
203-625-9	108-88-3	Toluene	192	50	384	100
202-849-4	100-41-4	Ethylbenzene	442	100	884	200
215-535-7	1330-20-7	Xylene (mixture isomers, pure)	221	50	442	100

Table 2.5 Occupational Exposure Limit Values of Benzene (in RHSPWCMA)

EINECS	**CAS**	**Substance**	**Limit Value TWA (8 hr)**	
			mg/m^3	**ppm**
200-753-7	71-43-2	Benzene	3.25	1

2.5.2 International Legislation

The EU has *Council Directive 1999/13/EC on the limitation of emissions of VOCs due to the use of organic solvents in certain activities and installations* establishing emission limit values for 20 different categories of “installations” that use solvents. The purpose of the Directive is “to prevent or reduce the direct and indirect effects of emissions of volatile organic compounds into the environment, mainly into air, and the potential risks to human health, by providing measures and procedures to be implemented for the activities defined in Annex I, in so far as they are operated above the solvent consumption thresholds listed in Annex IIA”. Mentioned activities of Annex I are coating, cleaning or printing activities generally in which solvents are used and VOCs may be emitted. Yet, threshold solvent consumption (tons/yr) and emission limits (g/kg or g/m^2) given in Annex IIA for VOCs are not compound specific.

There is also another EU Directive named as *Directive 2004/42/CE on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing products and amending Directive 1999/13/EC.* The purpose of this Directive is “to limit the total content of VOCs in certain paints and varnishes and vehicle refinishing products in order to prevent or reduce air pollution resulting from the contribution of VOCs to the formation of tropospheric ozone”. The Directive limits the VOC contents of various products. The Directive is generally applicable for decorative architectural paints, vehicle refinishing and protective paints applied on buildings. Permitted maximum VOC limits for paints and varnishes for 12 subcategories are given as g/l for both water-borne coatings and solvent-borne coatings. Furthermore, this directive regulates the overall VOC amount, but not compound specific.

EU has enforced the adaptation of OSH logic to all fields in work life. In order to achieve success in this manner, *Council Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work* was published. The scope of the Directive is to define “minimum requirements for the protection of workers from risks to their safety and health arising, or likely to arise, from the effects of chemical agents that are present at the workplace or as a result of any work activity involving chemical agents.”

To provide guidance for member states, EU published *Commission Directive 2000/39/EC establishing a first list of indicative occupational exposure limit values (IOELV) in implementation of Council Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work.* This Commission Directive includes IOELV in its Annex. The values given in the Annex for BTEX are the same with those given in Table 2.4.

USA; on the other hand, has a primary federal law which governs OSH in the private sector titled as the Occupational Safety and Health Act of 1970. The aim is stated as “by encouraging employers and employees in their efforts to reduce the number of occupational safety and health hazards at their places of employment, and to stimulate employers and employees to institute new and to perfect existing programs for providing safe and healthful working conditions; and by providing that employers and employees have separate but dependent responsibilities and rights with respect to achieving safe and healthful working conditions” (Occupational Safety and Health Act of 1970, 2004).

With respect to chemical exposure, OSHA (2013) has regulatory arrangements in its database. This database includes specific information of each hazardous chemical with respect to chemical identification, physical properties, exposure limits, health issues, public safety, clothing, evacuation when large spill occurs, response fire caution, first aid, etc. (URL 14).

The establishment of U.S. National Institute for Occupational Safety and Health (NIOSH), an independent research institute, was realized according to Occupational Safety and Health Act of 1970. There is a partnership with OSHA and NIOSH.

OSHA is under the U.S. Department of Labor. It develops and enforces workplace safety and health regulations. NIOSH is under the U.S. Centers for Disease Control and Prevention of the U.S. Department of Health and Human Services.

The exposure limits of benzene, toluene, ethylbenzene and xylene according to U.S. OSHA and NIOSH are given in Table 2.6 (URL 13, URL 14, URL 15, URL 16 and URL 17).

Table 2.6 Exposure Limits of BTEX According to OSHA and NIOSH

Benzene			
OSHA		**NIOSH**	
PEL*-TWA mg/m^3	3.19	REL**-TWA mg/m^3	0.32
Carcinogenicity	Yes	Carcinogenicity	Yes
Toluene			
OSHA		**NIOSH**	
PEL-TWA mg/m^3	754	REL-TWA mg/m^3	375
Carcinogenicity	NA	Carcinogenicity	NA
Ethylbenzene			
OSHA		**NIOSH**	
PEL-TWA mg/m^3	435	REL-TWA mg/m^3	435
Carcinogenicity	NA	Carcinogenicity	NA
Xylene			
OSHA		**NIOSH**	
PEL-TWA mg/m^3	435	REL-TWA mg/m^3	435
Carcinogenicity	NA	Carcinogenicity	NA

** PEL: U.S. OSHA's Permissible Exposure Limit expressed as a TWA; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8-h/workday or a 40-h/workweek.*
***REL: U.S. NIOSH's Recommended Exposure Limit for up to 10-h TWA exposure.*

As can be seen in Table 2.6, there are differences (i.e. an order of magnitude) in benzene and toluene exposure limits in OSHA and NIOSH (i.e. NIOSH limit is half of the OSHA’s limit), although they are established in the same country. One of the main reasons for the difference in these limit values (i.e. PEL and REL of OSHA and NIOSH, respectively) is that REL assumes TWA exposures up to 10 h/day whereas PEL assumes TWA exposures for 8 h/day (URL 18).

Utilization of “permissible” and “recommended” give an idea about the differences between exposure limits of OSHA and NIOSH. NIOSH, responsible for recommending health and safety standards, has joined OSHA in 1974. OSHA’s jurisdictions include promulgation and enforcement activities in developing a series of occupational health standards. NIOSH evaluates all known and available medical, biological, engineering, chemical, trade, and other information relevant to the hazard in order to derive the PELs (URL 18).

U.S. OSHA stated at its website that the Agency has not limited its initial consideration of appropriate limits to those levels established by the American Conference of Governmental Industrial Hygienists (ACGIH) or NIOSH (URL 19). However, the Agency has carefully evaluated the exposure limits recommended by NIOSH, the OSHA's sister agency. In cases where both NIOSH and the ACGIH have recommended substantially different limits for the same substance, OSHA has thoroughly analyzed the evidence presented by each organization and has made its own judgment of the appropriate exposure limits.

Methods have been developed to permit any chemical to be handled safely. This is conducted either via limiting the dose or controlling the exposure. However, before the necessary degree of control can be determined for a particular exposure or situation, the toxicity of the substance in question must be known and investigated thoroughly. Main factors affecting the exposure limit concentrations are: route of exposure, duration and frequency of exposure, variation in response and dose-response analysis (i.e. lethality studies), form of the response (i.e. trend of dose-response relationship), type of toxicological evidence (i.e. clinical observations or epidemiological studies) and quality of evidence (URL 19).

For all substances addressed in rule making, OSHA has evaluated the extensive evidences (i.e. scientific studies, dose-response analysis results etc.) in record which are given above. Thus, “the limits being established today represent, in the Agency's professional judgment, those levels found to be most consistent with the best available toxicological data, dose-response analysis, OSHA's mandate, and the case law that has subsequently developed to interpret that mandate” (URL 19). However, OSHA recognizes that many of its PELs are outdated and inadequate for ensuring protection of worker health. Most of OSHA’s PELs were issued shortly after adoption of the Occupational Safety and Health Act of 1970, and have not been updated since that time (URL 20).

There are other OSH institutions in the world. For instance, Health and Safety Executive (HSE) in England, Department of Occupational Safety and Health in Malaysia, Finnish Institute of Occupational Health in Finland, National Institute for Occupational Safety and Health, Japan in Japan, Institut National De Recherché Et De Sécurité in France and Italian National Institute for Occupational Safety and Prevention in Italy. All of these organizations have their own action plans, precautions, methodologies and standards in terms of OSH and human and environmental health.

Example legislative exposure limits and standards with respect to BTEX exposure in workplaces are provided in Table 2.7. It can be seen from Table 2.7 that, exposure limits could vary from country to country. Furthermore, the limit values of England, a member of EU, are same as the Turkish legislative limits.

Table 2.7 Exposure Limits of BTEX in Different Countries

Country	Exposure Limit Values of Compounds (mg/m^3)			
	Benzene	**Toluene**	**Ethylbenzene**	**Xylene**
England [a]	3.25	191	442	221
ACGIH, USA [b]	1.60	192	-	442
Alberta, Canada [c]	3.20	375	434	434
France [d]	3.25	375	442	442
Japan [e]	3.25	188	217	217

[a] *Health and Safety Executive, EH40/2005 Workplace exposure limits, Second Edition, 2011, England.*
[b] *http://www.worksafebc.com/regulation_and_policy/*
[c] *http://www.canlii.org/en/ab/laws/regu/alta-reg-393-1988/latest/alta-reg-393-1988.html*
[d] *Institut National De Recherché Et De Sécurité, Valeurs Limites D'exposition Professonnielle Aux Agents Chimiques en France, 2012, France.*
[e] *Japan Society for Occupational Health, 2013.*

Although above legislation focus on OSH and personal exposure, they can also provide references for the level of relevant constituent concentrations that should not be exceeded in indoor air at the workplaces. Therefore, in this study, they will be used as references to evaluate the indoor BTEX concentrations at selected industries in Turkey in which paint is manufactured or used.

CHAPTER 3

METHODOLOGY

The methodology used in this study is explained in this chapter. Detailed information on sampling and analysis of BTEX compounds is also provided. Furthermore, HRA methodology used in this study is presented in detail.

3.1 Data Collection

In Turkey, employers are required to provide employees a healthy and safe work life according to relevant regulations. MoLSS is the authorized institution to control this requirement in workplaces. For this reason, ISGUM of General Directorate of Occupational Health and Safety (GDOHS), collects air samples from employees' breathing zone and analyze these samples at ISGUM's own accredited laboratories for various pollutants and dust. Sometimes physical factors like noise, vibration etc. are measured at workplaces as well. Results of the analysis are reported by ISGUM. Sample collection methodology is explained in the next paragraph.

Sampling procedure involves collection of 3 types of samples: ambient air samples, 8-hour exposure samples and short term exposure samples. The exposure samples are gathered via aromatic hydrocarbon sampling pumps with a flow rate of 0.01-1 L/min (for BTEX measurement a flow rate of 0.2 L/min is used), with flexible connecting tubes which are attached on the employee. Thus, active sampling is conducted.

NIOSH Method 1501 (NIOSH, 1984) which provides information on the determination of peak (level of exposure above the ceiling level that is allowed to occur one time for a short interval, Nims D., 1999), ceiling (level of exposure that cannot be exceeded at any time during the work shift, Nims D., 1999), and TWA of aromatic hydrocarbons is used as the guidance for both sampling and analysis. After calibrating each personal sampling pump with a representative sampler in line, a known volume of air is let to pass through the sample tube containing activated carbon with the aid of the pump (see Figure 3.1). Organic vapor is collected on this active carbon. The end of the tube is settled to the breathing zone of the paint worker. Breathing zone is the zone within a 0.3 m radius of a sphere of worker's nose and mouth, and it has been generally assumed that a contaminant in the breathing zone is homogeneous and its concentration is equivalent to the concentration inhaled by the worker (Ojima, 2012). Samples are collected in sorbent tubes generally for 2 hours and then they are transported via cold chain (4-5 ^{0}C) and stored until the analysis.

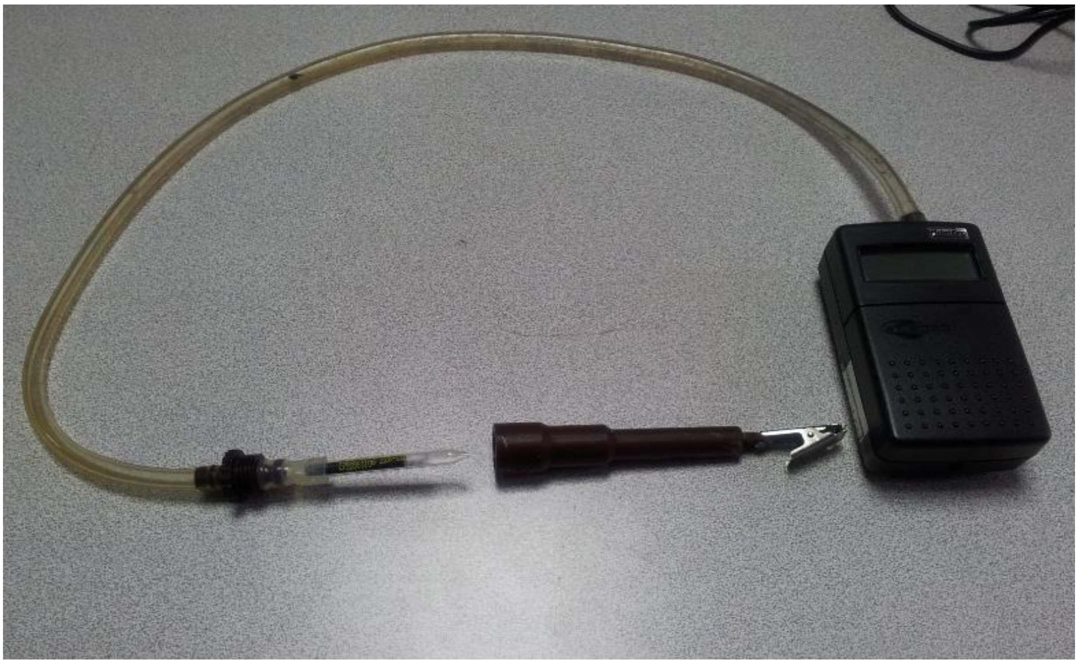


Figure 3.1 Personal Sampling Pump and Tube

According to TS EN 140 (Standard for half face mask) and TS EN 141 (Standard for gas-vapor filters), paint production and application employees should wear half face masks (gas masks) as personal protective equipment (PPE) during work hours. The masks should include A type filter which is suitable for paint related works (Drager, 2011). Based on an interview made with a member of MoLSS (2014), it has been noted that; unfortunately, painting workers do not use the appropriate PPE in the workplace environment. Furthermore, although they should wear appropriate filtered gas masks, dust masks (which are exactly inappropriate for painting activities) are provided to them because dust masks are cheaper than half faced masks. Additionally, employees wear these masks during inspections but not during regular work hours. However, the situation is better at the industry leader workplaces. In addition, a gas mask has a lifetime for usage. When its filter reaches its capture capacity, the filter should be changed. Wearing an appropriate gas mask will protect an employee from being exposed to high amount of chemicals only during the lifetime of filter. Thus, PPE usage has no effect on BTEX emissions sourced by painting and paint manufacturing, it only decreases the inhaled concentration since filters absorbs the pollutants. However, in this study it is assumed that the worker does not wear a mask and the air concentration is equal to the inhaled concentration.

In NIOSH 1501 (NIOSH, 1984), all measurement details like analyte, desorption, injection temperature, injection volume, carrier gas, calibration and accuracies are given. In order to conduct the analysis, Gas Chromatography (GC-VARIAN CP 3800) and Flame Ionization Detector (FID) were used by authorized personnel to conduct experiments. Thereby, concentrations of compounds in the sample were determined quantitatively.

In this study, reports belonging to paint related industries prepared by ISGUM between 2006 and 2013 are used. A total of 57 different workplaces in Turkey are evaluated in this study. Out of 57, 43 of them are located in Kocaeli, 2 workplaces in İstanbul, 1 workplace in Sakarya, 1 workplace in Yalova and 1 workplace in Çanakkale, Marmara Region while 9 of them are located in İzmir, Aegean Region.

Through 2006-2013 some of the 57 workplaces were visited once and the rest of workplaces were visited multiple times. A total of 73 visits are conducted. In each of these visits, a single or multiple samples were collected and this resulted in a total of 195 samples.

3.2 Evaluation

The goal of this study is to evaluate BTEX concentrations and associated health risks at selected paint industry related workplaces as well as industries that employ painting as a step in production process. However, due to the confidentiality agreements between the investigated workplaces and ISGUM, full names of the workplaces are not given in the study.

In this study, BTEX concentrations and associated health risks are evaluated with respect to two classifications:

1. Type of industry as given in Table 3.1, and
2. Type of action in paint production or application as given in Figure 3.2.

Table 3.1 Type of Industry

Workplace	Industry
Paint Production	A
Public-owned (Application of paint)	B
Maintenance and Repair (Land) Maintenance and Repair (Aircraft) Shipyard	B1 B2 B3
Automotive Painting	C
Shipyard	D
Furniture Painting	E
Others (Painting i.e. metal offset, ceramic, pipe etc.)	F

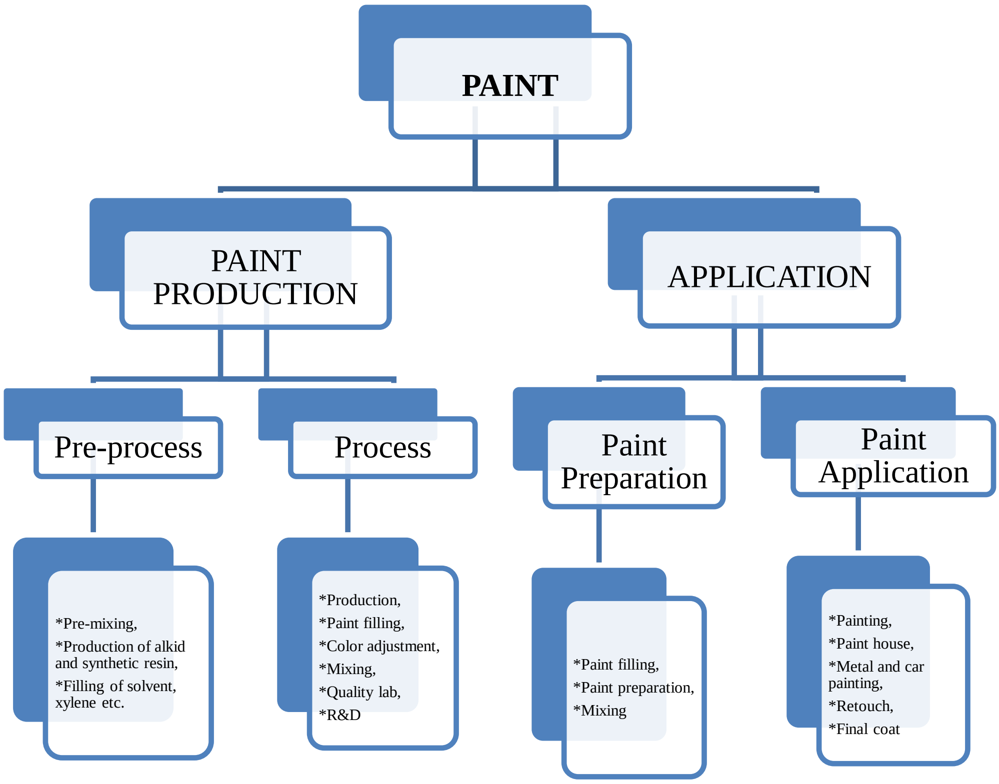


Figure 3.2 Type of Action

In the first category, industries are classified according to the type of industry (see Table 3.1). These industries are comprised of private sector and public-owned. Paint production workplaces are classified as A type industries. Public-owned institutions where painting exists are classified as B type industries. They are divided into three sub classes as B1, B2 and B3 type industries. B1 and B2 type industries represent maintenance and repair facilities of land and aircraft, respectively. B3 type industry specifies the public-owned shipyards; whereas D type industry represents private shipyards where painting is done. Other types of industries (i.e. C, E and F type industries) represent private sector workplaces which have paint application process.

In the second category, workplaces are classified according to action done in the workplaces (i.e. paint production and application). For this purpose, four main groups are considered: (i) paint production/pre-processing, (ii) paint production/processing, (iii) application/paint preparation, and (iv) application/paint application. BTEX concentrations and associated health risks are evaluated with respect to these two classifications in order to make a comparison through different industries and processes.

ISGUM controls the conformity of a workplace in terms of occupational health via comparing the pollutant concentrations in the employees' breathing zone based on the legislative limit values (TWA and mg/m^3) set in the Regulation on Health and Safety Measures for Works Involving Chemical Substances (RHSMWCS) and the Regulation on Health and Safety Precautions on Works Involving Carcinogenic or Mutagenic Agents (RHSPWCMA) as given in Table 3.2. Recently, in different countries HRA studies are used for this purpose as well (Lerner et al., 2012; Daengthongdee and Soralump, 2013). Furthermore, the health risks of emerging or existing environmental pollutants are subjected to close examination by many regulatory authorities with more evidences on adverse health effects appeared in the scientific communities and public media. Thus, assessment of health risks became a crucial step in setting regulatory actions (Cao et al., 2011).

In this study suitability of the paint industry related workplaces is evaluated with respect to both indoor air BTEX concentrations and their associated health risks. Health risks associated with BTEX exposure are calculated using the procedures provided in RAGS, Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment) (U.S. EPA, 2009). This procedure is explained in the following section.

Table 3.2 Summary of Legislative Limit Values

Regulations	Limit Value (mg/m^3)			
	Benzene	Toluene	Ethylbenzene	Xylene
RHSMWCS*	-	192	442	221
RHSPWCMA**	3.25	-	-	-
OSHA (TWA)	3.19	754	435	435
NIOSH (TWA)	0.32	375	435	435

**Regulation on Health and Safety Measures for Works with Chemical Substances*
***Regulation on Health and Safety Precautions on Works with Carcinogenic or Mutagenic Agents*

3.3 Health Risk Assessment

Health risks are calculated for both cancer and non-cancer effects. Thus, HRA study is divided in two parts: cancer risk assessment and non-cancer risk assessment. Since it is known that benzene has both carcinogenic and non-carcinogenic effects, both cancer and non-cancer risk assessments are conducted for benzene. On the other hand for toluene, ethylbenzene and xylene, only non-cancer risk assessment is conducted.

The excess cancer risk for a receptor exposed via inhalation is calculated by Equation 3.1; whereas Equation 3.2 is used for non-cancer risk which is represented by the hazard quotient, (U.S. EPA, 2009):

$$\text{Risk} = \text{IUR} \times \text{EC} \tag{3.1}$$

where IUR is the inhalation unit risk ($\mu g/m^3)^{-1}$; EC is the exposure concentration ($\mu g/m^3$).

$$HQ = \frac{EC}{RfC \times 1000} \tag{3.2}$$

where HQ is the hazard quotient (unitless); EC is the exposure concentration (μg/m^3) and RfC (mg/m^3) is the reference concentration which is an indication of inhalation toxicity. The "1000" in the denominator of Equation 3.2 is the conversion factor from mg to μg.

If the receptor is exposed to multiple chemicals through inhalation, first the HQ value for each chemical is calculated, and then they are summed to calculate cumulative non-cancer health risks. This cumulative value is referred to as the Hazard Index (HI) (U.S. EPA, 2009).

EPA defines IUR in the IRIS dictionary (U.S. EPA, 2009) as "the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 μg/m^3 in air" and RfC as "an estimate of a continuous inhalation exposure to the human population that is likely to be without appreciable risk of deleterious effects during a lifetime". IUR and RfC values are specific to chemicals and IUR of benzene and RfC values of BTEX used in this study are gathered from EPA-IRIS database (URL 21).

3.3.1 Estimation of EC for Cancer Risk

According to RAGS approach (U.S. EPA, 2009), first EC should be estimated. Estimation of EC for cancer risk characterized by an IUR involves the concentration of pollutant measured at an exposure point as well as exposure scenario specific parameters, such as the exposure duration and frequency. Thus, EC is estimated as follows (U.S. EPA, 2009):

$$EC = \frac{CA \times ET \times EF \times ED}{AT} \quad (3.3)$$

where EC is the exposure concentration (μg/m^3); CA is the contaminant concentration in air (μg/m^3); ET is the exposure time (hours/day); EF is the exposure frequency (days/year); ED is the exposure duration (years) and AT is the averaging time (70 years x 365 days/year x 24 hours/day).

