VILNIAUS GEDIMINO TECHNIKOS UNIVERSITETAS
APLINKOS INŽINERIJOS FAKULTETAS
APLINKOS APSAUGOS KATEDRA

Žana Bikbajeva

LAKIŲJŲ ORGANINIŲ JUNGINIŲ TYRIMAS NUO BENZINO DEGALINIŲ

RESEARCH OF VOLATILE ORGANIC COMPOUNDS FROM PETROL FILLING STATIONS

Baigiamasis magistro darbas

Aplinkos apsaugos vadybos ir švariosios gamybos studijų programa, valstybinis kodas 62404T103
Aplinkos inžinerijos mokslo kryptis

Vilnius, 2008

TABLE OF CONTENTS

Introduction 9
1. THEORETICAL PART 11
  1.1. Clarifying issues of air pollution with VOCs 11
    1.1.1. The magnitude of health impacts associated with VOCs from petrol 14
    1.1.2. Tropospheric ozone issue 17
    1.1.3. PM formation issue 20
  1.2. VOC emissions dependence on petrol composition 23
    1.2.1. Petrol nature 23
    1.2.2. Factors of petrol VOC emissions 26
  1.3. Typical petrol filling station 29
    1.3.1. Environmental legislation for petrol station 29
    1.3.2. Typical petrol station’s technology layout 30
    1.3.3. VOC emissions from petrol station 33
  1.4. VOCs’ estimation methods 36
    1.4.1. Total VOC approach 36
    1.4.2. Trends in VOCs concentrations in Europe 36
    1.4.3. Seasonal, diurnal variation and urban implication of VOCs 39
    1.4.4. Methods for VOCs measurement 41
    1.4.5. VOCs measurement worldwide 43
    1.4.6. Modelling approach 46
  Conclusions 49
2. RESEARCH PART 50
  2.1. Research sites 50
  2.2. Sampling 51
  2.3. Summary of method 54
    2.3.1. Scope and application 54
    2.3.2. Equipment and supplies 55
    2.3.3. Gas chromatograph preparation 57
    2.3.4. Analytical procedure 59
3. ANALITICAL PART 60
  3.1. Experiment results 60
  3.2. Results evaluation 64
  3.3. Results discussion 75
  3.4. Comparative analysis 77
  Conclusions 78
4. MODELLING PART 79
  4.1. Model description 79
  4.2. Results and graphical pictures of solving models 81
  4.3. Models output interpretation 88
  Conclusions 90
5. General conclusions and recomendations 91
References
Articles
Appendixes

LIST OF TABLES

Table 1.1 Lifetimes of VOCs due to gas-phase reactions
Table 1.2 Petrol, all grades exposure limits
Table 1.3 Petrol, all grades toxic content
Table 1.4 Basic chemical-physical properties of petrol
Table 1.5 Factors of petrol vapour and benzene emission for a typical petrol station
Table 1.6 VOC emissions from typical petrol station with annual 2000 m^3 petrol throughput
Table 2.1 Research sites of VOCs' from petrol filling stations in Vilnius
Table 2.2. Sampling points of VOCs from petrol filling station
Table 2.3 Meteorological conditions during sampling (1 h average)
Table 2.4. Material‘s suspension time
Table 3.1 VOC emission report for RS1 and RS2
Table 3.2 Experiment results quality assurance data
Table 4.1 Simulation scenarios

LIST OF FIGURES

Figure 1.1 Migration of persistent organic pollutants in the global atmosphere
Figure 1.2 VOCs issues at different temporal and spatial scales in atmosphere
Figure 1.3 Environmental benzene transformation product in air
Figure 1.4 Schematic ozone photochemistry driven by VOCs
Figure 1.5 Modelled VOCs relative reactivity
Figure 1.6 Ozone yields of individual petrol VOCs in the atmosphere
Figure 1.7 Chemical links between the VOC, ozone and PM formation processes
Figure 1.8 Mass-balance-based estimate of the global budget for atmospheric VOCs
Figure 1.9 Relative solubility and Henry's law constants for selected VOCs and fuel oxygenates
Figure 1.10 Vapour pressure chart
Figure 1.11 Typical petrol filling station's technology layout
Figure 1.12 Vapour recovery system with refrigeration technique
Figure 1.13 Annual VOC emissions in Europe from petrol evaporation and fuel as fugitive emissions
Figure 1.14 Benzene and NMVOC long-term trend in EMEP area
Figure 1.15 Petrol-related VOC emission dependence on ambient temperature
Figure 2.1 Research sites of VOCs' from petrol filling stations in Vilnius
Figure 2.2 Sampling points' location at petrol station's territory
Figure 2.3 Sampling equipment
Figure 2.4 Wind Rose for Vilnius, January
Figure 2.5 SRI capillary FID GC with built-in hydrogen generator
Figure 3.1 Relative percent differences in air VOC samples
Figure 3.2 Maximum, medium and minimum values of VOC concentrations in ambient air of petrol stations
Figure 3.3 Maximum, medium and minimum values of benzene concentrations in ambient air of petrol stations
Figure 3.4 VOC concentrations in ambient air of petrol stations
Figure 3.5 Benzene concentrations in ambient air of petrol stations
Figure 3.6 Toluene, ethylbenzene, m,p-xylene concentrations in ambient air of petrol station, RS1
Figure 3.7 Ethyl acetate concentrations in ambient air of petrol station, RS1
Figure 3.8 VOC composition in sampling points, RS1
Figure 3.9 VOC composition in ambient air of petrol station, RS1
Figure 3.10 VOC concentrations in ambient air of petrol stations, RS1 and RS2
Figure 4.1 Modelled ethylbenzene source strength (evaporation rate)
Figure 4.2 Modelled ethylbenzene threat zone