In order to evaluate health risks associated with exposures through inhalation, receptor specific exposure scenarios need to be used. Various exposure scenarios include: residential receptor, commercial-industrial/occupational receptor, construction worker and recreational receptor. These scenarios vary in terms of exposure duration and exposure frequencies. Thus, alteration of values used in the related equations occurs (see Equation 3.3) (U.S. EPA, 2009). Since the goal of this study is to evaluate health risks on workers in paint industry and application related works, “commercial-industrial/occupational receptor” is selected for evaluations.

3.3.2 Estimation of EC for Non-cancer Risk

The flowchart given in Figure 3.3 can be used in estimating EC for non-cancer health risks (i.e. HQ values) (U.S. EPA, 2009). Estimation of EC requires three steps:

1. Identification of the duration of the exposure scenario,
2. Identification of the exposure pattern of the exposure scenario and
3. Determining the scenario-specific EC.

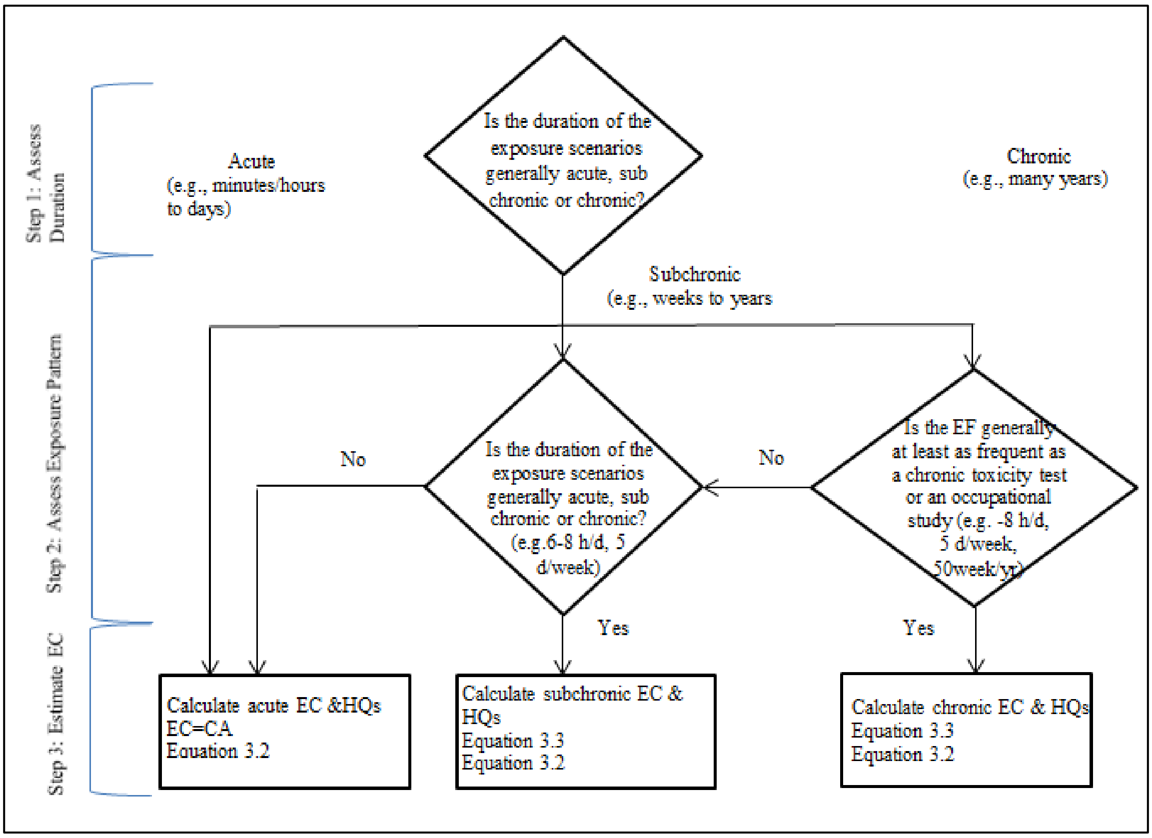


Figure 3.3 Procedure for Deriving Exposure Concentrations and Hazard Quotient (U.S.EPA, 2009)

Based on the selected path chosen in Figure 3.3, Equation 3.3 (for subchronic or chronic) is used to estimate EC (U.S. EPA, 2009). Once EC is estimated, Equation 3.2 is used to calculate HQ.

It should be added at this point that, according to the first Risk Assessment Guidance for Superfund (RAGS, 1989) approach[1], the inhalation exposure estimate was typically calculated by using chronic daily "air intake" (mg/kg-day) (see Equation 2.1). This is why past studies have used that equation for risk calculations. However, The Superfund Program has updated its inhalation risk paradigm to be compatible

[1] *The approach was outlined in RAGS, Part A, developed before U.S. EPA issued the Inhalation Dosimetry Methodology. This describes the Agency's refined recommended approach for interpreting inhalation toxicity studies in laboratory animals or studies of occupational exposures of humans to airborne chemicals.*

with the *Inhalation Dosimetry Methodology*, which represents the EPA's current methodology for inhalation dosimetry and derivation of inhalation toxicity values. It is recommended in Chapter 3 of EPA's Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual/Part F (2009) that when estimating risk via inhalation pathway, risk assessor should use the concentration of the chemical in air as the exposure metric (i.e. mg/m^3), rather than inhalation intake of a contaminant in air based on IR and BW (i.e., mg/kg-day). Thus, the former intake equation (Equation 2.1) is no longer consistent with the principles of U.S. EPA's *Inhalation Dosimetry Methodology* due to the fact that the amount of the chemical that reaches the target site is not just a simple function of IR and BW (U.S. EPA, 2009).

In paint production and application actions, it is assumed that employees work with 8-hour shifts in a day. U.S. EPA (2009) declares that a commercial-industrial/occupational receptor is exposed to pollutants for 5 to 25 years (see Table 3.3.). Thus, in this study, it is assumed that an employee works around 25 years in this sector. So, the duration of exposure is chosen as "chronic" in the study. Also average lifetime of an employee is taken as 70 years (Guo, 2004) while the duration of exposure to chemicals is taken as 25 years in the study (U.S. EPA, 2009). Additionally, when evaluating cancer risk, the AT is equal to lifetime in years. When evaluating non-cancer hazard, the AT is equal to EDs for exposure period (U.S. EPA, 2009).

The recommended acceptable cancer risk by EPA is $1x10^{-6}$ (U.S. EPA, 2009). It is stated in National Oil and Hazardous Substances Pollution Contingency Plan (NCP, 1994) that for known or suspected carcinogens, acceptable exposure levels are generally the concentration levels that represent lifetime cancer risk to an individual at the levels ranging between 10^{-4} (1 in 10,000) and 10^{-6} (1 in 1,000,000). When HI exceeds 1, it can be said that there may be a concern of potential non-cancer health effects (EPA-RAGS, Part A, 1989). In this study, to be on the conservative side, $1x10^{-6}$ is used as the acceptable cancer risk and 1 is used as the acceptable limit for non-cancer health risks.

Different values are suggested by different researchers for the variables used in cancer and non-cancer risk calculation. A summary of these values is given in Table 3.3 Additionally, values of all the variables used in the risk calculations in this study are provided in the last column of Table 3.3.

Table 3.3 Health Risk Related Variable Values given in Literature and Used in this Study

Variable	Explanation	Literature		EPA	Value Used in this Study
		Range	Reference	Value	
ET	Exposure Time (h/d)	5-8	Guo, 2004; Lerner, 2012	8 [a]	8
EF	Exposure Frequency (d/y)	240, 252, 365	Lerner, 2012; Daengthongdee, 2013; Guo, 2004	250 [a] (5d/week x 50weeks/y)	300 [c] (6d/week x 50weeks/y)
ED	Exposure Duration (y)	8-25, 40, 25	Lerner, 2012; Guo, 2004; Tsai, 2001	5-25 [a]	25
AT	Averaging Time (h)	411720(47*365*24), 613200(70*365*24)	Lerner, 2012; Guo, 2004	43800-219000 (5-25 y) [a]	613200 (Cancer: 70 y is used [d]) 175200 (Non-cancer:25 y is used [d])
IUR	Inhalation Unit Risk	$2.2*10^{-6} m^3/\mu g$	Guo, 2004	$2.2*10^{-6} m^3/\mu g$ [b]	$2.2*10^{-6} m^3/\mu g$
$RfC_{benzene}$	Reference Conc.	0.03 mg/m^3	Huang, 2013	0.03 mg/m^3 [b]	0.03 mg/m^3
$RfC_{toluene}$	Reference Conc.	0.4 mg/m^3	Lerner, 2012	5 mg/m^3 [b]	5 mg/m^3
$RfC_{ethlybenzene}$	Reference Conc.	0.3 mg/m^3	Lerner, 2012	1 mg/m^3 [b]	1 mg/m^3
RfC_{xylene}	Reference Conc.	0.3 mg/m^3	Lerner, 2012	0.1 mg/m^3 [b]	0.1 mg/m^3

[a] *EPA RAGS Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment, 2009).*
[b] *EPA IRIS, http://www.epa.gov/IRIS/*
[c] *In Turkey, employees work for 6 days/week at the industries in the scope of the study (Labor Law No:4857, 2003).*
[d] *1 year: 365 days*

CHAPTER 4

RESULTS AND DISCUSSION

The results of the study are presented with respect to two classifications: type of industry and type of action. BTEX concentrations and associated health risks are evaluated with respect to these two classifications.

4.1 Evaluations based on the Type of Industry

4.1.1 BTEX Concentrations

Reported BTEX concentrations are given in Table 4.1. ISGUM checks compliance of a workplace in terms of occupational health via comparing the pollutant concentrations in the employees' breathing zone with the legislative limit values set in the Regulation on Health and Safety Measures for Works Involving Chemical Substances (RHSMWCS, 2013) and the Regulation on Health and Safety Precautions on Works Involving Carcinogenic or Mutagenic Agents (RHSPWCMA, 2013) in Turkey. The total number of samples collected and analyzed is given in the third column of Table 4.1. In the last column, percentages of the number of samples which are below RHSMWCS and RHSPWCMA regulatory limits are provided.

Table 4.1 BTEX Concentrations with respect to the Type of Industry

TI	NW	NS	Compound	Min TWA (mg/m^3)	Max TWA (mg/m^3)	Compliance (%) RHSMWCS/RHSPWCMA*
A	16	28	Benzene	0.02	4.07	96
		60	Toluene	0.05	291.37	93
		58	Ethylbenzene	0.09	64.39	100
		60	Xylene	0.41	200.00	100
B1	3	5	Benzene	0.07	0.45	100
		10	Toluene	1.32	300.00	80
		5	Ethylbenzene	0.58	12.41	100
		13	Xylene	2.00	250.00	92
B2	4	3	Benzene	19.03	19.03	67
		6	Toluene	13.79	976.28	67
		3	Ethylbenzene	361.72	361.72	100
		6	Xylene	0.39	1,832.13	67

Table 4.1 BTEX Concentrations with respect to the Type of Industry (continued)

TI	NW	NS	Compound	Min TWA (mg/m^3)	Max TWA (mg/m^3)	Compliance (%) RHSMWCS/RHSPWCMA*
B3	14	20	Benzene	0.07	242.35	80
		31	Toluene	0.65	747.66	80
		30	Ethylbenzene	0.25	251.85	100
		31	Xylene	0.03	754.79	80
C	10	20	Benzene	0.132	5.92	95
		30	Toluene	0.08	656.97	97
		30	Ethylbenzene	0.07	19.06	100
		30	Xylene	0.05	67.61	100
D	7	4	Benzene	0.226	51.47	75
		13	Toluene	0.50	14.66	100
		13	Ethylbenzene	7.28	999.52	85
		13	Xylene	36.68	3,232.89	54

Table 4.1 BTEX Concentrations with respect to the Type of Industry (continued)

TI	NW	NS	Compound	Min TWA (mg/m^3)	Max TWA (mg/m^3)	Compliance (%) RHSMWCS/RHSPWCMA*
E	3	10	Benzene	-**	-**	-***
		10	Toluene	4.28	137.52	100
		10	Ethylbenzene	0.23	10.55	100
		10	Xylene	0.94	40.08	100
F	16	15	Benzene	0.16	13.59	87
		32	Toluene	0.33	1,474.31	91
		31	Ethylbenzene	0.08	18.85	100
		32	Xylene	0.29	100.00	100

**Limit values of RHSMWCS for Toluene: 192 mg/m^3, Ethylbenzene: 442 mg/m^3, Xylene: 221 mg/m^3 & RHSPWCMA for Benzene: 3.25 mg/m^3*
*** Not detected: Measured concentration is lower than the detection limit. So there is no result for that compound in the type of industry.*
****Not calculated: Since there is no measurement result in this type of industry, the compliance could not be calculated.*

(TI: Type of Industry, NW: Number of Workplace visit times, NS: Number of Samples Analyzed).

(Type A: Paint production; Type B1: Maintenance and repair; Type B2: Maintenance and repair-aircraft; Type B3: Shipyard (Public-owned); Type C: Automotive painting; Type D: Shipyard (Private); Type E: Furniture painting; Type F: Others-application of paint).

As demonstrated in Table 4.1, more than 90% compliance is achieved for all compounds (i.e. benzene, toluene, ethylbenzene and xylene) for A (paint production), C (automotive painting) and F (others-application of paint) type industries. Low BTEX emission is expected in paint production rather than paint application because during paint production generally closed containers (i.e. tanks, mixers) are used for pre-mixing, mixing or paint filling steps of production which minimizes the emissions of solvents (Şengül et al., 2003). Thus, high compliance percentages for A type facilities are reasonable. On the other hand, high compliance at C and F type facilities might be due to advanced and environmentally friendly technologies used in these industries. Furthermore, the workplaces under the automotive painting industry considered in this study are known as the industry leader companies. As expected, high technology ventilation and automation systems assuring minimum exposure to employees are used at these workplaces. Thus, workplace conditions and precautions taken to minimize exposure to indoor BTEX at type C industry should be taken as good practice in point of BTEX exposure.

For B1 type industry (maintenance and repair-land), 100% compliance is achieved for benzene and ethylbenzene. Toluene and xylene regulatory limits are exceeded in 20% and 8% of the samples, respectively. However, only 5 to 13 samples are collected and analyzed from B1 type industries. Furthermore, out of 10 only 2 samples and out of 13 only 1 sample are above the regulatory limits for toluene and xylene, respectively (see Appendix A). Therefore, more samples are required to be conclusive about compliance with relevant regulations.

The total number of samples collected from B2 (maintenance and repair-aircraft) (i.e. 3 samples for benzene and ethylbenzene and 6 samples for toluene and xylene) and E (furniture painting) type industries are also low (i.e. 10 samples for benzene, toluene, ethylbenzene and xylene) as given in Table 4.1. Only in one of the four samples benzene concentrations exceed the limit at shipyard industry (type D) however the number of sample is not sufficient. Thus, to be able to derive general results for these facilities, more samples need to be collected and analyzed. Again for shipyards xylene concentrations are above the regulatory limits in more than half of the samples collected. When all concentrations of industries are investigated, it has been seen that painting at private- and public-owned shipyards is problematic with respect to benzene and xylene emissions. For toluene 100% compliance is achieved only for private shipyards whereas for public-owned shipyard only ethylbenzene has 100% compliance. The possible reason for low compliance for the rest of the compounds is that in shipyard industry, paints without SDS (datasheet of chemical ingredients) of the chemicals, or solvent based ones which include high levels of VOC are generally used (interview made by a member of Ministry of Labor and Social Security, 2014). In order to decrease the BTEX emissions and exposures in the mentioned problematic industries (i.e. type B3 and type D), rather than solvent based paints, waterborne paints having less amount of VOC should be used (URL 22).

4.1.2 Health Risks

HRA of chronic BTEX exposure for different industries in which paint is produced or applied is conducted. Calculated cancer risks and chronic non-cancer risks are given in Table 4.2 and Table 4.3, respectively. Since only benzene has carcinogenic effect among BTEX, the cancer risks are only calculated for benzene. In the last columns of Table 4.2 and Table 4.3, the percentage of samples for which the carcinogenic health risks are below the acceptable cancer risk of $1x10^{-6}$ (U.S. EPA, 2009) and non-cancer risks are below 1 (U.S. EPA, 2009) are provided, respectively. Furthermore, for each sampling location HI values (cumulative of HQs) of each industry are calculated and given in Table 4.4.

Table 4.2 Cancer Risks for Benzene with respect to the Type of Industry

TI	NW	NS	Min	Max	Compliance (%) (Acceptable cancer risk: 10^{-6})
A	16	28	4.35×10^{-6}	8.85×10^{-4}	0
B1	3	5	1.48×10^{-5}	9.87×10^{-5}	0
B2	4	3	4.13×10^{-4}	4.13×10^{-4}	0
B3	14	20	1.59×10^{-5}	5.27×10^{-2}	0
C	10	20	2.87×10^{-5}	1.28×10^{-3}	0
D	7	4	4.92×10^{-5}	1.20×10^{-2}	0
E	3	10	-*	-*	-**
F	16	15	3.56×10^{-5}	2.95×10^{-3}	0

**Not detected: Since measured concentration is lower than the detection limit, cancer risk could not be calculated.*
***Not calculated: Since there is no measurement result in this type of industry, the compliance could not be calculated.*

(TI: Type of Industry, NW: Number of Workplace visit times, NS: Number of Samples).

(Type A: Paint production; Type B1: Maintenance and repair; Type B2: Maintenance and repair-aircraft; Type B3: Shipyard (Public-owned); Type C: Automotive painting; Type D: Shipyard (Private); Type E: Furniture painting; Type F: Others-application of paint).

Table 4.3 Non-cancer Risks (i.e. HQ values) with respect to the Type of Industry

TI	NW	NS	Compound	Min	Max	Compliance (%) (Acceptable non-cancer risk: 1)
A	16	28	Benzene	0.18	37.19	18
		60	Toluene	0.003	15.97	55
		58	Ethylbenzene	0.03	17.64	83
		60	Xylene	1.12	547.95	0
B1	3	5	Benzene	0.62	4.15	60
		10	Toluene	0.07	15.12	15
		5	Ethylbenzene	0.16	3.40	40
		13	Xylene	5.48	684.93	0
B2	4	3	Benzene	173.82	173.82	0
		6	Toluene	0.76	53.49	17
		3	Ethylbenzene	99.10	99.10	0
		6	Xylene	1.07	5,019.54	0

Table 4.3 Non-cancer Risks (i.e. HQ values) with respect to the Type of Industry (continued)

TI	NW	NS	Compound	Min	Max	Compliance (%) (Acceptable non-cancer risk: 1)
B3	14	20	Benzene	0.67	2,213.22	10
		31	Toluene	0.04	40.97	55
		30	Ethylbenzene	0.06	68.99	27
		31	Xylene	0.08	2,067.91	5
C	10	20	Benzene	1.21	54.06	0
		30	Toluene	0.004	35.99	57
		30	Ethylbenzene	0.02	5.22	30
		30	Xylene	0.13	185.24	23
D	7	4	Benzene	2.06	470.03	0
		13	Toluene	0.03	0.80	100
		13	Ethylbenzene	1.99	273.84	0
		13	Xylene	100.49	8,857.25	0

Table 4.3 Non-cancer Risks (i.e. HQ values) with respect to the Type of Industry (continued)

TI	NW	NS	Compound	Min	Max	Compliance (%) (Acceptable non-cancer risk: 1)
E	3	10	Benzene	-*	-*	-**
		10	Toluene	0.24	7.54	31
		10	Ethylbenzene	0.06	2.89	70
		10	Xylene	2.58	109.82	0
F	16	15	Benzene	1.49	124.10	0
		32	Toluene	0.02	80.78	46
		31	Ethylbenzene	0.02	5.16	48
		32	Xylene	0.79	273.97	3

** Not detected: Since measured concentration is lower than the detection limit, non-cancer risk could not be calculated.*
***Not calculated: Since there is no measurement result in this type of industry, the compliance could not be calculated.*

(TI: Type of Industry, NW: Number of Workplace visit times, NS: Number of Samples).

(Type A: Paint production; Type B1: Maintenance and repair; Type B2: Maintenance and repair-aircraft; Type B3: Shipyard (Public-owned); Type C: Automotive painting; Type D: Shipyard (Private); Type E: Furniture painting; Type F: Others-application of paint).

Table 4.4 Cumulative Non-cancer Risks (i.e. HI values) with respect to the Type of Industry

TI	NW	NS	Min	Max	Compliance (%) (Acceptable non-cancer risk: 1)
A	16	28	0.02	562.29	3
B1	3	5	6.58	701.37	0
B2	4	3	0.76	5,345.96	17
B3	14	20	0.63	4,350.30	3
C	10	20	0.02	192.24	20
D	7	4	102.57	9,473.84	0
E	3	10	5.74	118.03	0
F	16	15	0.03	374.40	6

(TI: Type of Industry, NW: Number of Workplace visit times, NS: Number of Samples).

(Type A: Paint production; Type B1: Maintenance and repair; Type B2: Maintenance and repair-aircraft; Type B3: Shipyard (Public-owned); Type C: Automotive painting; Type D: Shipyard (Private); Type E: Furniture painting; Type F: Others-application of paint).

As demonstrated in Table 4.2, even the minimum cancer risk of benzene within all types of industries considered in this study is above the acceptable cancer risk of $1x10^{-6}$. Though almost all benzene concentrations of A (paint production), C (automotive painting) and F type industries (others-application of paint) are complying with the regulatory limit (see Table 4.1), calculated cancer risks are higher than the acceptable limit. This result is an indication of the necessity of HRA rather than concentration based comparisons for decision making and evaluations.

Hazard Indexes calculated via summation of non-cancer risks (Hazard Quotient) of BTEX exposures are provided in Table 4.3. All HIs are above the limit value of 1 except in automotive painting (type C). It should be realized that, even if the concentrations are acceptable with respect to regulatory limits, non-cancer health risks of BTEX are significant according to the HRA study. For instance, for automotive painting; although more than 95% compliance is achieved for all compounds (i.e. benzene, toluene, ethylbenzene and xylene) (see Table 4.1); only 20% of the samples comply with the non-cancer limit. B1 (maintenance and repair), B2 (maintenance and repair-aircraft), D (shipyard-private) and E (furniture painting) types of industries generates similar results. Additionally, as mentioned before, since few samples are collected from B1, B2, D and E type of industries, the results may not reflect the general situation. Thus, in order to derive general conclusions from the HRA study more samples need to be collected.

This analysis showed that compliance comparisons based on health risks and concentration based comparisons produce different results. Although compliance of concentration based comparison is high, health risks of BTEX exposure at given concentrations state significantly low compliance. This means that concentration based comparison as given in RHSMWCS and RHSPWCMA may not be sufficient in terms of providing a healthy work place if it is not supported with HRA; therefore, decision makers should conduct HRA as well. Moreover, the regulatory limits stated in RHSMWCS and RHSPWCMA may need revision.

4.2 Evaluations based on the Type of Action

4.2.1 BTEX Concentrations

Reported BTEX concentrations according to type of action (paint production and paint application) are compiled from the data set and given in Table 4.5.

Table 4.5 BTEX Concentrations with respect to the Type of Action

TA	NW	NS	Compound	Min TWA (mg/m^3)	Max TWA (mg/m^3)	Compliance (%) RHSMWCS/RHSPWCMA*
Paint Production/ Pre-Process	10	5	Benzene	0.25	0.97	100
		17	Toluene	0.44	200.00	94
		15	Ethylbenzene	0.03	30.59	100
		17	Xylene	1.70	200.00	100
Paint Production/ Process	16	23	Benzene	0.02	4.07	96
		50	Toluene	0.05	291.37	94
		50	Ethylbenzene	0.09	195.57	100
		50	Xylene	0.41	654.21	94

Table 4.5 BTEX Concentrations with respect to the Type of Action (continued)

TA	NW	NS	Compound	Min TWA (mg/m^3)	Max TWA (mg/m^3)	Compliance (%) RHSMWCS/RHSPWCMA*
Application/ Paint Preparation	12	10	Benzene	0.07	5.92	90
		15	Toluene	0.33	139.83	100
		14	Ethylbenzene	0.57	30.64	100
		17	Xylene	3.68	100.00	100
Application/ Paint Application	50	58	Benzene	0.07	242.35	86
		110	Toluene	0.08	2,760.00	86
		101	Ethylbenzene	0.07	999.52	98
		111	Xylene	0.03	3,232.89	87

**Limit values of RHSMWCS for Toluene: 192 mg/m^3, Ethylbenzene: 442 mg/m^3, Xylene: 221 mg/m^3 & RHSPWCMA for Benzene: 3.25 mg/m^3*

(TA: Type of Action, NW: Number of Workplace visit times, NS: Number of Samples).

As demonstrated in Table 4.5, nearly 100% compliance is achieved for all compounds (i.e. benzene, toluene, ethylbenzene and xylene) at paint production. For paint preparation step of application, all compounds except benzene which was analyzed in fewer samples compared to other compounds, fully complied with the regulatory limits. Thus, to be able to derive general results for benzene, number of workplaces visited and samples collected should be increased. On the other hand, for paint application step, lower compliance is achieved compared to paint preperation although number of samples (i.e. 58, 110, 101 and 110 for benzene, toluene, ethylbenzene and xylene, respectively) are considerably more than paint preparation.

According to the results, BTEX concentrations measured for paint application process are higher than paint production process. Employees working at paint application areas are exposed to BTEX compounds more than paint production employees. The possible reason for this condition is that production is usually carried out in enclosed equipment such as tanks or mixers so the evaporation of the solvents is minimized (McCann, 2011). Furthermore, due to the nature of the work, employees directly work with paint during paint application and paint can be ejected into the environment which results in higher exposure to BTEX.

Results indicate that taking precautions against BTEX emissions and exposure, thereby improvement of IAQ in paint application workplaces should be among the priorities. Adequate ventilation rates, high technology painting systems (i.e. painting in cabinets with ventilation) and proper use of PPE are considered as the mentioned crucial precautions (U.S. Army Public Health Command, 2012). Reducing work hours spent on paint application, trainings of employees, monitoring IAQ and exposures periodically could help to minimize adverse health effects of BTEX exposure, as well.

4.2.2 Health Risks

Cancer risks and chronic non-cancer risks calculated according to type of action are given in Table 4.6 and Table 4.7, respectively. In the last column of Table 4.6 and Table 4.7, the percentage of samples for which the health risks are below the acceptable cancer risk of $1x10^{-6}$ and non-cancer risk of 1 are provided, respectively. Furthermore, for each sampling location HI values (cumulative of HQs) of each industry are calculated and given in Table 4.8.

Table 4.6 Cancer Risks with respect to the Type of Action

TA	NW	NS	Min	Max	Compliance (%) (Acceptable cancer risk: 10^{-6})
Paint Production/ Pre-Process	10	5	5.44×10^{-5}	2.10×10^{-4}	0
Paint Production/ Process	16	23	4.35×10^{-6}	8.85×10^{-4}	0
Application/ Paint Preparation	12	10	1.48×10^{-5}	1.29×10^{-3}	0
Application/ Paint Application	50	58	1.59×10^{-5}	5.26×10^{-2}	0

(TA: Type of Action, NW: Number of Workplace visit times, NS: Number of Samples).

Table 4.7 Non-cancer Risks (i.e. HQ values) with respect to the Type of Action

TA	NW	NS	Compound	Min	Max	Compliance (%) (Acceptable non-cancer risk: 1)
Paint Production/ Pre-Process	10	5	Benzene	2.28	8.85	0
		17	Toluene	0.02	10.96	65
		15	Ethylbenzene	0.00	8.38	53
		17	Xylene	4.67	547.95	0
Paint Production/ Process	16	23	Benzene	0.18	37.19	22
		50	Toluene	0.003	15.97	32
		50	Ethylbenzene	0.03	53.58	62
		50	Xylene	1.12	1,792.36	0

Table 4.7 Non-cancer Risks (i.e. HQ values) with respect to the Type of Action (continued)

TA	NW	NS	Compound	Min	Max	Compliance (%) (Acceptable non-cancer risk: 1)
Application/ Paint Preparation	12	10	Benzene	0.62	54.06	10
		15	Toluene	0.02	7.66	53
		14	Ethylbenzene	0.043	8.39	57
		17	Xylene	10.08	273.97	0
Application/ Paint Application	50	58	Benzene	0.67	2,213.22	3
		110	Toluene	0.004	151.23	49
		101	Ethylbenzene	0.02	273.84	39
		111	Xylene	0.08	8,857.25	7

(TA: Type of Action, NW: Number of Workplace visit times, NS: Number of Samples).

Table 4.8 Cumulative Non-cancer Risks (i.e. HI values) with respect to the Type of Action

TA	NW	NS	Min	Max	Compliance (%) (Acceptable non-cancer risk: 1)
Paint Production/ Pre-Process	10	5	4.99	558.90	0
Paint Production/ Process	16	23	0.02	1,846.02	4
Application/ Paint Preparation	12	10	10.26	279.45	0
Application/ Paint Application	50	58	0.02	9,473.84	9

(TA: Type of Action, NW: Number of Workplace visit times, NS: Number of Samples).

As demonstrated in Table 4.6, calculated cancer risks for benzene for all types of actions exceed the acceptable cancer risk level of $1x10^{-6}$. Although 100% and more than 85% compliance are achieved in BTEX concentrations at paint production and paint application with regard to legislative limits, the high non-compliance levels for cancer risks proves that HRA studies provide useful information for decision making. It should be noted that the lower numbers of workplaces visited may be a drawback for evaluations of pre-process and process activities under paint production. More samples should be collected and analyzed to be able to derive general conclusions. Results provided in this study are restricted by the facilities and the number of samples considered.

It can be seen from Table 4.7 that there are significant differences between minimum and maximum non-cancer risks of xylene exposures at paint production/process and application/paint application actions. However, there are few high concentrations making both maximum concentrations and non-cancer health risks extremely high. For instance, maximum xylene concentration at application/paint application (see Table 4.5) is more than 3,000 mg/m^3 where minimum concentration is 0.03 mg/m^3. When Table A.47 in Appendix A, where the distributions of measured concentrations at all type of industries and type of action considered in this study are given, is investigated, it is seen that out of 111 there are only 4 samples measured as that high (i.e. more than 1000 mg/m^3). Using high VOC paints or paint application (i.e. spraying) in a cabinet which does not have water curtain could cause these high concentrations.

According to Table 4.7, almost all HIs exceed the non-cancer risk limit of 1. This is also another indication that although concentrations comply with the legislative limits, adverse health effects can be observed. Therefore, HRA clearly helps to evaluate the indoor air pollutant concentrations.

Evaluations conducted based on types of industries and activities conducted in paint production and application revealed that health risks evaluations rather than concentration based comparisons with respect to current legislative limits may be more reasonable for decision making on evaluation and improvement of IAQ (i.e. efficiency of ventilation system, PPE type selection etc.) and minimization of human exposures, as well. Since HRA take the cancer and non-cancer health risks of exposure into account, it is a more rational comparison mechanism when health of workers is considered. U.S. EPA (2014) declares that RA has led to decisions protecting human health and the environment from a range of threats. HRA is based on exposure scenarios that are consistent with the context, frequency, duration and pathway of exposures.

U.S. EPA uses RA as a key source of scientific information for evaluating risks and related outcomes associated with possible risk management options, and ultimately, informing the process of making sound decisions about managing risks to human health and the environment (U.S. EPA, 2014). In brief, HRA studies encourage the consideration of innovative technology and concepts in the still developing area of sustainability in environmental decision making.

Compliance of BTEX concentrations and HRA with respect to legislative and acceptable limits, respectively are significantly different from each other. Therefore, in the following sections, cancer and non-cancer risks of exposure to legislative limits and BTEX concentrations supplying acceptable cancer and non-cancer risks are provided (see Chapter 4.3 and Chapter 4.4, respectively).

4.3 Evaluation of Cancer and Non-Cancer Risks associated with Concentration Limits given in Relevant Regulations

First cancer and non-cancer risks associated with the current regulatory limit concentrations given in both national and international legislations are calculated given in Table 4.9 and Table 4.10, respectively.

Table 4.9 Cancer Risks Associated with Current Regulatory Limit Concentrations

Regulations	Limit Value (mg/m^3)	Cancer Risk
	Benzene	
RHSPWCMA*	3.25	7.10×10^{-4}
OSHA (TWA)	3.19	6.94×10^{-4}
NIOSH (TWA)	0.32	6.96×10^{-5}

**Regulation on Health and Safety Precautions on Works with Carcinogenic or Mutagenic Agents*

According to Table 4.9, limit values for benzene provided in the Turkish legislation (RHSPWCMA, 2013), OSHA and NIOSH limits result in significantly higher cancer risks than the acceptable cancer risk of $1x10^{-6}$. Thus, even if the legislative concentration limits are met; cancer risk higher than commonly accepted levels are due to inhalation of indoor contaminants. Acceptable cancer risk of $1x10^{-6}$ is a legislative choice; other values might be set as the limit value by the government.

However, it is the threshold adopted in the regulation for the control of sites contaminated with point sources and soil pollution control (Regulation on Soil Pollution Control and Sites Contaminated with Point Sources, Appendix 1, 2010). Besides risk values given in Table 4.9 are higher than $1x10^{-4}$ - another commonly used acceptable value for cancer risk - as well. These results indicate that the current limit values provided in RHSPWCMA, OSHA and NIOSH should be reevaluated.

An HRA based approach and acceptable limits based on cancer and non-cancer health risks need to be adapted in relevant regulations.

All HQs associated with current BTEX limits are above the acceptable limit of 1 when chronic non-cancer risks are taken into account (see Table 4.10). Thus, employees working at workplaces in which BTEX concentrations are at the limit values set in RHSPWCMA, OSHA or NIOSH may have non-cancer health problems.

Table 4.10 Non-cancer Risks (i.e. HQ values) Associated with Regulatory Limit Values

Regulations	Limit Value (mg/m^3)				Non-cancer Risk			
	Benzene	Toluene	Ethylbenzene	Xylene	Benzene	Toluene	Ethylbenzene	Xylene
RHSMWCS*	-	192	442	221	-	10.52	121.10	605.48
RHSPWCMA**	3.25	-	-	-	29.68	-	-	-
OSHA (TWA)	3.19	754	435	435	29.13	41.32	118.90	1,189.04
NIOSH (TWA)	0.32	375	435	435	2.93	20.55	118.90	1,189.04

**Regulation on Health and Safety Measures for Works with Chemical Substances*
***Regulation on Health and Safety Precautions on Works with Carcinogenic or Mutagenic Agents*

4.4 Suggested Limit Concentrations

Evaluation of current BTEX regulatory concentration limits based on cancer and non-cancer health risks suggests the need for lowering the limits in order to provide better indoor air quality and reduce health risks to employees at workplaces where paint is produced or applied. Since benzene causes both cancer and non-cancer health risks, two different concentration values are estimated for benzene. Benzene concentration which will result in an acceptable cancer risk of $1x10^{-6}$ is calculated and provided in Table 4.11. BTEX compounds concentration values which will result in acceptable non-cancer health effects are calculated and given in Table 4.12.

If the concentration limit is reduced in comparison to current limit value, then additional precautions can be enforced to provide better IAQ in terms of protecting human health. It is demonstrated that the benzene concentration providing the acceptable cancer risk is 0.0046 mg/m^3 (Table 4.11). This is significantly lower than the current limit values which are 3.25 mg/m^3 and 3.19 mg/m^3 in RHSPWCMA and OSHA, respectively. Reduction in the current regulatory limit value may be beneficial for the health of workers. During decision making, HRA should be conducted as well as the concentration based comparison through regulatory limits, since current limits may not be sufficiently protective in regard to human health.

Table 4.11 Concentration Providing the Acceptable Cancer Risk

Compound	Acceptable Cancer Risk	Concentration Providing the Acceptable Cancer Risk	RHSPWCMA
Benzene	$1x10^{-6}$	0.0046 mg/m^3	3.25 mg/m^3

EPA IRIS has calculated the air concentrations at specified risk levels for cancer risk (URL 22). According to this, exposure concentration (EC) that meets an acceptable cancer risk of $1x10^{-6}$ is founded as 0.45 µg/m^3. This EC is founded via dividing the acceptable cancer risk to IUR of benzene which is $2.2x10^{-6}$ m^3/µg. This value is exactly same as founded in this study. However, the safe amount of contaminant concentration in the air (CA) to which an employee is exposed in the workplace indoor air that would be causing acceptable cancer risk should be calculated. For this reason, cancer risk scenario used in this study (i.e. 8 hours shift, work for 300 days in a year and work for 25 years in the sector and having 70 years lifetime) is integrated into EC. Therefore, due to the assumed scenario conditions, CA which provides the EC of acceptable cancer risk (4.6 µg/m^3) is 3 orders of magnitudes lower than the current limit value (3.25 mg/m^3). In case it may not be lower the concentrations indoor to the given value, at least shift hours can be lowered, fewer workdays can be employed in a year, or even early retirement or frequent work alteration for employees of the paint industry can be suggested to reduce the impact of exposure.

Table 4.12 Concentrations Providing the Acceptable Non-cancer Risk

Compound	Acceptable Non-cancer Risk	Concentration Providing the Non-cancer Risk	RHSMWCS/ RHSPWCMA
Benzene	1	0.11 mg/m^3	3.25 mg/m^3
Toluene	1	18.25 mg/m^3	192 mg/m^3
Ethylbenzene	1	3.65 mg/m^3	442 mg/m^3
Xylene	1	0.36 mg/m^3	221 mg/m^3

BTEX concentrations calculated to provide acceptable non-cancer risks are given in Table 4.12. It is clearly demonstrated that suggested concentrations providing the acceptable threshold value are considerably lower than the legislative limit values. This is another indication of the potential need for re-evaluation of the limits set in relevant regulations.

In this study, there is no measurement result that is below the suggested limit concentrations and there is no cancer and non-cancer risk below the acceptable limit values, as well).

Two different limit benzene concentrations providing acceptable cancer and non-cancer risks are calculated. Since benzene is controlled under RHSPWCMA in Turkey, the new concentration providing the acceptable cancer risk (see Table 4.11) should be adapted in this Regulation.

4.5 Suggested Measures

The difference between current exposure limit concentrations and the calculated concentrations that will result in acceptable cancer and non-cancer risks (based on the scenario considered in this study) are highly different from each other. Furthermore, compliance levels according to acceptable cancer and non-cancer risk values are low for BTEX exposures at considered paint industries and paint application/production actions. In order to decrease these exposures BTEX emissions especially in paint application industries should be lowered. For this purpose, the Best Available Techniques (BAT) Reference Documents (BREF) suggested by European Commission, Joint Research Centre can be used as guiding document.

The main objectives of BREFs are to define applied techniques, emissions amounts and consumption levels, and techniques considered for the determination of BAT conclusions within a particular sector. Furthermore, BREFs aim to reflect accurately the exchange of information which has taken place and to provide reference information for regulators to take into account when determining permit conditions. A series of BREFs are published. Each of them focuses on a specific industry.

A specific BREF on the painting industry has not yet been implemented at the EU level. However, existing BREFs on chemical industry can give some general indication on valid measures that can be implemented, based on filtration systems and water and energy saving techniques (Grimaldi and Benedetti, 2010).

The BREF entitled as the "Surface Treatment Using Organic Solvents" (2007) reflects an information exchange on the objective of installations for the surface treatment of substances, objects or products using organic solvents (i.e. for dressing, printing, coating, waterproofing, sizing, painting or cleaning). This BREF is the most relevant document giving information on BAT of painting activities as mentioned above.

Water soluble paints as an alternative to solvent based ones is discussed in the document. The emission of solvents to air, water and groundwater, and soil are the main environmental issues mentioned. However, manufacture of paints, inks, adhesives, etc., which are not within the scope have not been considered in the document.

Solvent based paints are commonly applied in: the automotive industry, coating of trucks and commercial vehicles, coating of buses or trains, ships and yachts, aircraft metal packaging, furniture and wood materials sectors (BREF-Surface Treatment Using Organic Solvents, 2007). Recommended technologies as BAT in the document for painting (i.e. shipyard, aircraft etc.) are:

- Reducing solvent emissions by substitution of high VOC paints by high-solids or waterborne paints,
- Capturing and treating waste gases during paint application on components via extracting air from enclosed areas where painting (i.e. spraying) is carried out and using appropriate waste gas treatment techniques (i.e. good ventilation technologies),
- Reducing overspray and increasing application efficiency by a combination of techniques (i.e. the use of nets or water curtains),
- Enclosing main solvent using or painting areas,
- For new constructions, spray sections prior to assembly in enclosed areas with waste gas extraction and treatment techniques.

It has mentioned in Chapter 2 that spray painting is mostly performed during paint application in Turkey. Although "spraying carried out in closed cabinets" is known as the most basic and urgent precaution and sufficient, in all cases, the use of a further water curtain which capture water-paint mixture and treated in a reservoir below the spray booth is absolutely necessary (BREF-Surface Treatment Using Organic Solvents, 2007).

With the EU harmonization process, industries have started to change their technologies and policies in parallel with BATs which aid to minimize pollutants release to environment and decrease the adverse effects on both human and ecological health. Most paint manufacturers have developed waterborne paints having low VOC amounts to comply with the regulatory limits. Furthermore, automotive industry companies, which have OSH and environmental quality standards and policies on their own, have the approach of considering and adopting BATs to their investments. According to the interview conducted with one of the OSH expert of type C industry workplace, it is noted that since these workplaces generally use acrobat ventilation with high flow rate of suction (i.e. mobile ventilation systems which allows focusing on directly the point where painting is done), the VOC concentration in the workplace air, so personal exposure is low. Furthermore, since in automotive painting, small pieces like door hander, hoods or fenders are painted, closed paint cabinets and water curtains are generally used in the sector as BAT to decrease the VOC emissions. Therefore, BTEX emissions related with the mentioned sector almost comply with the limits (see Table 4.1).

According to interviews conducted with the OSH experts of workplaces of type B2 (maintenance and repair-air craft) and type B3 (shipyard, public-owned) (i.e. industries at which BTX emissions are comparatively higher than other industries), it is noted that there are some main reasons causing the high concentrations of VOC in these industries. Using low VOC paints and installing good ventilation in the workplace are the recommended technologies in BAT. OSH expert of the company said that, since using low VOC paint changes the quality of final product (i.e. brightness and durability etc.); clients prefer the use of solvent based paints. Additionally, low VOC paints are expensive than solvent based paints, which makes using solvent based ones more convenient. Therefore, BTEX concentrations in these industries and also exposures are higher and some precautions should be taken.

It has been noted in the field study that due to bureaucracy of public-owned institutions, changing the current systems (i.e. ventilation technology, design of the workplaces) is difficult. In terms of ventilation technologies, the OSH expert mentioned that the suction flow rate of the ventilation system is not enough to decrease VOC concentrations. Furthermore, changing the system with a new technology (i.e. ventilation which supplies fresh air from top and sucks the polluted air from bottom) is not a feasible solution in terms of both economical and ergonomic reasons. It is not ergonomically feasible because current workplaces of the industry have been built so many years ago and the design of the workplaces does not allow installing a new ventilation technology. According to the cost analysis done during the exploration, the expert stated that, a high technology ventilation system requires around 60.000 Turkish Liras, which can be considered as high amount for workplaces of mentioned industries (i.e. public-owned maintenance and repair and shipyard workplaces).

According to another conversation done by the OSH expert of a workplace under type D industry (shipyard-private sector), paint application in a closed system like paint cabinets is not feasible for shipyards with respect to applicability. The reason is that large pieces even entirely ships are painted in these workplaces. This situation makes cabinet usage which is especially suitable for small pieces painting impossible for this industry. Furthermore, she stated that again due to the first design conditions of the workplaces, paint houses are so small and inappropriate to install good ventilation technologies and water curtains.

Recommended BAT especially for paint application could be summarized as: use of low VOC paints, installing better ventilation technologies, painting in closed cabinets and installing water curtains into these cabinets. Number of possible BAT that could be applied to the industries of this study with respect to BTEX emissions is given in Table 4.13. As can be seen from Table 4.13, type A has already applied 2 of the recommendations which are good ventilation and closed system works. However type B workplaces only use low VOC paint as better housekeeping while type F industry has closed cabinets without water curtain. Type C workplaces are good examples with respect to BAT since all recommended technologies have been already applied. For type E workplaces, only use of water curtains is need to be applied as further BAT.

Technically feasible recommendations and related benefits can be seen in Table 4.14. According to Table 4.14, installing better ventilation systems (i.e. supplying more fresh air with higher flow rate and sucking the polluted air with higher flow rate) and using low VOC paints instead of solvent based paints during paint application are the mostly recommended available technologies for the mentioned industries. However, painting in closed cabinets with water curtains are not technically feasible as mentioned above. The main benefit of adapting the recommendations is decreasing the BTEX emissions originating from painting and thus decreasing the exposure to these chemicals and related adverse health effects.

Table 4.13 Number of Possible BAT that can be Applied in the Selected Industries

Type of Industry	Already applied	Can be applied	Technically not feasible
Type A	2	-	-
Type B1	1	1	2
Type B2	-	2	2
Type B3	-	2	2
Type C	4	-	-
Type D	-	2	2
Type E	3	1	-
Type F	1	2	1

(Type A: Paint production; Type B1: Maintenance and repair; Type B2: Maintenance and repair-aircraft; Type B3: Shipyard (Public-owned); Type C: Automotive painting; Type D: Shipyard (Private); Type E: Furniture painting; Type F: Others-application of paint).

Table 4.14 Technically Feasible Recommendations and Related Benefits

Type of Industry	Recommendations	Benefits
Type A	-	-
Type B1	Better ventilation technology	BTEX emission reduction
Type B2	Better ventilation technology	BTEX emission reduction
	Use of low VOC paints	BTEX emission reduction
Type B3	Better ventilation technology	BTEX emission reduction
	Use of low VOC paints	BTEX emission reduction
Type C	-	-
Type D	Better ventilation technology	BTEX emission reduction
	Use of low VOC paints	BTEX emission reduction
Type E	Use of water curtains	BTEX emission reduction
Type F	Better ventilation technology	BTEX emission reduction
	Use of low VOC paints	BTEX emission reduction

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

All four compounds of BTEX, which cause poor IAQ, at selected industries/facilities producing and/or applying paint are evaluated based on human health risks through inhalation with the methodology suggested by U.S. EPA. The BTEX measurements at selected industries measured between 2006 and 2013 are evaluated for potential cancer and non-cancer health risks in addition to the current approach of comparing the concentrations with the legislative limit values. BTEX concentrations (mg/m^3) and associated health risks are evaluated with respect to two classifications: type of industries and type of actions.

Main conclusions of the study are summarized as follows:

1. Compliance of measured BTEX concentrations at indoor workplaces with legislative limits versus compliance of HRA results and acceptable cancer and non-cancer risks are different from each other. Although compliance of concentration based comparison is high, health risks of BTEX exposure have significantly low compliance with health risk limits. This means that concentration based comparisons might be misleading in terms of cancer and non-cancer health risks.

2. Since there is no specific industrial IAQ legislation in Turkey, a regulation which provides acceptable emission limit values of IAQ disruptive chemicals based on HRA approach should be published. This regulation should include all industries.

3. Considering type of industry, number of workplaces visited and thereby number of samples collected at type B1 (maintenance and repair), type B2 (maintenance and repair-aircraft), type D (shipyard-private) and type E (furniture painting) industries are not sufficient to derive general conclusions. More data need to be collected.

4. BTEX concentrations measured at paint application process are higher than paint production process. The reason for this condition is that production is usually performed in enclosed equipment (i.e. tanks or mixers) so the evaporation of the solvents is minimized at paint production so emission of pollutants and exposures are limited.

5. Considering type of action, number of samples and workplaces visited at paint production workplaces are limited to make a general conclusion. More data need to be collected.