LIST OF APPENDIXES

Appendix A MSDS of petrol from “Mazeikiu Nafta”
Appendix B Vapour recovery system with add-on control device
Appendix C Hazardous areas of typical petrol station
Appendix D Presentation of research project

ACRONYMS AND ABBREVIATIONS

ALOHA	Areal locations of hazardous atmospheres
CFD	Computational Fluid Dynamics
FID	Flame ionization detector
GC	Gas chromatography
HC	Hydrocarbons
MSDS	Material safety data sheet
MTBE	Methyl-tertiary butyl ether
NMVOC	Non-methane volatile organic compounds
PAHs	Polycyclic aromatic hydrocarbons
PM	Particulate matter
POPs	Persistent organic pollutants
PVR	Petrol vapour recovery
RFG	Reformulated gasoline
RS	Research site
RVP	Reid Vapour Pressure
SOA	Secondary organic aerosol
STEL	Short-term exposure limit (15 min)
TVOCs	Total volatile organic compounds
TWA	Time weighted average (8 h)
VOCs	Volatile organic compounds

Vilnius Gediminas technical university
Faculty of Environment Engineering
Department of Environment protection

ISBN ISSN
No. of copies: 1
Date 2008-06-05

Final paper for master degree
Title: Research of volatile organic compounds from petrol filling stations

Author: Žana Bikbajeva, gr. AVGmu06

Language

☐ Lithuanian

☒ English

SUMMARY

The research focuses on the environmental problem of volatile organic compounds in ambient air of petrol filling stations. The literature review of the issues, arising from petrol-related VOCs, with actual and proposed VOC emissions trends in Europe, have been performed. Besides petrol filling station's typical technology layout, petrol nature and composition, applicable petrol vapour recovery solutions and their efficiency were examinated. The volatile organic compounds' experimental research in two petrol stations of typical technology layout in Vilnius city under similar extreme meteorological conditions (VOC air pollution episodes with low winds, stable stratification and suspended photochemical removal) is done. The emitted from petrol stations VOC experiment is based on air pumped sampling in glass gas pipette and further determination using gas chromatography with flame ionization detector. The experimental results, presented by means of tables and diagrams, are analysed and discussed. The available results of the experiment are loaded into the environmental model "ALOHA" for air pollution evaluation and concentrations prediction in the ambient air under different meteorological conditions and technological emergency situations (petrol spillage) at petrol filling station. The research is summarized in conclusions and recommendations.

KEYWORDS

Volatile organic compounds (VOC), VOC emission, VOC mixture, VOC dispersion, air pollution, ambient air, air quality, photochemical smog formation, ground-level ozone formation, evaporation, petrol vapour recovery, petrol filling station.

Vilnaus Gedimino Technikos Universitetas
Aplinkos inžinerijos fakultetas
Aplinkos apsaugos katedra

ISBN ISSN
Nr. kopijų: 1
Date 2008-06-05

Baigiamas magistro darbas
Pavadinimas: Lakiųjų organinių junginių tyrimas nuo benzino degalinių