6. Concentrations corresponding to acceptable cancer and non-cancer risks (1x10-6 and 1, respectively) are lower than the current legislative concentration limits. Thus, the legislative limit values should be reevaluated.

7. HRA is a scenario based approach (i.e. exposure pathways, duration and frequency of exposure) with respect to chemical exposures. It takes into account cancer and non-cancer health risks of exposures by these scenarios. So, it is a more rational comparison mechanism than comparing the measured concentrations with fixed legislative limits. Thus, HRA based comparisons will provide more information about the safety of workers.

The recommendations for future studies are as follows:

1. One of the limitations of this study is limited number of workplaces visited and number of samples collected. In order to derive general results, further study should be conducted with more samples and more workplaces especially on maintenance and repair, shipyard and furniture painting industries and paint production facilities as well.

2. The study is conducted using only concentrations of BTEX obtained from measurements conducted at workplaces. Impact of factors such as ventilation technologies, automation systems, protective measures used in the workplaces should be evaluated simultaneously and measures to reduce potential health problems should be developed.

3. Since there is no industrial IAQ regulation that controls the indoor BTEX concentrations especially at paint industry workplaces, if such a regulation published in the future, it is recommended to perform a further HRA study in accordance with the new regulation.

4. Workplaces visited at type C industry (automotive painting) and paint production actions are known as the industry leader companies so the compliance of concentrations are high at these workplaces. To identify technology related advantages, a more detailed study need to be carried out. Extensive data from high technology facilities and SMEs need to be collected to compare exposures and related inhalation health risks at these different types of workplaces.

5. A further study is highly recommended in order to see the impact of appropriate PPE use on BTEX exposures and related health effects.

REFERENCES

Arslan Tatar Ç. P. (2012). Process safety in the industry working with different types of solvents, MSc Thesis, Ege University, İzmir.

Bahadar H., Mostafolou S., Abdollahi M. (2014). Current understandings and perspectives on non-cancer health effects of benzene: A global concern. *Toxicology and Applied Pharmacology, 276,* 83–94.

Bono R., Scursatone E., Schilirò T., Gilli G. (2003). Ambient Air Levels and Occupational Exposure to Benzene, Toluene, and Xylenes in Northwestern Italy. *Journal of Toxicology and Environmental Health, Part A, 66,* 519–531.

Branco, P.T.B.S., Alvim-Ferraz, M.C.M., Martins, F.G., Sousa, S.I.V. (2013). Indoor air quality in urban nurseries at Porto city: Particulate matter assessment. *Atmospheric Environment, 84,* 133-143.

Cao Q., Yu Q., Connel D. W. (2011). Health risk characterisation for environmental pollutants with a new concept of overall risk probability. *Journal of Hazardous Materials, 187,* 480-487.

Charretton M. and Vincent R. (1997). Occupational exposure to organic solvents during paint stripping and painting, In N. P. Cheremisinoff (Ed.). *Advances in Environmental Control Technology: Health and Toxicology*. (251-305). Portland: Book News Inc.

Chen C., Campbell K., D., Negi I., Iglesias R. A., Owens P., Tao N., Tsowa F., Forzani E. S. (2012). A new sensor for the assessment of personal exposure to volatile organic compounds, *Atmospheric Environment, 54*, 679-687.

Conseil Européen de l'Industrie des Peintures, CEPE. (2011). A Guide to VOC Reduction in Decorative Coatings. Retrieved from: http://www.cepe.org/

Council Directive 98/24/EC of 7 September 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC) [2003] OJ L131/11.

Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of VOCs due to the use of organic solvents in certain activities and installations [2004] OJ L85/1.

Council Directive 2004/42/CE of 21 April 2004 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing products and amending Directive 1999/13/EC [2004] OJ L143/87.

Commission Directive 2000/39/EC of 8 June 2000 establishing a first list of indicative occupational exposure limit values (IOELV) in implementation of Council Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work [2000] OJ L142/47.

Corvalán C., Briggs D., Zielhuis G. (2000). *Decision Making in Environmental Health: From evidence to action* (1st ed). London, England: E&FN Spon.

Çelebi U., B., Vardar N. (2008). Investigation of VOC emissions from indoor and outdoor painting processes in shipyards, *Atmospheric Environment, 42*, 5685– 5695.

Çökelek E. (2008). Determination of Volatile Organic Compound (VOC) Levels in the Center of Kocaeli and Risk Assessment. MSc Thesis. Kocaeli University, Kocaeli.

Daengthongdee C., and Soralump C. (2013). Health risk assessment of volatile organic compounds in painting process in the automotive industry, *EHSM-02,* 1-6.

Drägerwerk AG & Co. KGaA. 2011. Germany.
Retrieved from:
http://www.draeger.com/sites/assets/PublishingImages/Products/com_x-plore_bayonet/Attachments/9045782_AB_Selection_Guide_Atemschutz_en-121211-fin.pdf)

Du Z., Mo J., Zhang Y., Xu Q. (2014). Benzene, toluene and xylenes in newly renovated homes and associated health risks in Guangzhou, China. *Building and Environment, 72,* 75-81.

Environment Australia. (1998). *Emission Estimation Technique Manual for Paint and Ink Manufacturing, National Pollutant Inventory.* Queensland, Australia.

Erkmen, J. (2012). Solvent bazlı inşaat boyalarında pigment boyutunun etkilerinin uzun zaman aralığında incelenmesi, MSc Thesis, Atatürk University, Erzurum.

European Commission. (2013). Methodology for the Derivation of Occupational Exposure Limits Scientific Committee on Occupational Exposure Limits (SCOEL): Key Documentation (Version 7).

European Commission. (2007). Reference Document on Best Available Techniques on Surface Treatment Using Organic Solvents.

Fernández L. C., Alvarez R., F., González-Barcala F. J., Rodríguez Portal J. (2013). Indoor Air Contaminants and Their Impact on Respiratory Pathologies, *Arch Bronconeumol, 49*(1), 22–27.

Grimaldi G and Benedetti G. (2010). Capacity Building and Strengthening Institutional Arrangement Workshop: "Best Available Techniques (BAT) on Painting Industry".

Gunatilaka M. (2003). Hazardous air pollutants Concentrations of Benzene, Toluene, Ethylbenzene and Xylene (BTEX) in Christchurch 2001/2002. *Environment Canterbury Technical Report,* Christchurch.

Guo H., Lee S.C., Chan L.Y., Li W.M. (2004). Risk assessment of exposure to volatile organic compounds in different indoor environments, *Environmental Research, 94*, 57–66.

Güllü G. (2013, November). *Indoor Air Pollution: Volatile Organic Compounds.* Paper presented at the TSE Symposium, Turkey.
(Retrieved from: http://sempozyum2013.tse.org.tr/docs/c5/g%C3%BClen-g%C3%BCll%C3%BC.pdf?sfvrsn=2)

Health Protection Agencys (HPA). (2007). Toxicological Overview of Toluene. United Kingdom.

Health and Safety Executive. (2011). EH40/2005 Workplace exposure limits containing the list of workplace exposure limits for use with the control of substances hazardous to health regulations. Second Edition. England.

Huang L, Mo J, Sundell J, Fan Z, Zhang Y. (2013). Health risk assessment of inhalation exposure to formaldehyde and benzene in newly remodeled buildings, Beijing, *Plosone, 8*(11), e79553.

Institut National De Recherché Et De Sécurité. (2012). Valeurs Limites D'exposition Professonnielle Aux Agents Chimiques en France. France.

Japan Society for Occupational Health. (2013). Occupational Exposure Limits. *Journal of Occupatioanl Health, 55:* 422–441.

Jones, A.P. (1999). Indoor air quality and health, *Atmospheric Environment, 33,* 4536-4564.

Lan T. T. N., Liem N. Q.,Binh N. T. T. (2013). Personal exposure to benzene of selected population groups and impact of commuting modes of in Ho Chi Minh, Vietnam. *Environmental Pollution, 175,* 56-63.

Labour Law, Law No: 4857. Official Gazette Date: 10.06.2003 No: 25134.

Law on Occupational Health and Safety, Law No: 6331. Official Gazette Date: 30.06.2012 No: 28339.

Law on Organization and Duties of Ministry of Labor and Social Security Law No: 3146. Official Gazette Date: 18.01.1985 No: 18639.

Lerner C. J. E., Sanchez E.Y., Sambeth J. E., Porta A. A. (2012). Characterization and health risk assessment of VOCs in occupational environments in Buenos Aires, Argentina, *Atmospheric Environment, 55,* 440-447.

Leusch, F., Bartkow, M. (2010). A short primer on benzene, toluene, ethylbenzene and xylenes (BTEX) in the environment and in hydraulic fracturing fluids. [online] http://www.ehp.qld.gov.au/management/coal-seam-gas/pdf/btex-report.pdf

Liu H., Liang Y., Bowes S., Xu H., Zhou Y., Armstrong T., Wong O., Schnatter A.R., Fang J., Wang L., Nie L., Fu H., Irons R. (2009). Benzene Exposure in Industries Using or Manufacturing Paint in China- A Literature Review, 1956-2005. *Journal of Occupational and Environmental Hygiene*, *6*:11, 659-670.

Liu Q., Liu Y., Zhang M. (2014) Source Apportionment of Personal Exposure to Carbonyl Compounds and BTEX at Homes in Beijing, China, *Aerosol and Air Quality Research: 11*, 330-337.

Malherbe L., Mandin C. (2007). VOC emissions during outdoor ship painting and health-risk assessment, *Atmospheric Environment, 41*, 6322–6330.

Manuela C., Gianfranco T., Maria F., Tiziana C., Carlotta C., Giorgia A., Assunta C., Pia M.S., Jean-Claude A., , Francesco T., Angela S. (2012). Assessment of occupational exposure to benzene, toluene and xylenes in urban and rural female workers. *Chemosphere, 87*, 813-819.

McCann M. (2011). Paint and Coating Manufacture. *Encyclopedia of Occupational Health and Safety.* International Labor Organization, Geneva.
(Retrieved from: http://www.ilo.org/oshenc/part-xii/chemical-processing/examples-of-chemical-processing-operations/item/380-paint-and-coating-manufacture)

Ministry of Environment and Urban Affairs. (2009). *Paint Production Guidance: Project of Improving the Management of Hazardous Waste from Industries in Turkey.* Ankara, Turkey.

Ministry of Environment and Urban Affairs, Regulation on Air Quality Assessment and Management. Official Gazette Date: 06.06.2008 No: 26898.

Ministry of Environment and Urban Affairs, Regulation on Industrial Air Pollution Control. Official Gazette Date: 03.07.2009 No: 27277.

Ministry of Environment and Urban Affairs, Regulation on Soil Pollution Control and Sites Contaminated with Point Sources. Official Gazette Date: 08.06.2010 No: 27605.

Ministry of Labor and Social Security. (2005). *Labor Inspection Board, Project Evaluation Report of Occupational Health and Safety Inspection for Paint Production Workplaces.* Ankara, Turkey.

Ministry of Labor and Social Security, Regulation on Health and Safety Measures for Works with Chemical Substances. Official Gazette Date: 12.08.2013 No: 28733.

Ministry of Labor and Social Security, Regulation on Health and Safety Precautions on Works with Carcinogenic or Mutagenic Agents. Official Gazette Date: 06.08.2013 No: 28730.

Ministry of Labor and Social Security, Regulation on Occupational Health and Safety Risk Assessment. Official Gazette Date: 29.12.2012 No: 28512.

National Oil and Hazardous Substances Pollution Contingency Plan (NCP). (1994). Part 300, Subchapter J-Superfund, Emergency Planning, and Community Right-To-Know Programs, Subpart E-Hazardous Substance Response. p.70.

Nims D. (1999). *Basics of Industrial Hygiene*. The United States of America: Preserving the Legacy.

NIOSH. (1984). Hydrocarbons, Aromatic: Method 1501. In: Eller PM, ed. NIOSH Manual of Analytical Methods. 4th rev. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

Occupational Safety and Health Act of 1970, Pub. L. No. 91-596, 84 STAT. 1590, 91^{st} Congress, S.2193, Sec 2(b)(1) (2004).

Occupational Safety and Health Administration. (2011). *Indoor Air Quality in Commercial and Institutional Buildings*. U.S.A.

Ojima J. (2012).Gaseous contaminant distribution in the breathing zone. *Industrial Health, 50*(3), 236-238.

Oregon Department of Human Services, 1994, Technical Bulletin on Health Effects Information on BTEX, Portland.

Parra M. A. Elustondo D., Bermejo R., Santamaria J. M. (2008). Quantification of indoor and outdoor volatile organic compounds (VOCs) in pubs and cafes in Pamplona, Spain, *Atmospheric Environment*, *42,* 6647–6654.

Robertson S. (2011). Greener Paint. Sanctuary, 71-74. Retrieved from: https://www.livos.com.au/uploads/187/48/Sanctuary16_Paints.pdf, on June 2014.

Qian H., Fiedler N., Moore F., Weisel C. P. (2010). Occupational Exposure to Organic Solvents during Bridge Painting, *Ann. Occupational Hygienist*, Vol. 54, No. 4, 417–426.

Rentz O., Peters N., Nunge S., Gelderman J. (2002). Best Available Techniques (BAT) for the Paint and Adhesive Application in Germany, Volume I Paint Application, Karlsruhe-Strasbourg.

Seeber A., Sietman B., Zupanic M. (1996). In Search of Dose-Response Relationships of Solvent Mixtures to Neurobehavioral Effects in Paint Manufacturing and Painters, *Food and Chemical Toxicology, 34,* 1113-1120.

Sofuoğlu S., C., Aslan G., İnal F., Sofuoğlu A. (2011). An assessment of indoor air concentrations and health risks of volatile organic compounds in three primary schools, *International Journal of Hygiene and Environmental Health, 214,* 36–46.

Soldatos A. P., Bakeas B. E., and Siskos P. A. (2010). Occupational Exposure to BTEX of Workers in Car Parking and Gasoline Service Stations in Athens, Greece. (Retrieved from: http://www.siskos.gr/pegasus/content04/show.php?hert20=3000079&pcode=HERT20_CD3000079)

State Planning Organization. (2006).*9th Development Plan, Specialization Commission of Chemical Industry, Report of Paint Work Group,* Ankara, Turkey.

Şengül, F., Dursun D., Çatalkaya E., Dinçer A., Kargı F. (2003). Solvent İçerikli Boya Sanayi Atıksularının Arıtımı, *Çevre Bilim ve Teknoloji, 1* (3), 1-9.

Tsaia P., Shiehb H., Leec W., Lai S. (2001). Health-risk assessment for workers exposed to polycyclic aromatic hydrocarbons (PAHs) in a carbon black manufacturing industry, *The Science of the Total Environment, 278,* 137-150.

Uang S., Shih T., Chang C., Chang S., Tsai C., Deshpand C. G. (2006). Exposure assessment of organic solvents for aircraft paint stripping and spraying workers, *Science of the Total Environment, 356,* 38– 44.

U.S. Army Public Health Command. (2012). *Guidelines for Controlling Health Hazards in Painting Operations.* U.S.A.

U.S. Department of Defense. (2007). *Deployment Health and Family Readiness Library, Industrial Solvents.* U.S.A.

U.S. Environmental Protection Agency. (1989). Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A). Washington, D.C.: Office of Emergency and Remedial Response.

U.S. Environmental Protection Agency. (1994). Competitive Implications of Environmental Regulation in the Paint and Coatings Industry, Hochschule St. Gallen Copyright. 189-249.

U. S. Environmental Protection Agency. (2003). Benzene (CASRN 71-43-2). Retrieved from: http://www.epa.gov/iris/subst/0276.htm

U.S. Environmental Protection Agency-Integrated Risk Information System. (2009). Risk Assessment Guidance for Superfund, Volume I: Human Health Evaluation Manual (Part F) Supplemental Guidance for Inhalation Risk Assessment. Washington, D.C.: Office of Emergency and Remedial Response.

U.S. Environmental Protection Agency. (2014). Framework for Human Health Risk Assessment to Inform Decision Making.

Vitali M., Ensabella F., Stella D., Guidotti M. (2006). Exposure to organic solvents among handicraft car painters: A Pilot Study in Italy, *Industrial Health*, 44, 310–317.

Wang L., Liu M., Huang D., Wang Y. (2012). Cancer Risk Assessment for Occupational Exposure a Case Study in a Paint Production Process. *Advances in Biomedical Engineering, Volume 9.*

World Health Organization. (2000). *Air Quality Guidelines for Europe* (Second Edition, WHO Regional Publications, European Series, No. 91). Copenhagen.

World Health Organization. (1989*).IARC Monographs on the Evaluation of Carcinogenic Risks to Human Some Organic Solvents, Resin Monomers and Related Compounds, Pigments and Occupational Exposures in Paint Manufacture and Painting* (Volume: 47). Lyon, France.

Yin S.N., Li Q., Liu Y., Tian F., Du C., and Jin C. (1987). Occupational exposure to benzene in China, *Br. J. Ind. Med.*, *44,* 192–195.

Zhou J., You Y., Bai Z., Hu Y., Zhang J., Zhang N. (2011). Health risk assessment of personal inhalation exposure to volatile organic compounds in Tianjin, China, *Science of the Total Environment*, 409, 452–459.

Ziong J., Wang L., Bai Y., Zhang Y. (2013). Measuring the characteristic parameters of VOC emission from paints, *Building and Environment*, 66, 65-71.

Web Sources

URL 1: http://www.epa.gov/oaqps001/community/details/paint_manuf_addl_info.html, last visited on May 2014.

URL 2: Made How, http://www.madehow.com/Volume-1/Paint.html, last visited on December 2013.

URL 3: American Coatings Association,http://www.paint.org/about-our-industry/historical-context.html, last visited on December 2013.

URL 4: ICIS, http://www.icis.com/resources/news/2011/02/25/9439086/us-benzene-production-rises-19-in-2010-npra/, last visited on May 2014.

URL 5: U.S. Environmental Protection Agency, http://www.epa.gov/ttn/atw/hlthef/ethylben.html, last visited on December 2013.

URL 6: Programme for Workers' Activities (ACTRAV) - International Training Centre of the ILO, http://actrav.itcilo.org/actrav-english/telearn/osh/kemi/ctm1.htm, last visited on December 2013.

URL 7: The Canadian Center for Occupational Health and Safety, http://www.ccohs.ca/products/publications/iaq.html, last visited on December 2013.

URL 8: U.S. Environmental Protection Agency, http://www.epa.gov/iaq/ia-intro.html, last visited on December 2013.

URL 9: U.S. Environmental Protection Agency, http://www.epa.gov, last visited on December 2013.

URL 10: International Agency for Research on Cancer, http://monographs.iarc.fr/ENG/Classification, last visited on December 2013.

URL 11: National Institute of Environmental Health Sciences, http://ntpsearch.niehs.nih.gov, last visited on December 2013.

URL 12: Occupational Safety and Health Administration, https://osha.europa.eu/en/publications/reports/OELs_table, last visited on December 2013.

URL 13: Occupational Safety and Health Administration, https://www.osha.gov/chemicaldata/, last visited on December 2013.

URL 14: Centers for Disease Control and Prevention, http://www.cdc.gov/niosh/npg/npgd0049.html, last visited on December 2013.

URL 15: Centers for Disease Control and Prevention, http://www.cdc.gov/niosh/npg/npgd0619.html, last visited on December 2013.

URL 16: Centers for Disease Control and Prevention, http://www.cdc.gov/niosh/npg/npgd0264.html, last visited on December 2013.

URL 17: Centers for Disease Control and Prevention, http://www.cdc.gov/niosh/npg/npgd0669.html, last visited on December 2013.

URL 18: Centers for Disease Control and Prevention, http://www.cdc.gov/niosh/npg/pgintrod.html, last visited on July 2014.

URL 19: US. Occupational Safety and Health Administration https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_id=770&p_table=preambles, last visited on June 2014.

URL 20: US. Occupational Safety and Health Administration https://www.osha.gov/dsg/annotated-pels/index.html, last visited on July 2014.

URL 21: U.S. Environmental Protection Agency, http://www.epa.gov/iris/, last visited on February 2014.

URL 22: U.S. Environmental Protection Agency, http://www.epa.gov/oaqps001/community/details/paint_operations.html, last visited on June 2014.

URL 23: U.S. Environmental Protection Agency, Integrated Risk Information System, http://www.epa.gov/iris/subst/0276.htm, last visited on June 2014.

APPENDIX

A. FREQUENCY DISTRIBUTIONS WITH RESPECT TO THE TYPE OF INDUSTRIES AND TYPE OF ACTIONS

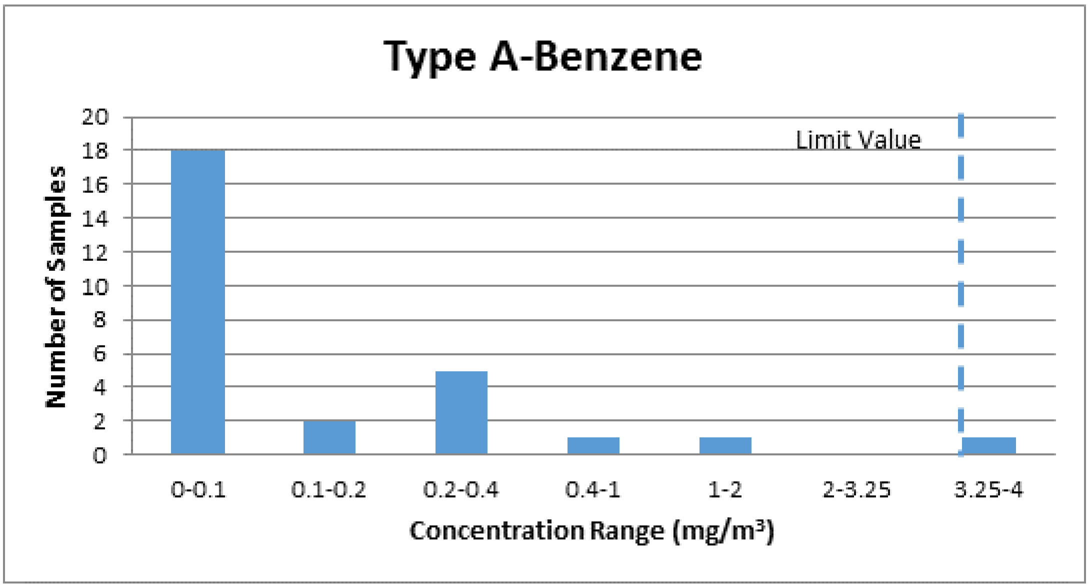


Figure A.1 Frequency Distribution of A Type Industry-Benzene

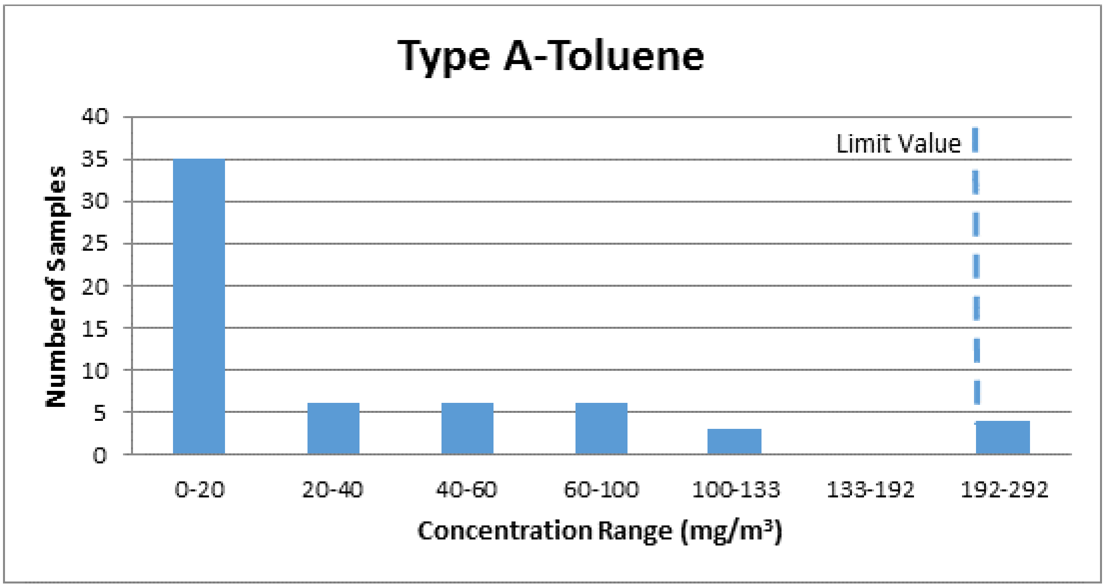


Figure A.2 Frequency Distribution of A Type Industry-Toluene

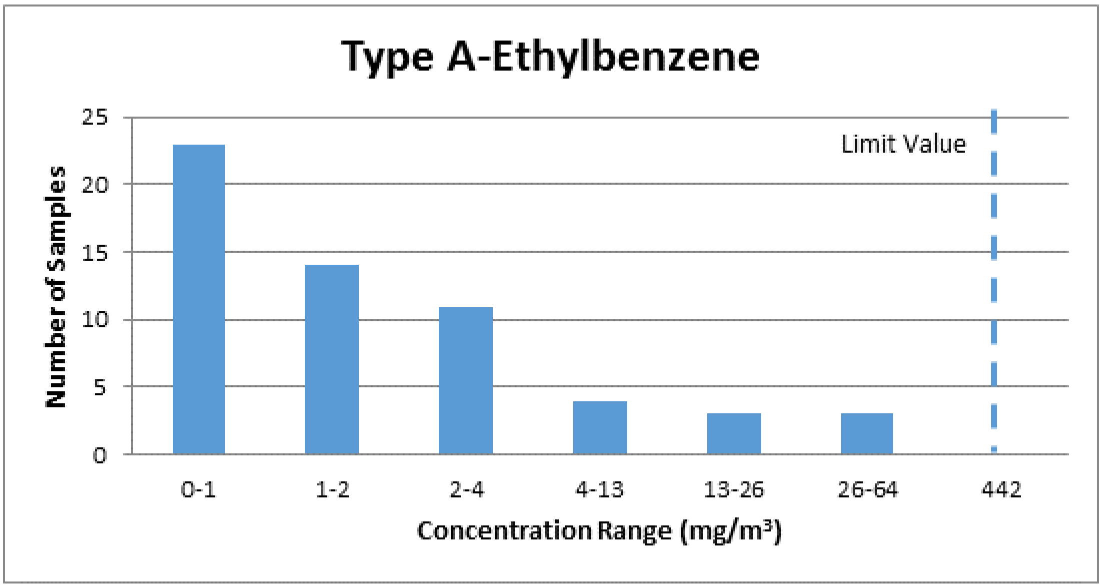


Figure A.3 Frequency Distribution of A Type Industry-Ethylbenzene

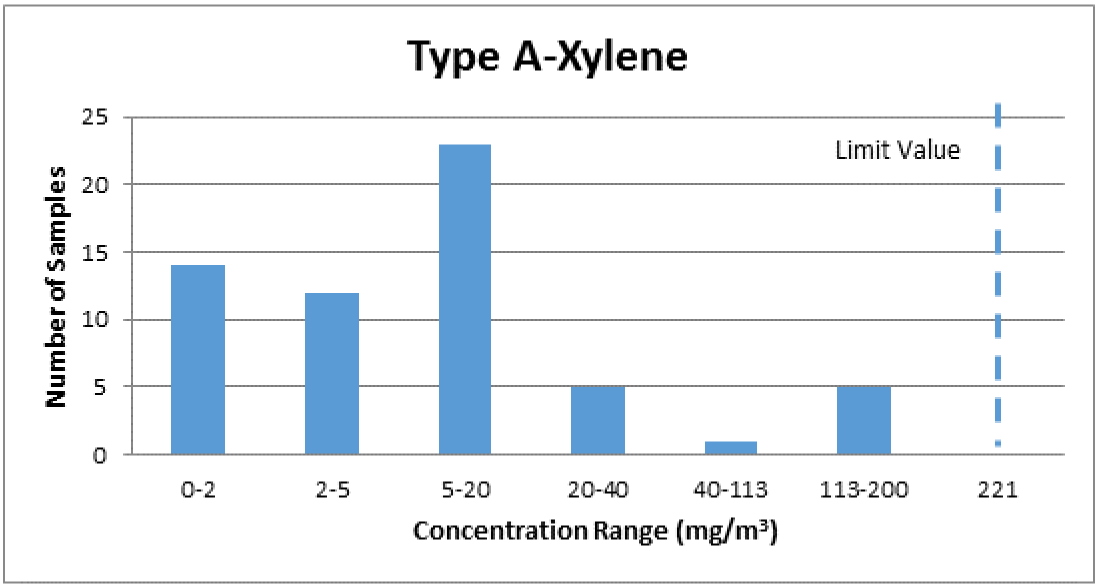


Figure A.4 Frequency Distribution of A Type Industry-Xylene

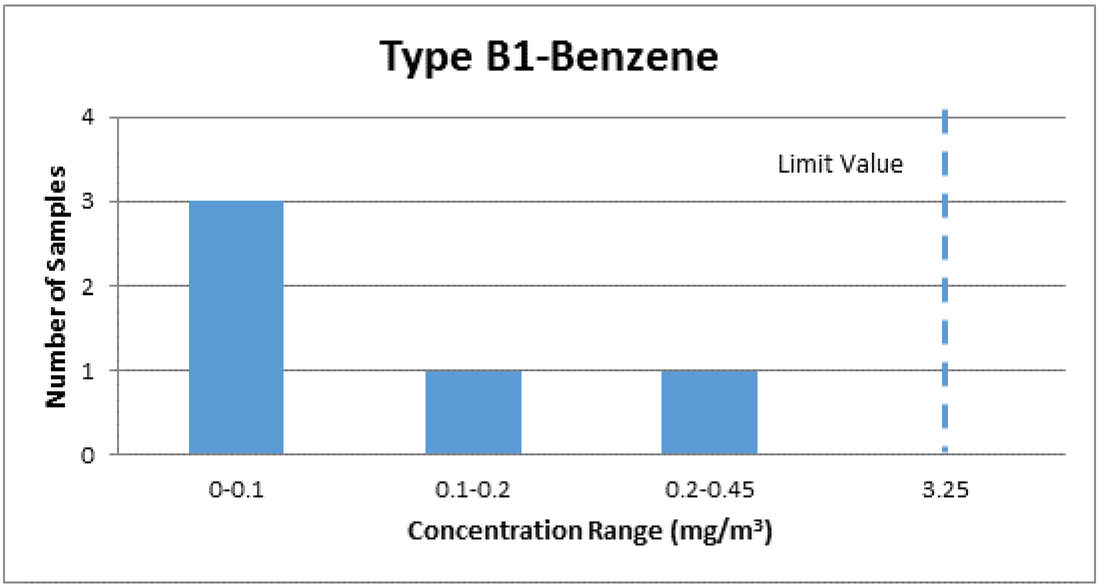


Figure A.5 Frequency Distribution of B1 Type Industry-Benzene

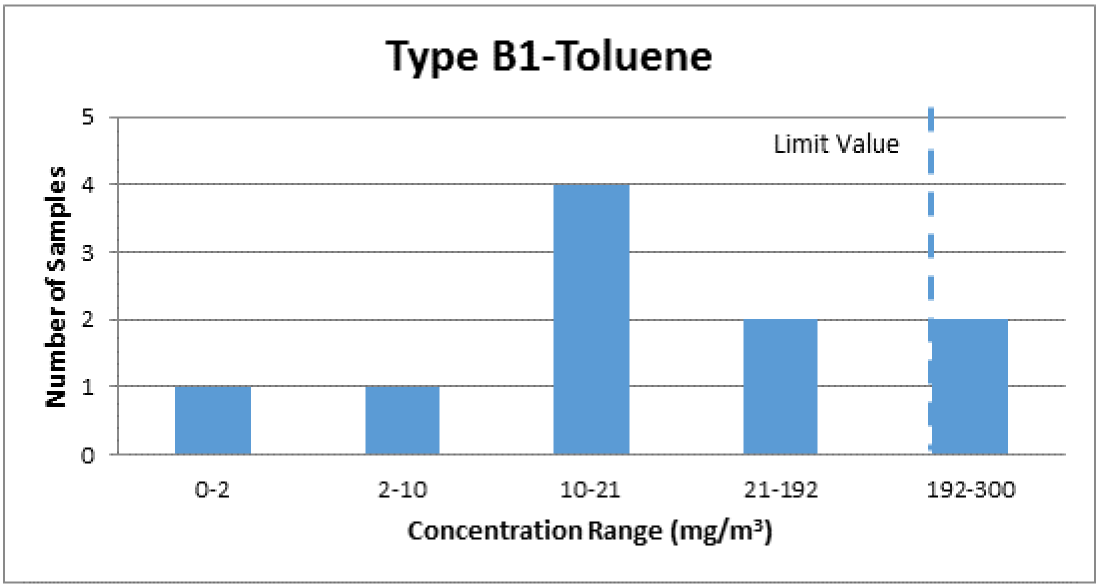


Figure A.6 Frequency Distribution of B1 Type Industry-Toluene

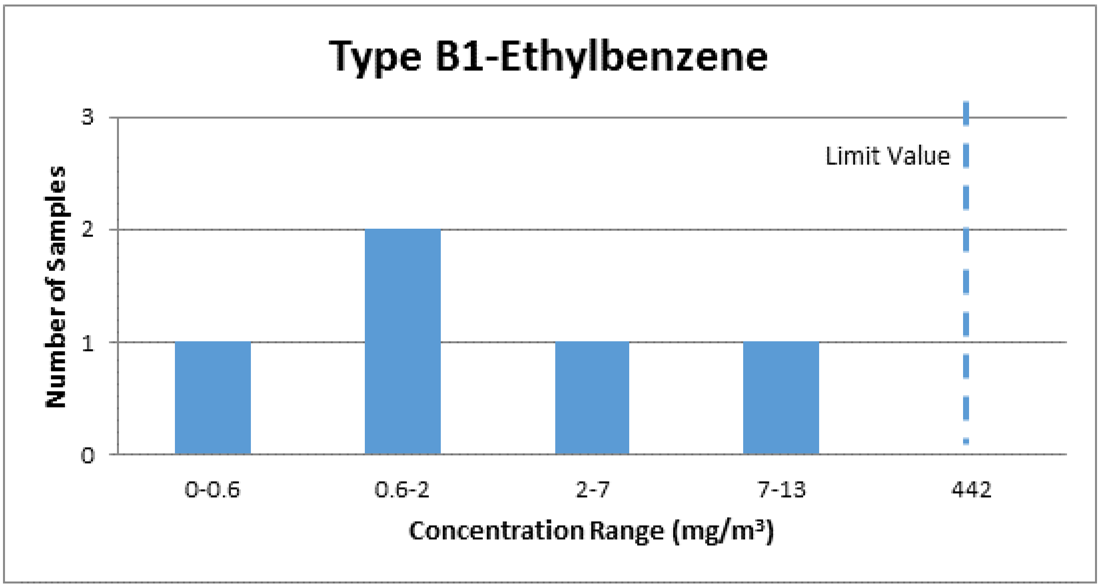


Figure A.7 Frequency Distribution of B1 Type Industry-Ethylbenzene

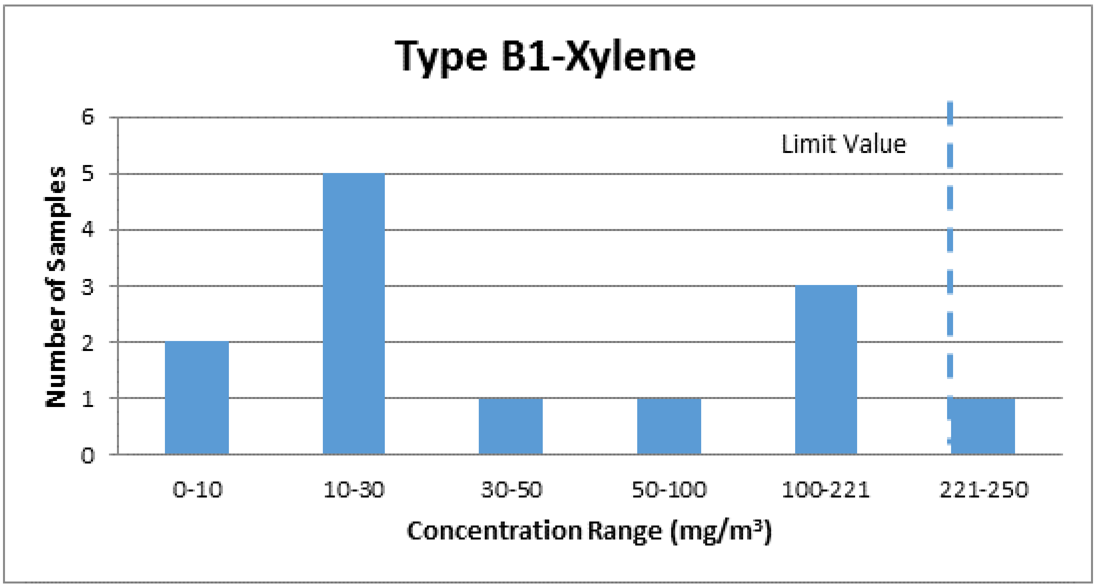


Figure A.8 Frequency Distribution of B1 Type Industry-Xylene

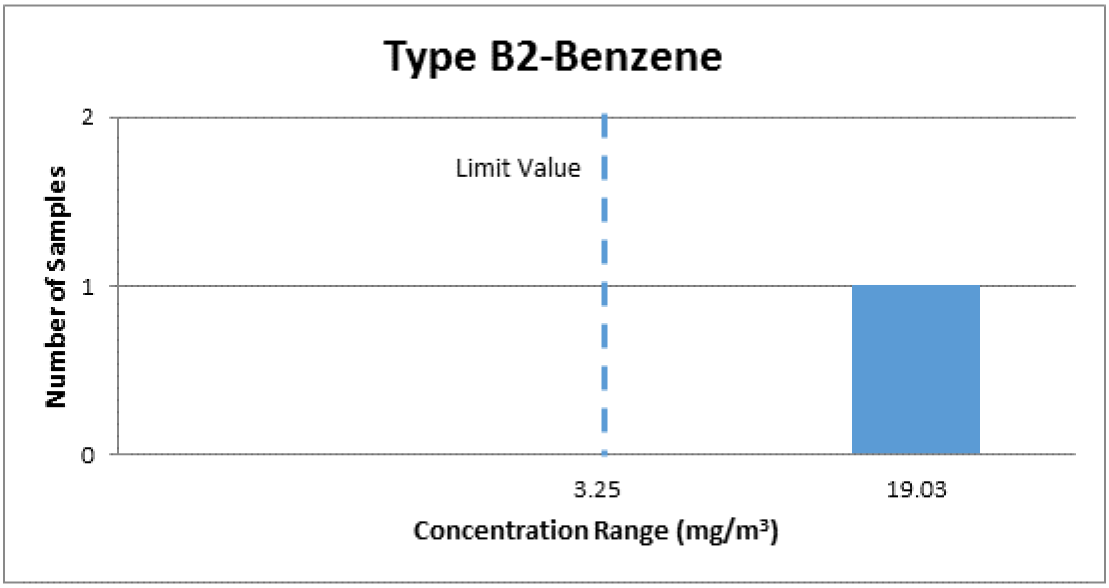


Figure A.9 Frequency Distribution of B2 Type Industry-Benzene

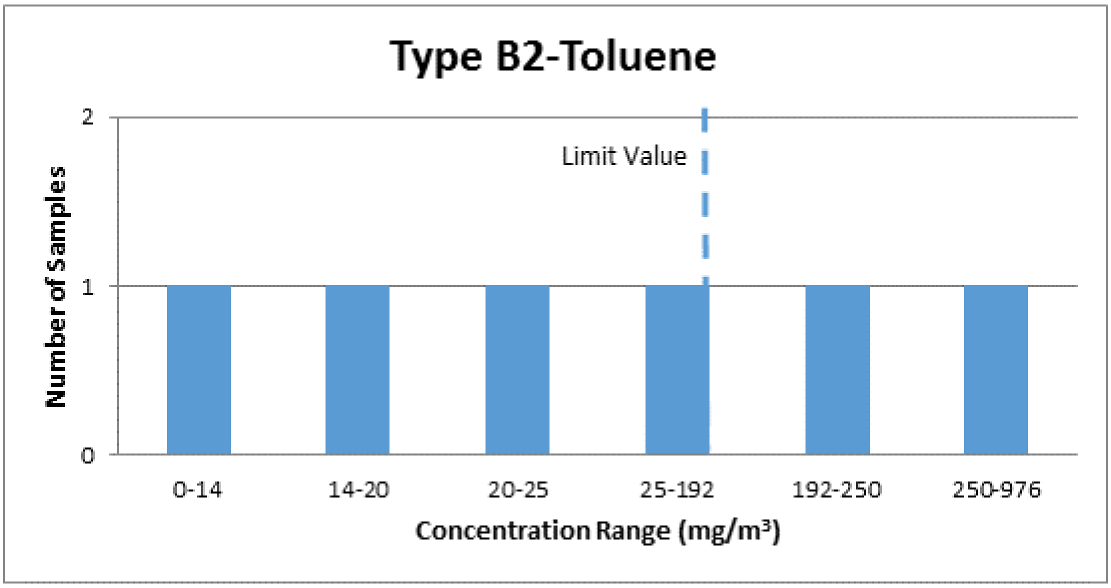


Figure A.10 Frequency Distribution of B2 Type Industry-Toluene

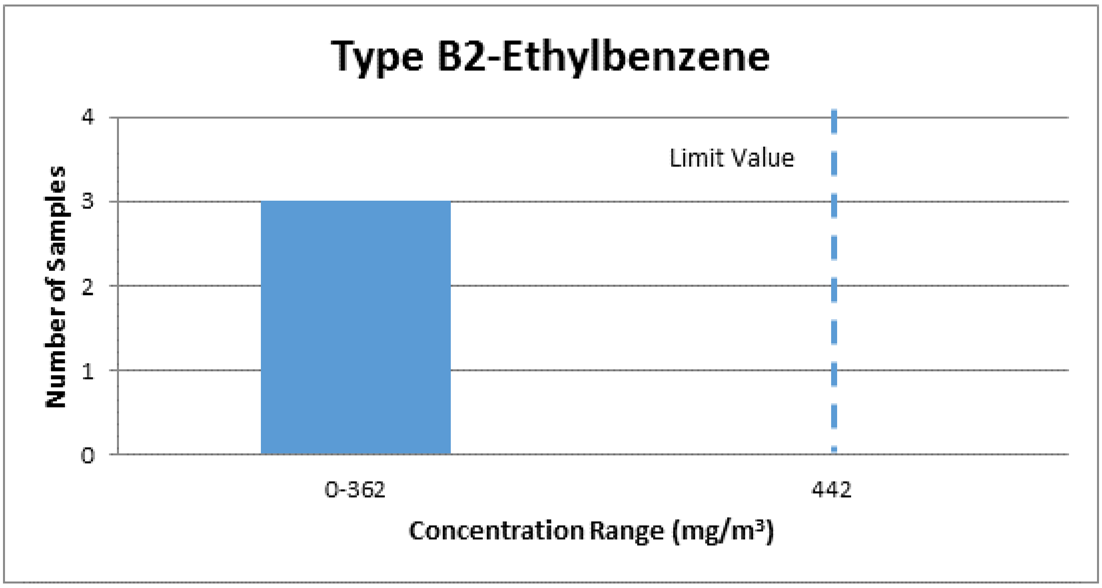


Figure A.11 Frequency Distribution of B2 Type Industry-Ethylbenzene

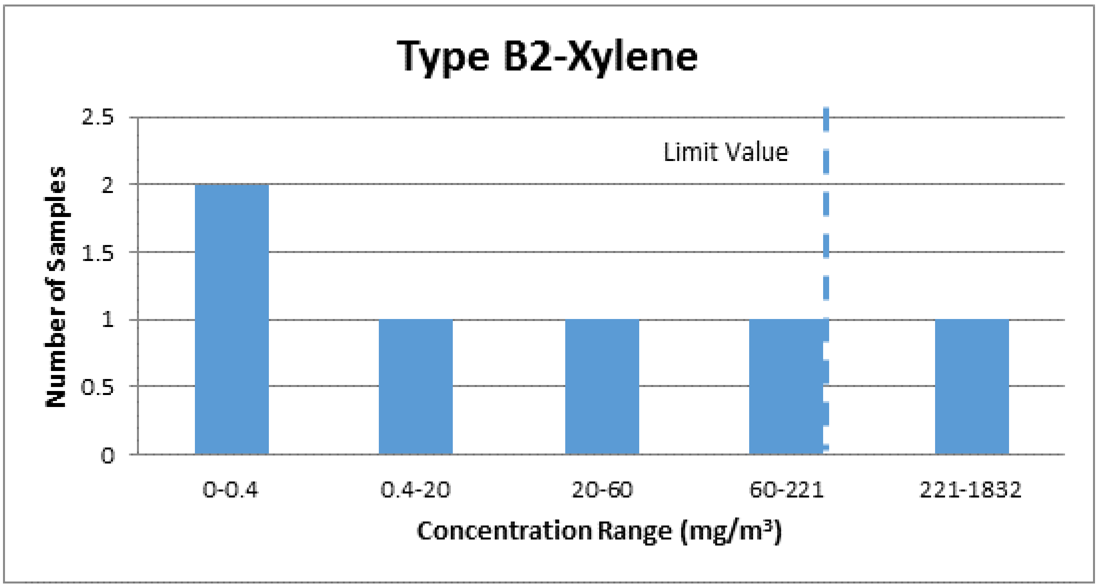


Figure A.12 Frequency Distribution of B2 Type Industry-Xylene

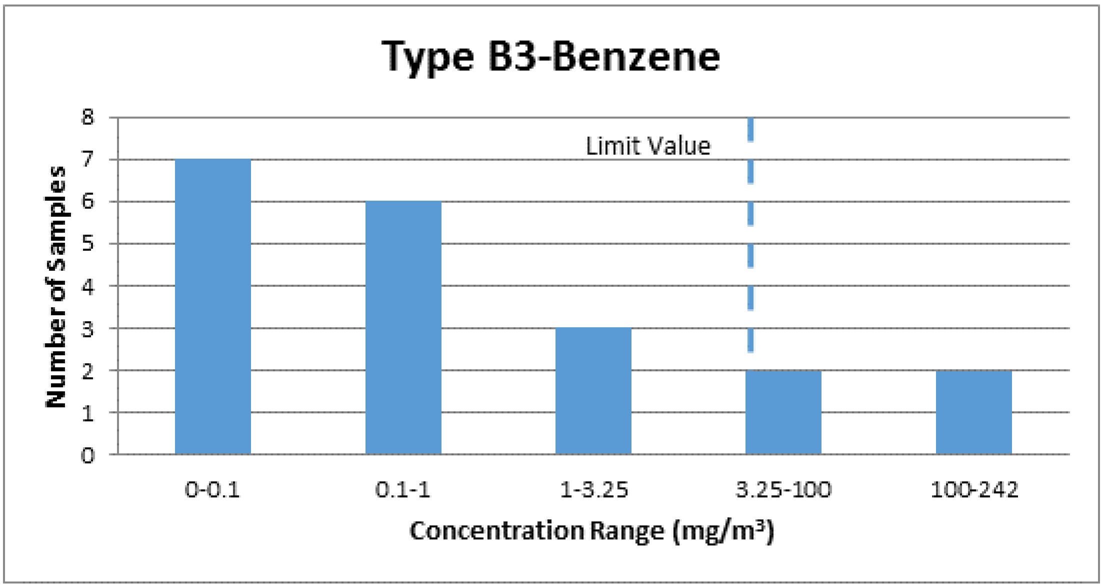


Figure A.13 Frequency Distribution of B3 Type Industry-Benzene

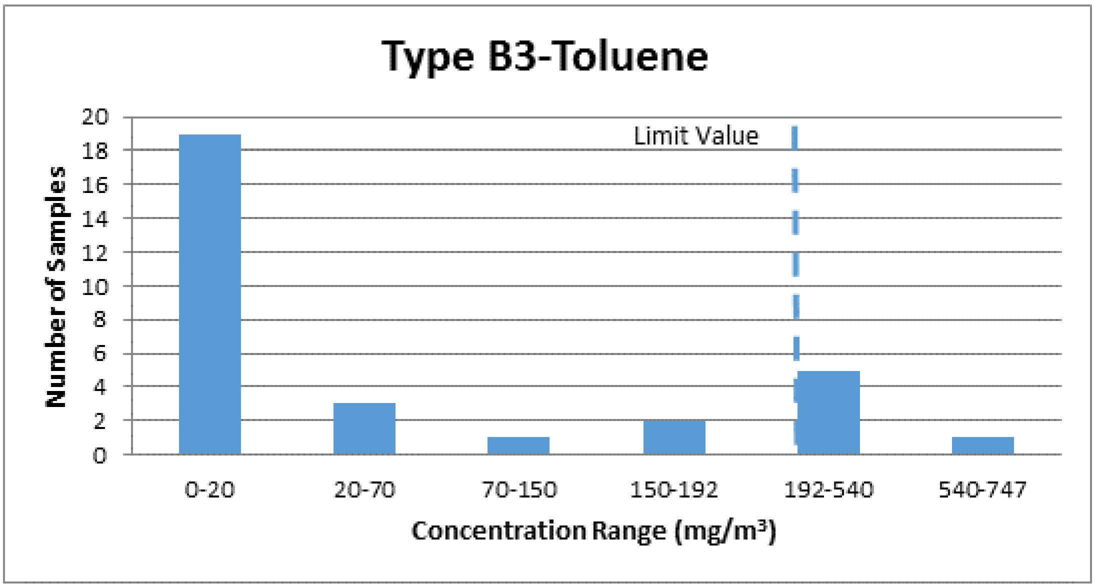


Figure A.14 Frequency Distribution of B3 Type Industry-Toluene

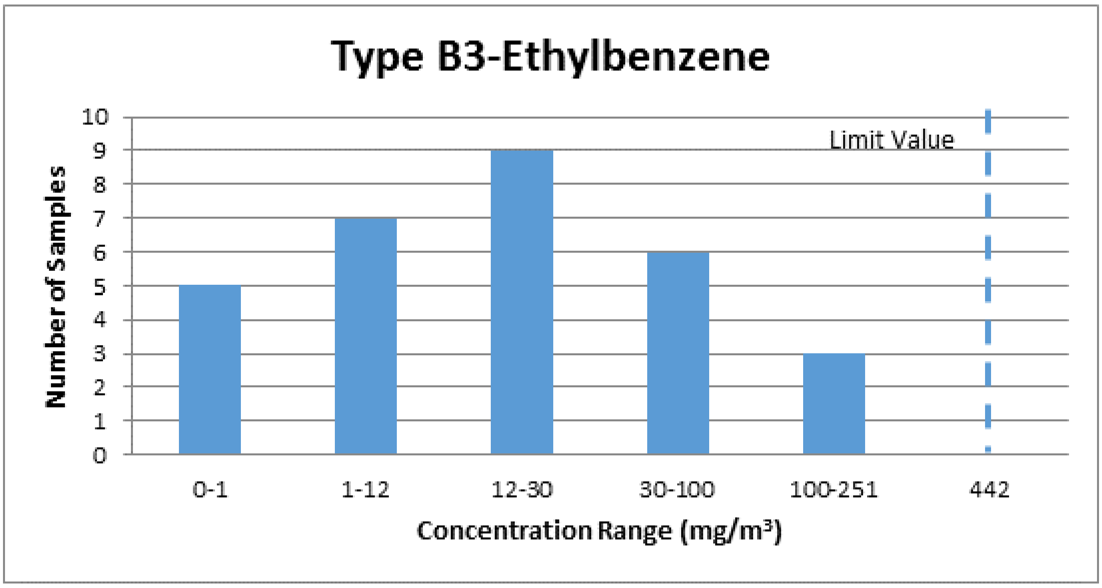


Figure A.15 Frequency Distribution of B3 Type Industry-Ethylbenzene

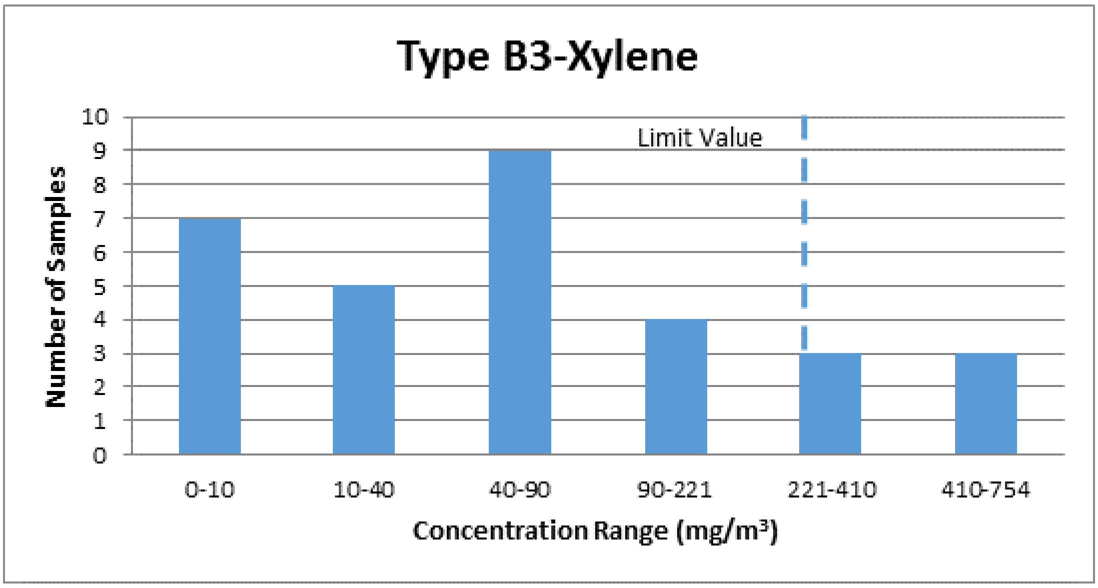


Figure A.16 Frequency Distribution of B3 Type Industry-Xylene

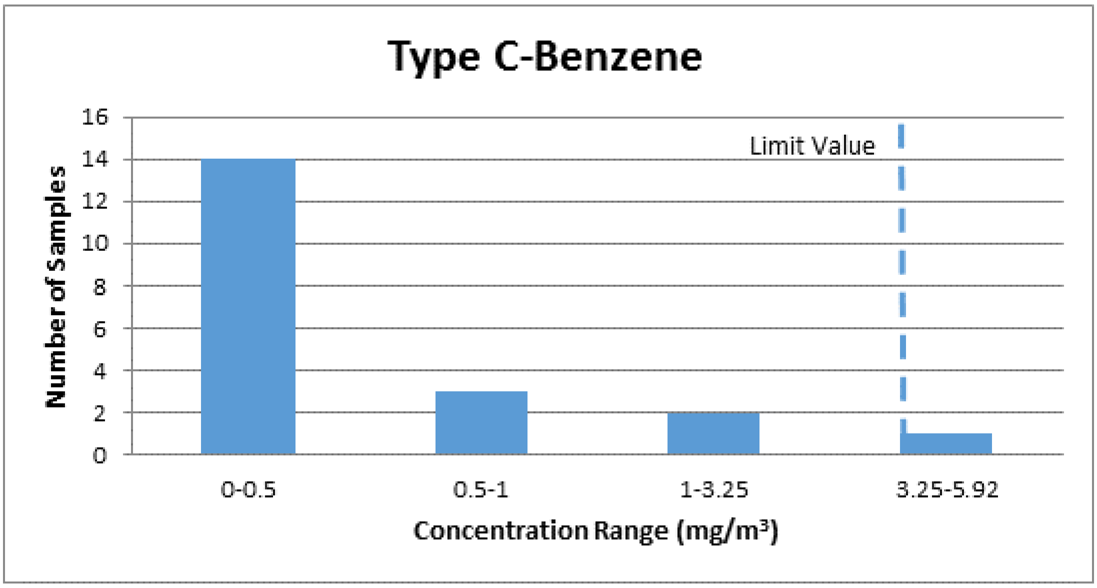


Figure A.17 Frequency Distribution of C Type Industry-Benzene

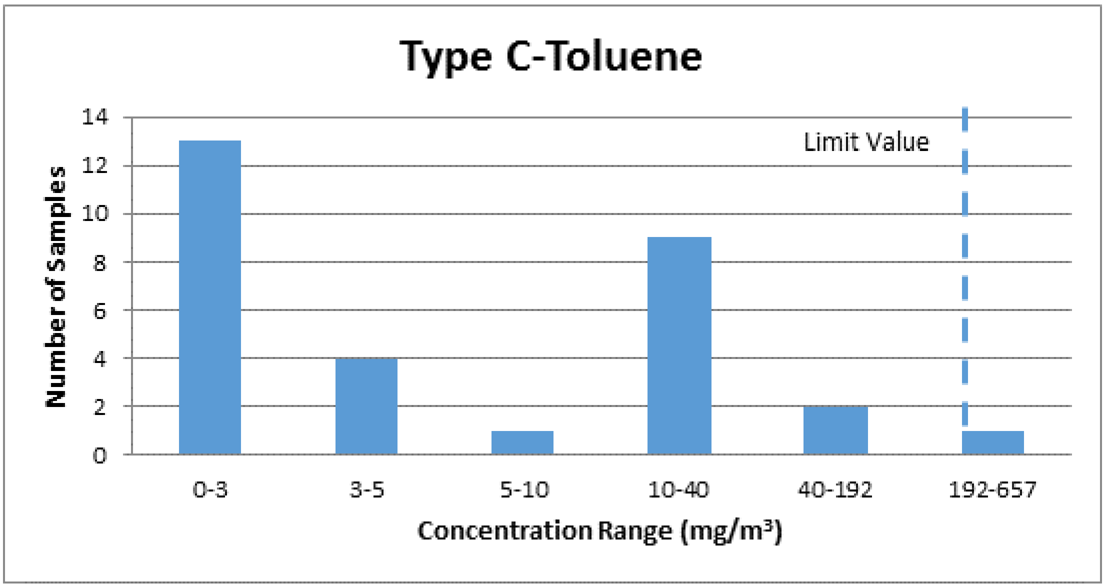


Figure A.18 Frequency Distribution of C Type Industry-Toluene

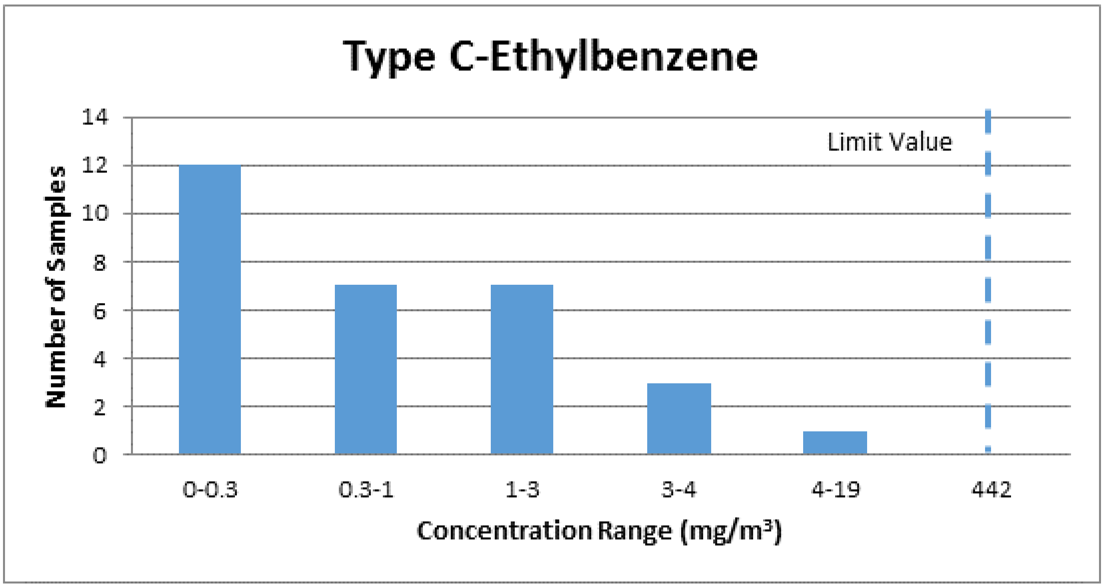


Figure A.19 Frequency Distribution of C Type Industry-Ethylbenzene

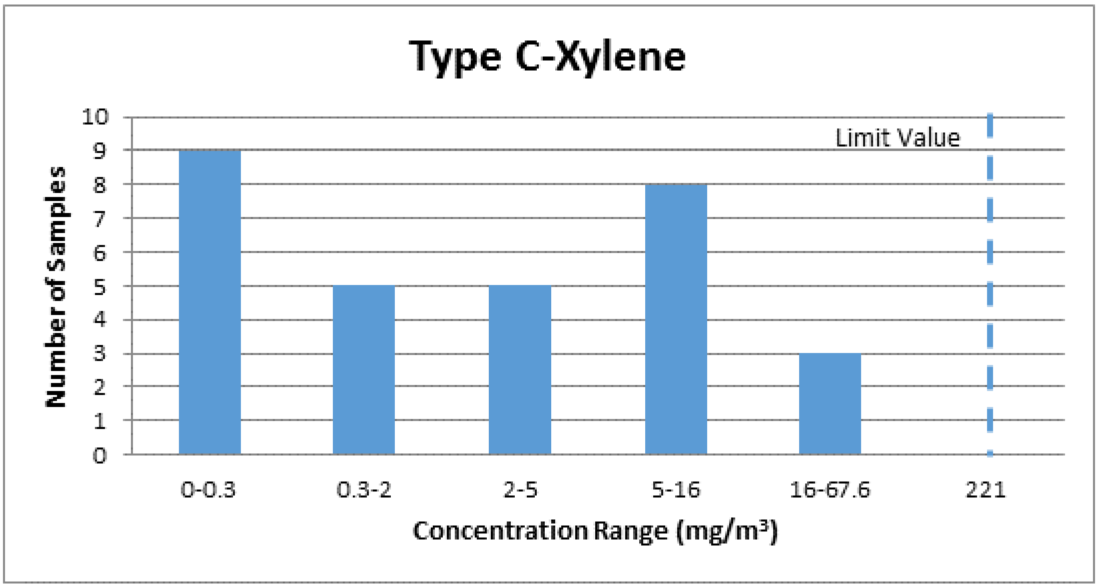


Figure A.20 Frequency Distribution of C Type Industry-Xylene

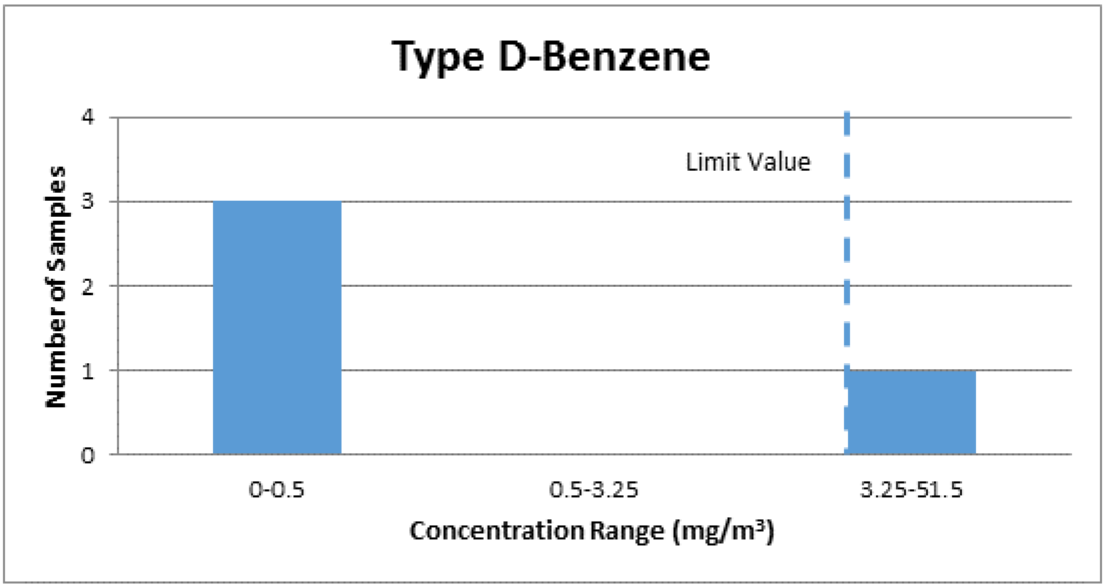


Figure A.21 Frequency Distribution of D Type Industry-Benzene

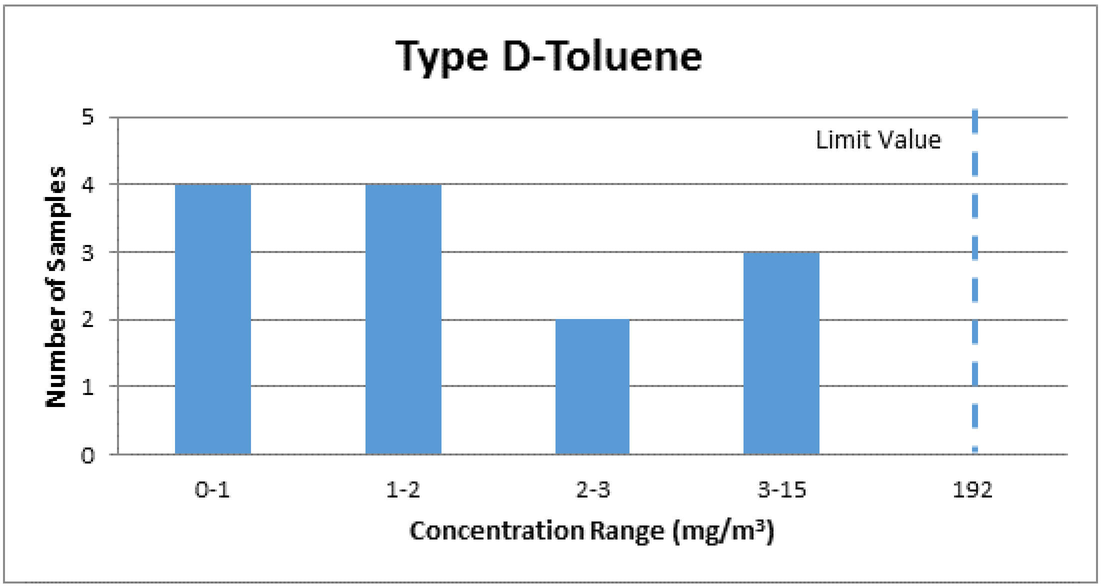


Figure A.22 Frequency Distribution of D Type Industry-Toluene

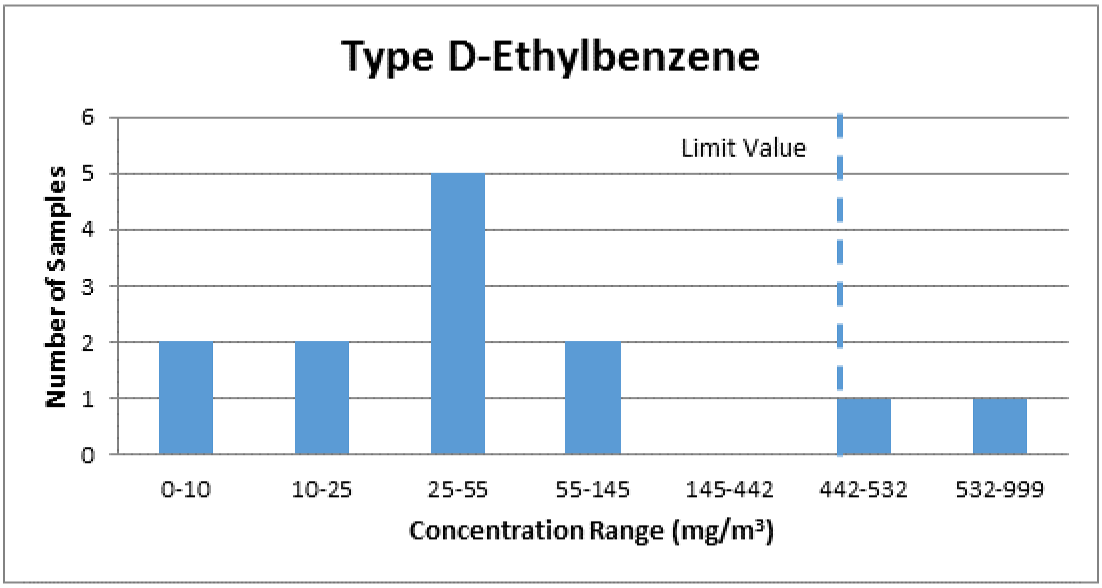


Figure A.23 Frequency Distribution of D Type Industry-Ethylbenzene

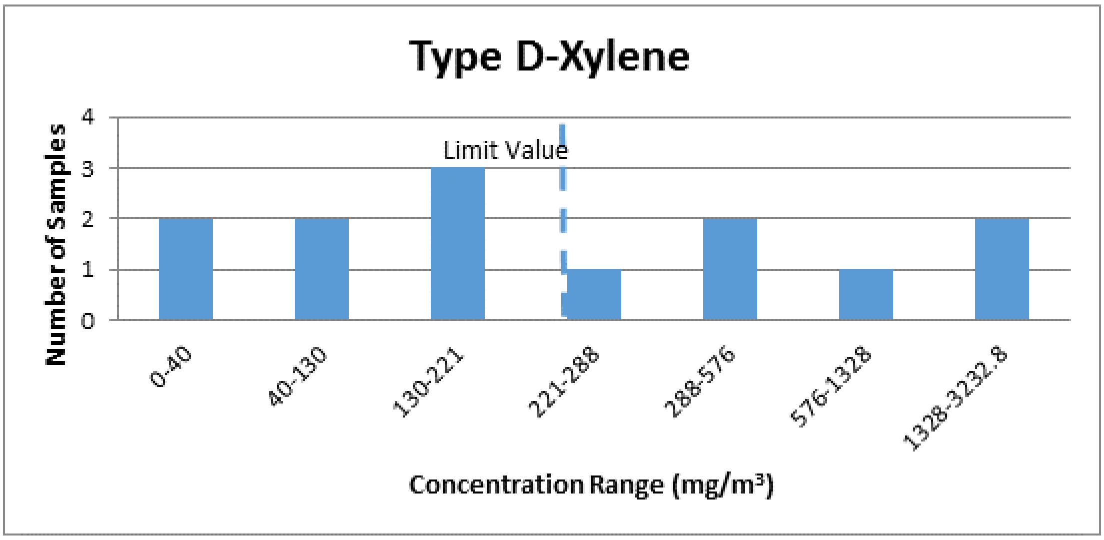


Figure A.24 Frequency Distribution of D Type Industry-Xylene

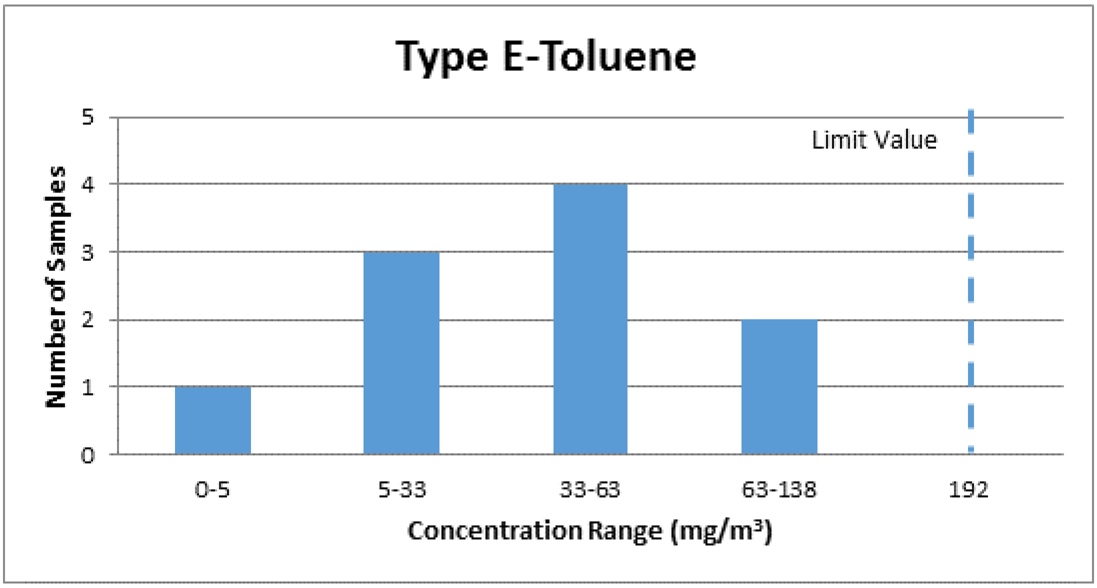


Figure A.25 Frequency Distribution of E Type Industry-Toluene

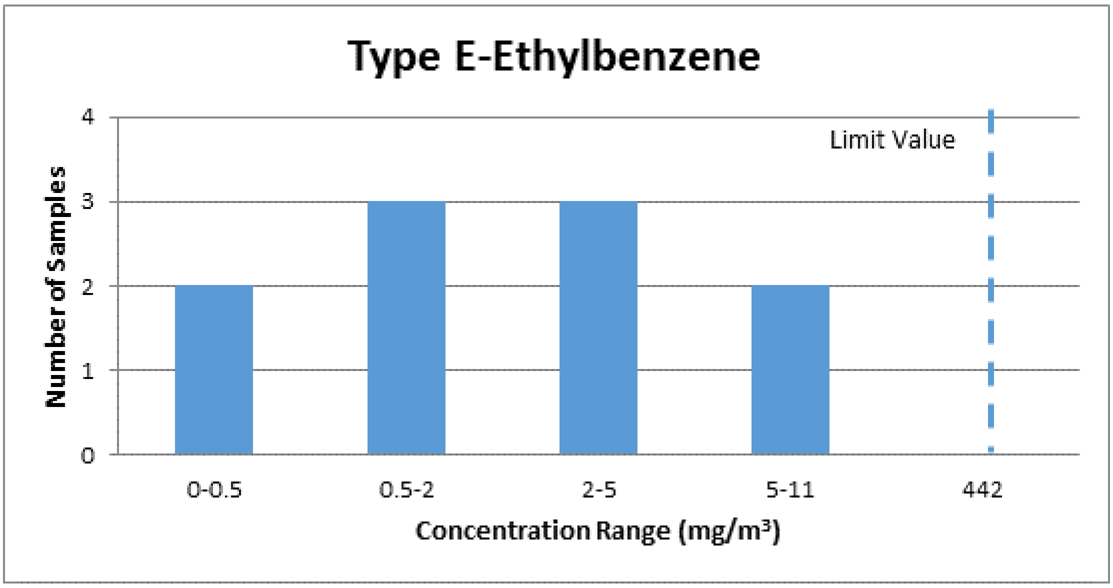


Figure A.26 Frequency Distribution of E Type Industry-Ethylbenzene

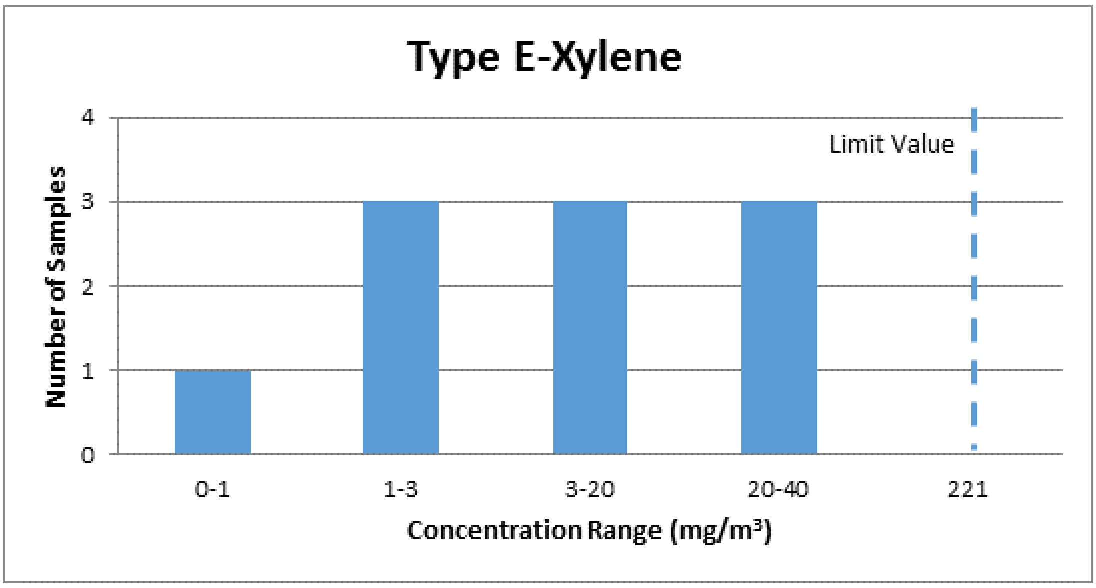


Figure A.27 Frequency Distribution of E Type Industry-Xylene

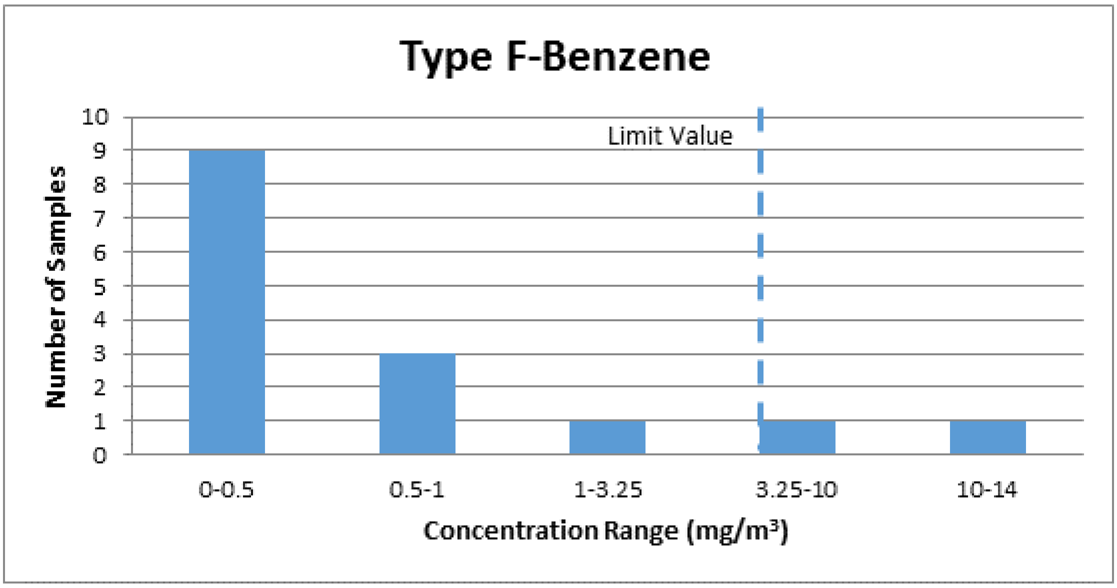


Figure A.28 Frequency Distribution of F Type Industry-Benzene

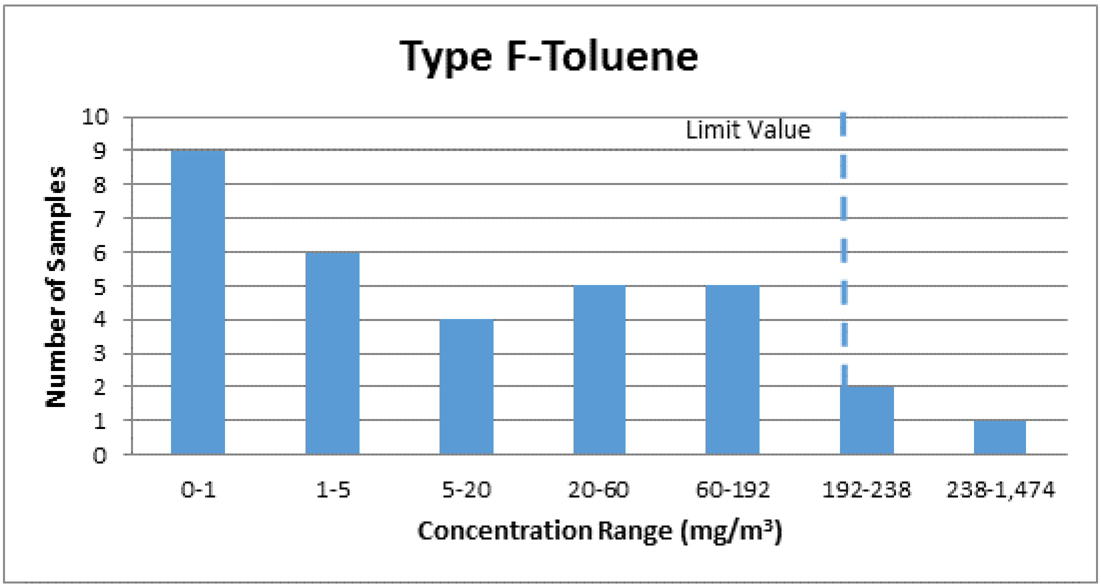


Figure A.29 Frequency Distribution of F Type Industry-Toluene

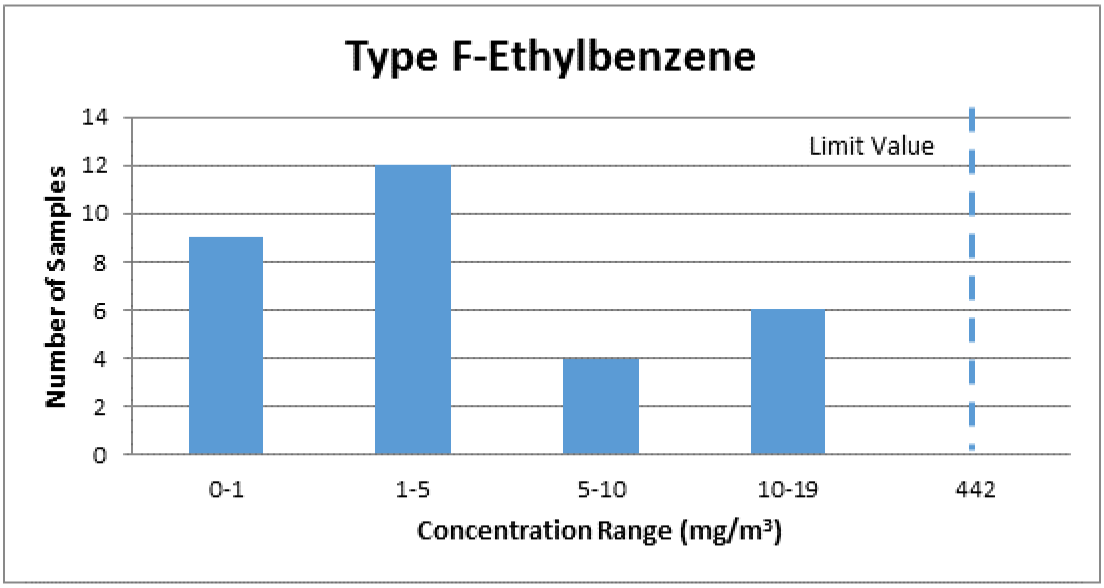


Figure A.30 Frequency Distribution of F Type Industry-Ethylbenzene

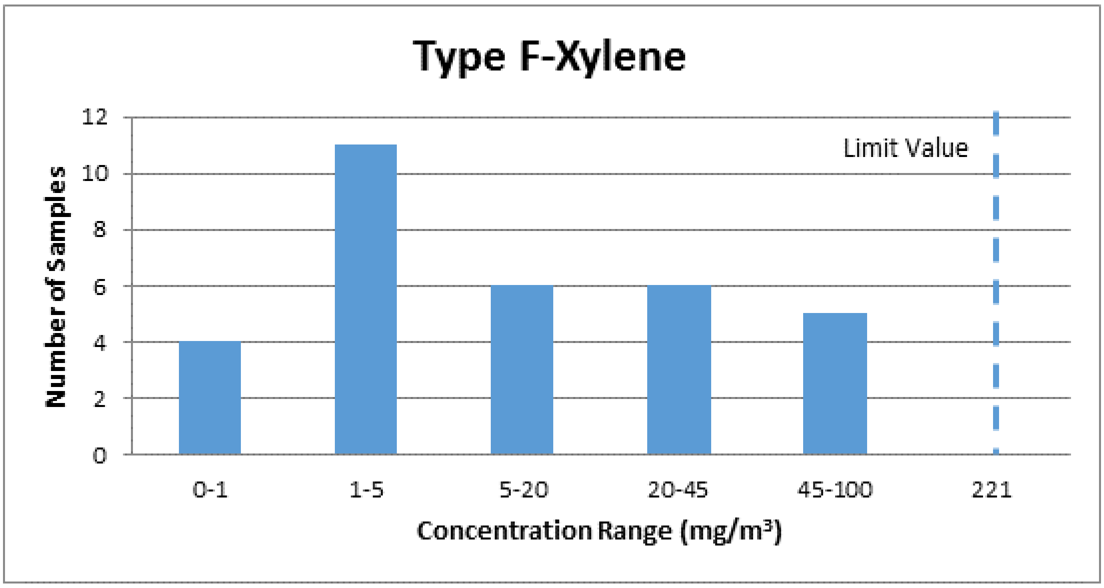


Figure A.31 Frequency Distribution of F Type Industry-Xylene

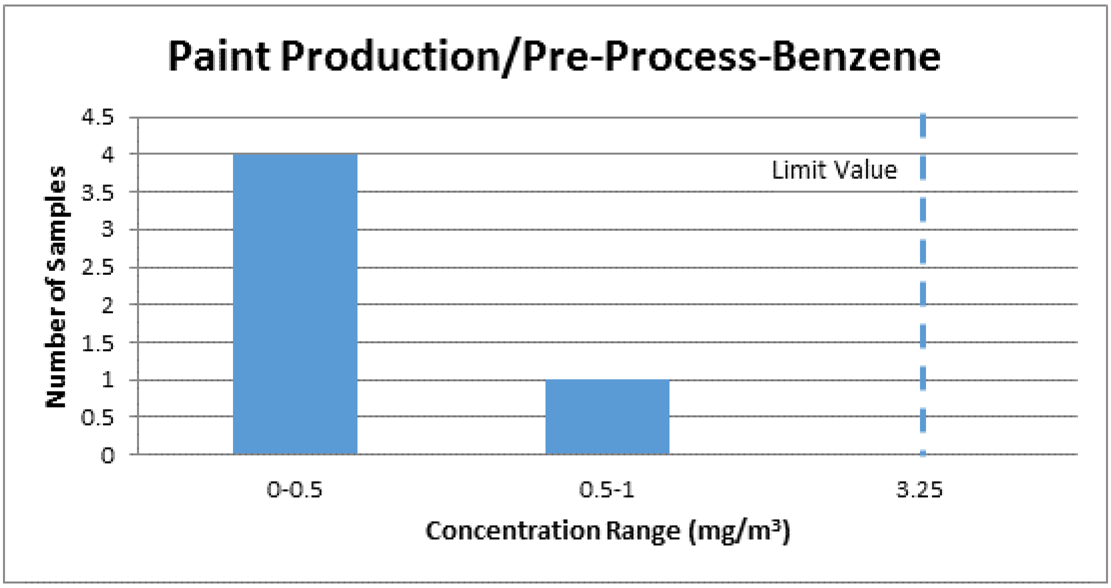


Figure A.32 Frequency Distribution of Paint Production/Pre-Process-Benzene

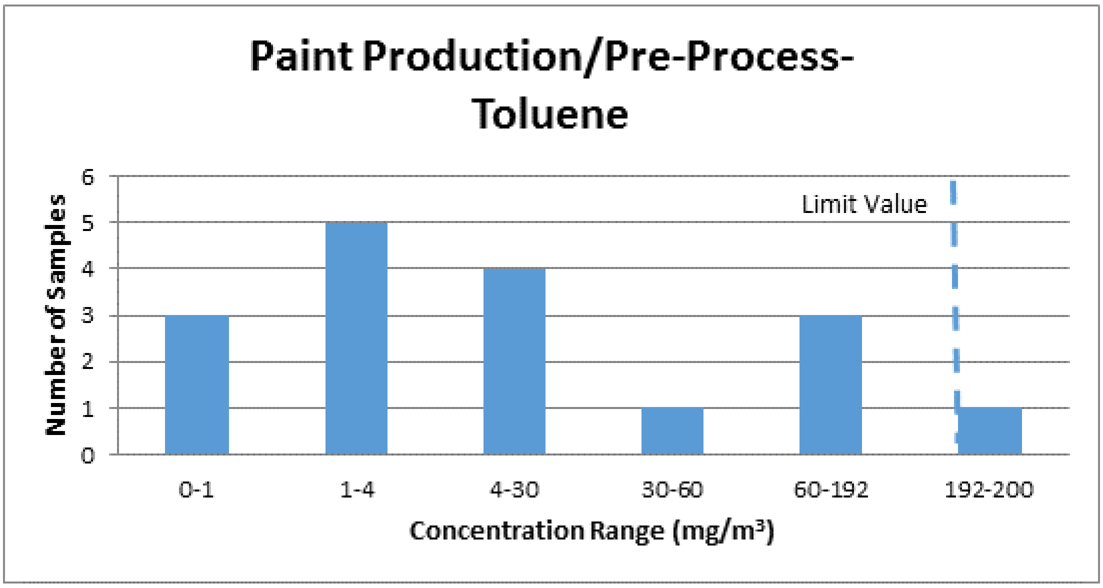


Figure A.33 Frequency Distribution of Paint Production/Pre-Process-Toluene

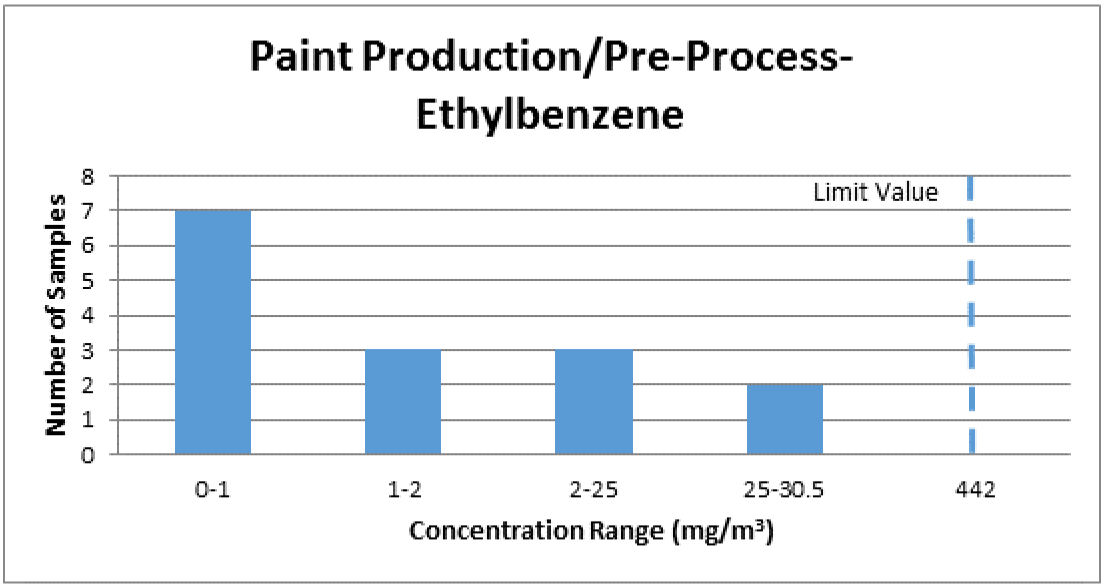


Figure A.34 Frequency Distribution of Paint Production/Pre-Process-Ethylbenzene

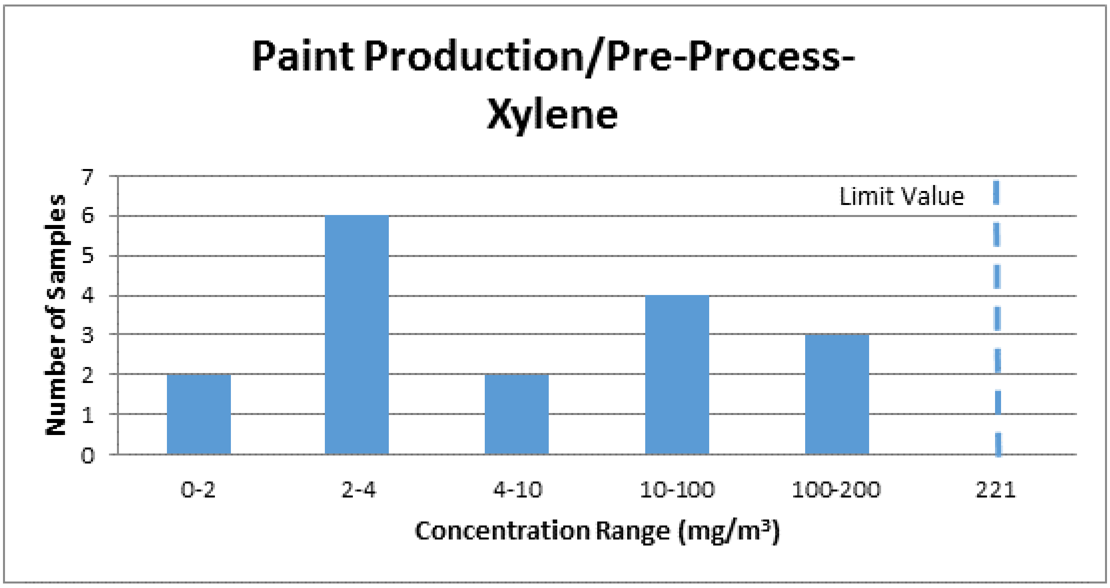


Figure A.35 Frequency Distribution of Paint Production/Pre-Process-Xylene

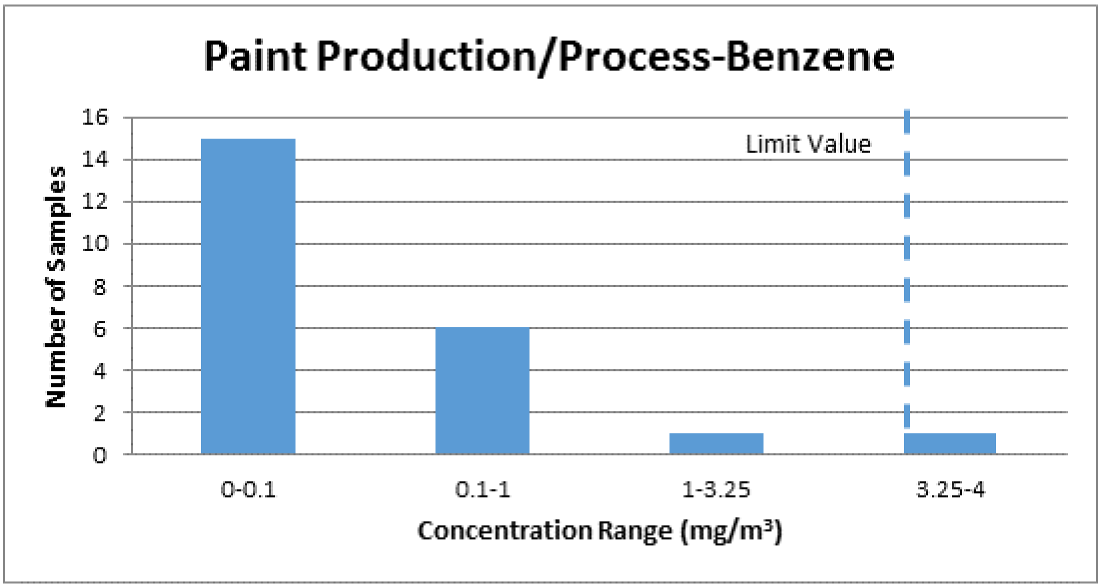


Figure A.36 Frequency Distribution of Paint Production/Process-Benzene

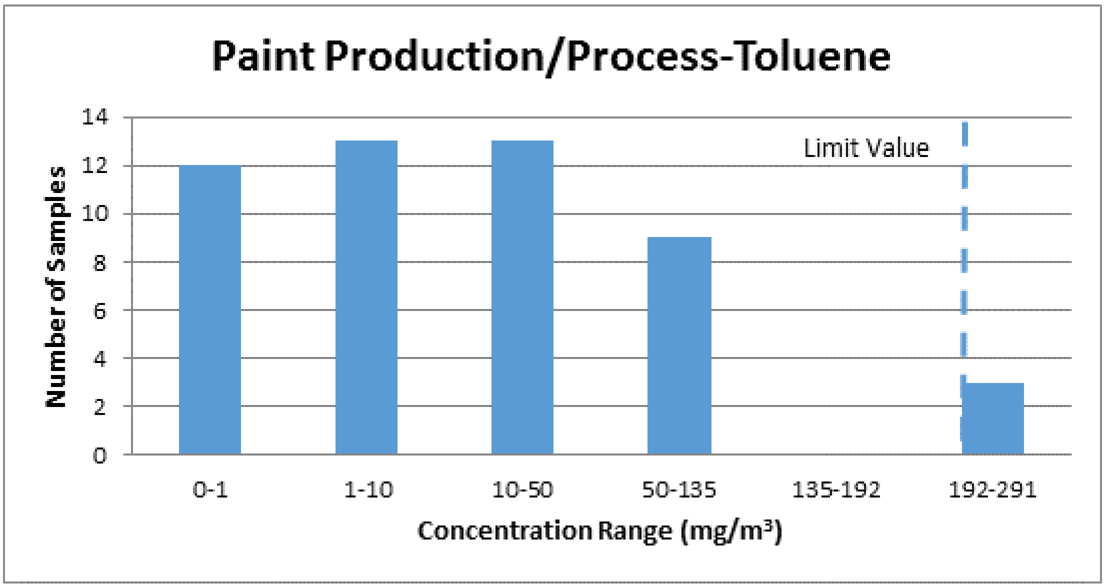


Figure A.37 Frequency Distribution of Paint Production/Process-Toluene

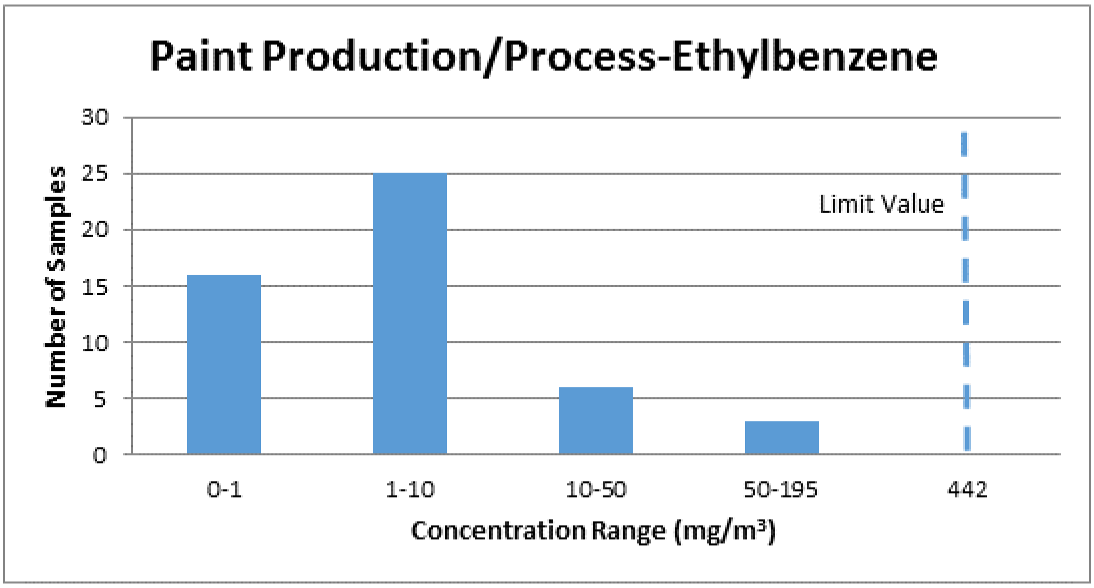


Figure A.38 Frequency Distribution of Paint Production/Process-Ethylbenzene

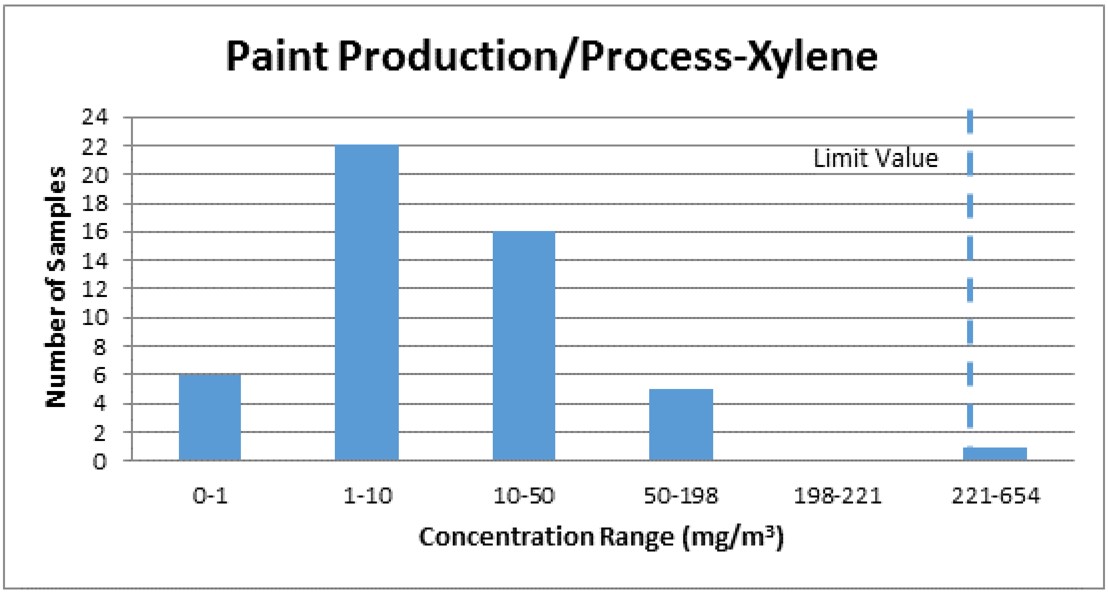


Figure A.39 Frequency Distribution of Paint Production/Process-Xylene

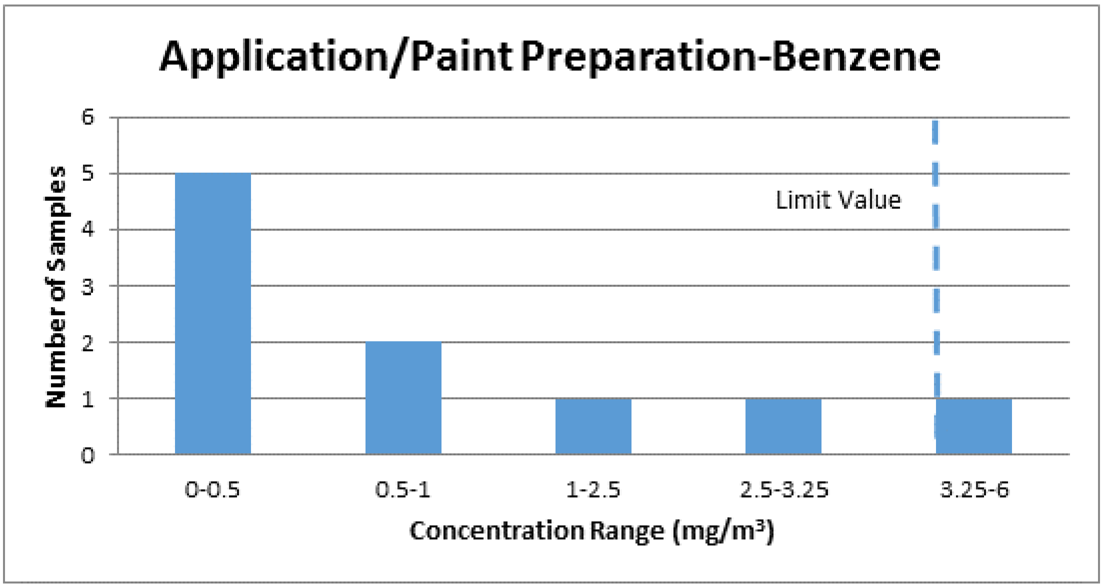


Figure A.40 Frequency Distribution of Application/Paint Preparation-Benzene

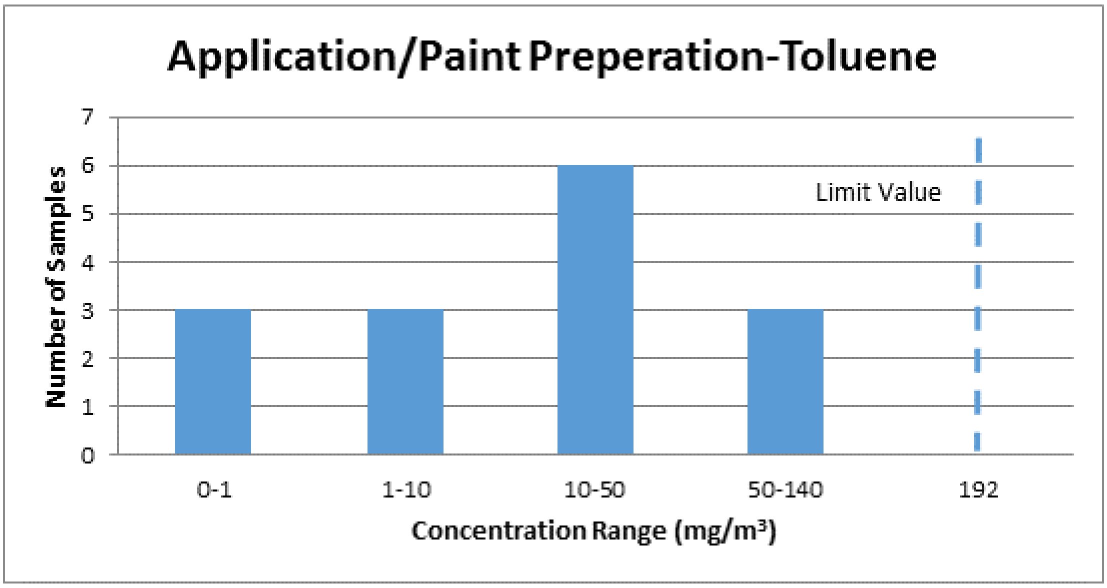


Figure A.41 Frequency Distribution of Application/Paint Preparation-Toluene

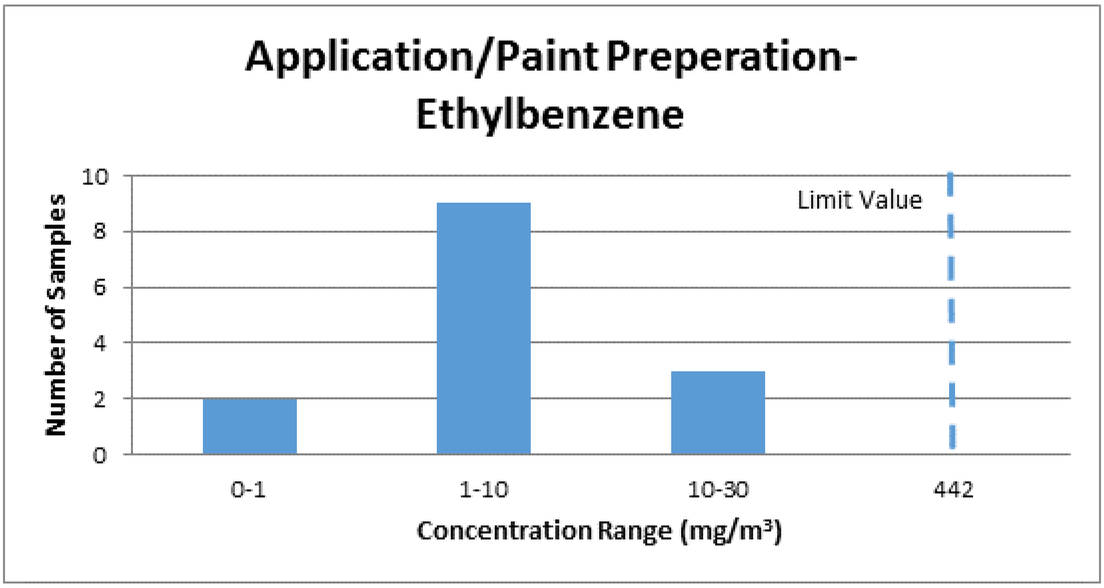


Figure A.42 Frequency Distribution of Application/Paint Preparation-Ethylbenzene

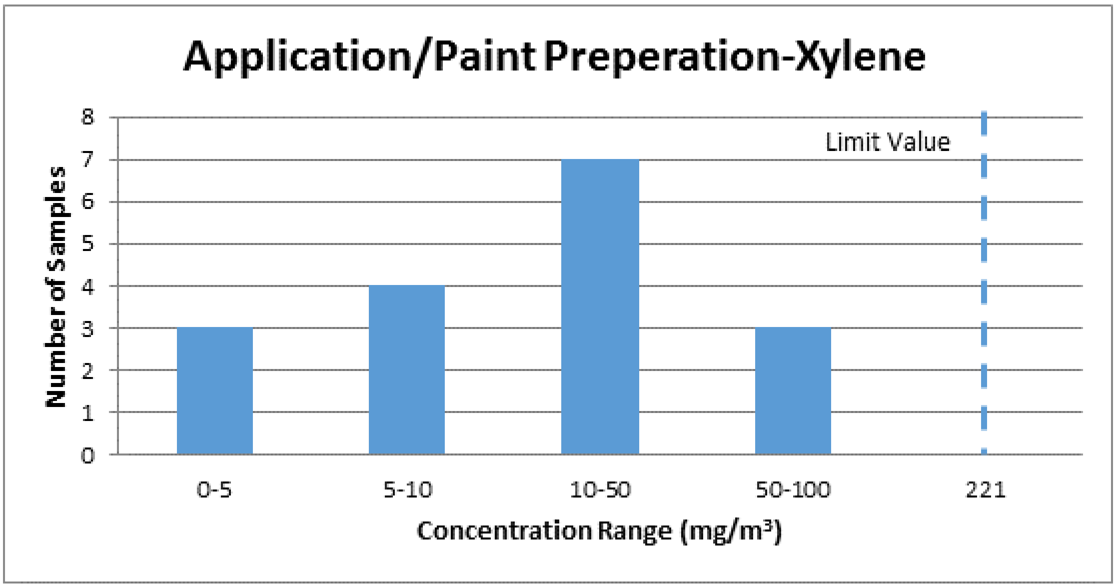


Figure A.43 Frequency Distribution of Application/Paint Preparation-Xylene

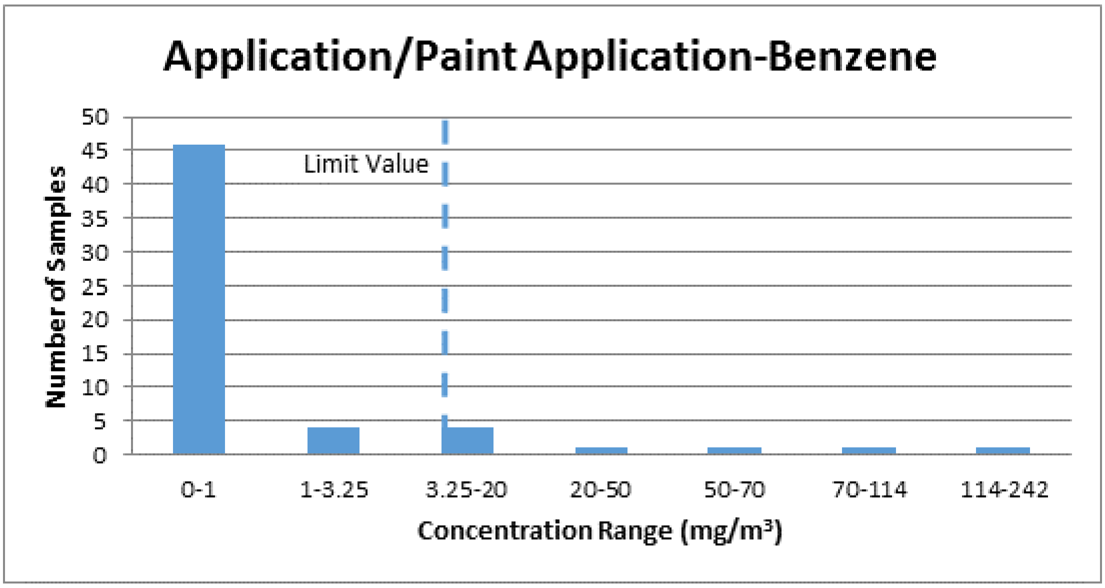


Figure A.44 Frequency Distribution of Application/Paint Application-Benzene

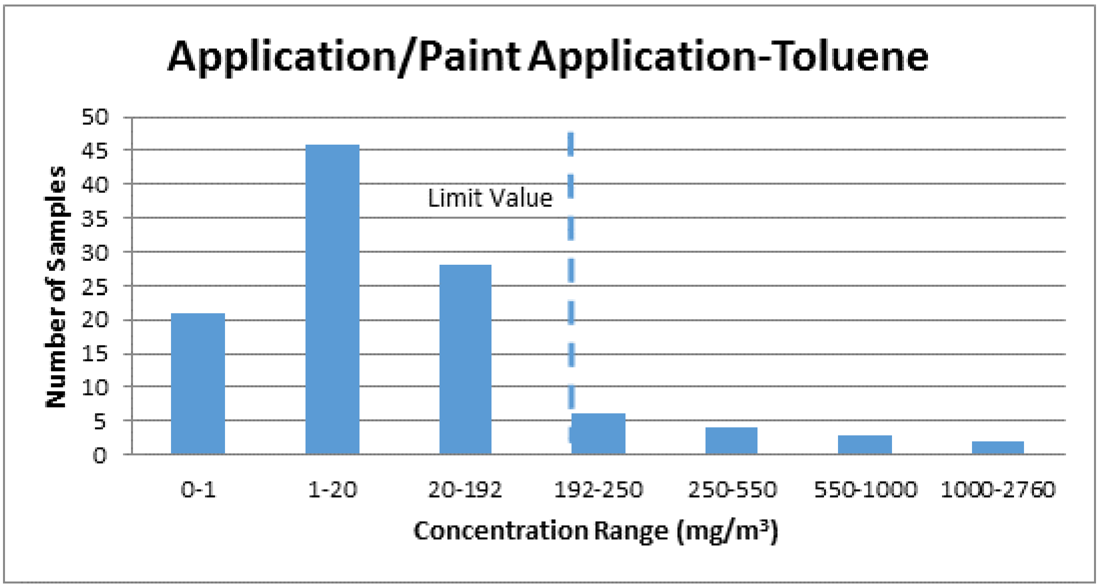


Figure A.45 Frequency Distribution of Application/Paint Application-Toluene

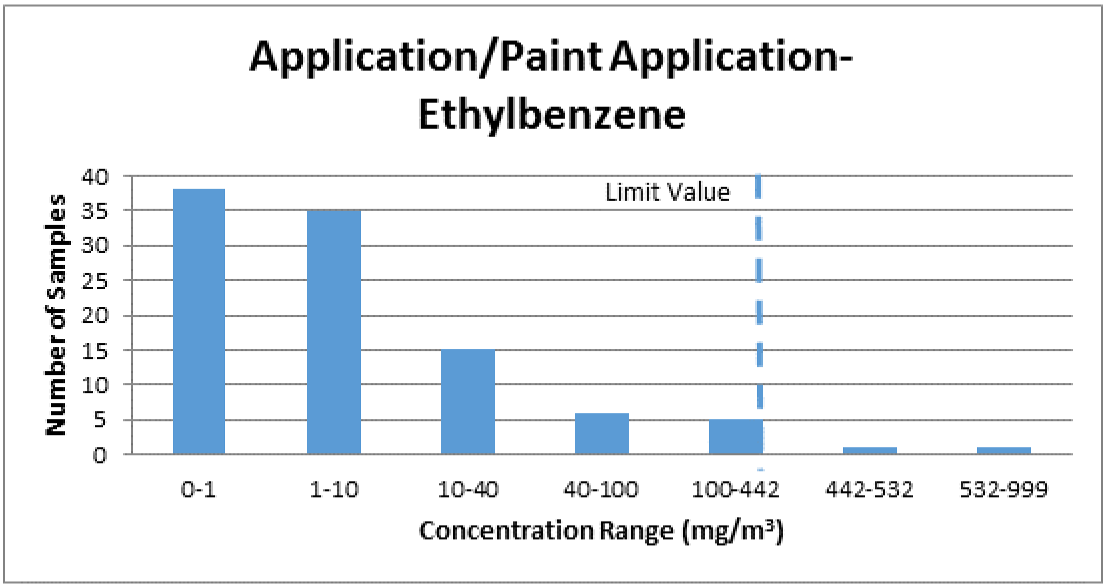


Figure A.46 Frequency Distribution of Application/Paint Application-Ethylbenzene

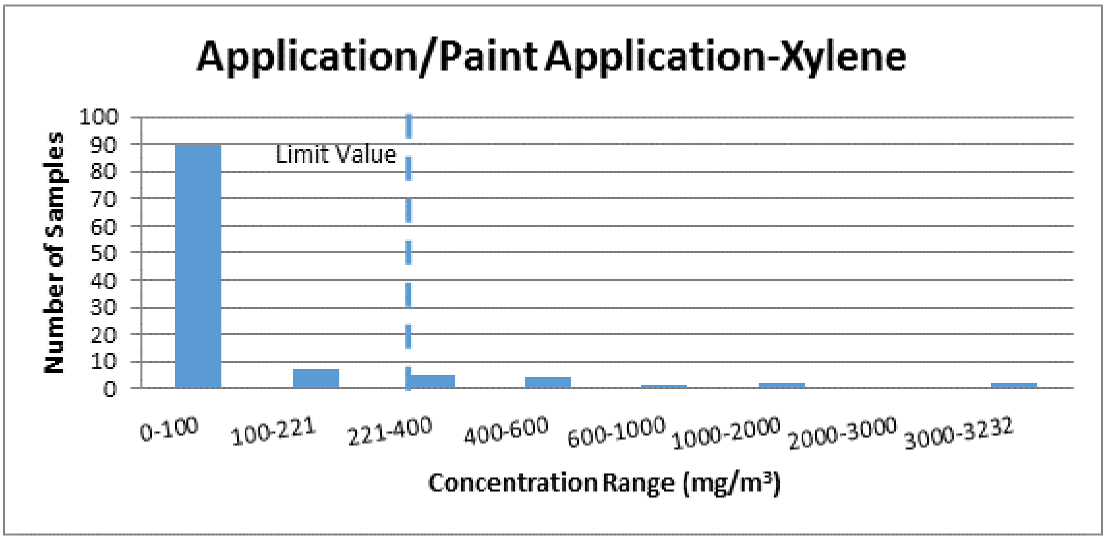


Figure A.47 Frequency Distribution of Application/Paint Application-Xylene