Autorius: Žana Bikbajeva, gr. AVGmu06

Kalba

☒ Lietuvių

☐ Anglų

ANOTACIJA

Tyrimas skirtas aplinkos oro taršos problemai lakiaisiais organiniais junginiais, išsiskiriančiais nuo benzino degalinių. Atlikta svarstomos aplinkosauginės problemos literatūros apžvalga. Apžvelgti oro taršos pasekmės skatinamos LOJ išsiskyrimų nuo benzino degalinių, aktualios ir numatomos LOJ emisijų tendencijos Europoje, tipinis benzino degalinės technologijos išsidėstymas, benzino sudėtis ir svarbiausios LOJ garų formavimui benzino savybės, taikomi garų grąžinimo sprendiniai ir jų efektyvumas. Detaliai aprašytas LOJ eksperimentinis tyrimas, atliktas dviejose Vilniaus miesto tipinės technologijos degalinėse esant panašioms kraštutinėms (LOJ taršos epizodai prie silpnų vėjų, stabilios stratifikacijos ir suspenduoto fotocheminio šalinimo) meteorologiniams sąlygoms. LOJ mėginių ėmimui panaudotas aktyvus metodas su aspiracija į dujines pipetes, LOJ koncentracijos nustatytos dujinės chromatografijos su liepsnos jonizacijos detektoriumi metodu. Tyrimo rezultatai, pateikti lentelių ir diagramų pavidalu, aptarti ir įvertinti. Eksperimento duomenys įkelti į oro kokybės modelį “ALOHA”, siekiant nustatyti LOJ pernašą ir sudaryti LOJ koncentracijų prognozė benzino degalinių aplinkos ore prie skirtingų meteorologinių parametrų ir avarinių technologinių situacijų (benzino išsiliejimas). Tiriamąjį darbą reziumuoja išvados ir rekomendacijos.

REIKŠMINIAI ŽODŽIAI

Lakieji organiniai junginiai (LOJ), LOJ emisija, LOJ mišinys, LOJ sklaida, oro tarša, oro kokybė, fotocheminio smogo susidarymas, pažemės ozono susidarymas, garavimas, benzino garų grąžinimas, benzino degalinė.

INTRODUCTION

The Problem. The 20th century has seen the births of three ages: Nuclear, Electronic and Chemical. The latter (beginning ca. 1930) has more thoroughly and deeply permeated into environment and eminently transformed human lives with manufacturing of petrol fuel, which heralded era of mobility. According to the EU Commission forecasts, nearly 16 million new cars were registered in Europe in 2007, or 1,1 % more than the year before, for Lithuania new passenger car registration value change in 2006-2007 years period is almost doubled. The nearest years the further increase of transport stock is expected. It urban sprawl’s after-effect puts pressure on an environment by constantly expanding a road infrastructure with construction of new petrol filling stations and also with reconstruction of old stations, so increasing petrol distribution and individual site throughput.

Petrol filling stations have become an integral part of urban landscape. There is an environmental contamination during petrol filling station’s service operations. Petrol is product classed as dangerous for the environment by distributing organic material over a volatility basis and contributing to volatile organic compounds’ (VOC) excessive concentrations in ambient air. Petrol stations emit vapours continuously due to usual activity – 24 hours per day, 365 days per year. Their prospective share is about 5 % in the general issue of cities air pollution.

A primary VOC evaporative emission is identified from the technological processes of petrol station: loading and breathing of fuel storage tank, dispensing petrol into the vehicle fuel tank. Additional emission is occurred from vehicles operation and hot-soak, accidental spills and leaks. Others polluting substances in ambient air of petrol stations alongside VOCs satiation appear as impurities, combustion products, or similar indirect polluting substances from traffic-generated pollutants. Technical measures are unable to liquidate VOC emission from petrol station operations totally. The significant uncontrolled volume of VOC emission from petrol stations enforces raise of their environmental performance.

The problem scope extends into air intensification in urban areas, because of VOCs’ high toxicity and extremely reactivity it’s directly and indirectly translates into environmental problems proliferation at personal, local, regional scales and moreover at global scale. VOCs in ambient air at personal scale conduct to exposure, causing health harm including long-term adverse carcinogenic health effects. VOCs at local to regional scales conduct to air toxics, ground-level ozone and photochemical smog formation like O_3 precursors, to fine particle formation like PM precursors. VOCs in atmosphere at global scale lead to free troposphere ozone formation, ozone depletion, and take part in climate change perspective.

The Relevance. The “ALOHA” heavy gas model can be used as the auxiliary tool for proposed petrol station’s VOC impact assessment and emergency plan preparation.

The Purpose. Complex research of VOCs’ environmental impact on ambient air quality around typical petrol filling stations, using the experimental and modelling approach.

The Tasks.

1) Measurement of VOC emissions in hazardous and non-hazardous areas of typical petrol filling stations.
2) Evaluation of VOC concentrations and petrol-related VOC species in ambient air of typical petrol stations.
3) Prediction of VOC emissions from petrol station’s emergency situations based on “ALOHA” heavy gas model.

The Novelty. The experimental and simulation evaluation of VOC emissions, acting in typical petrol stations’ ambient air, in Vilnius city under extreme meteorological conditions (VOC air pollution episodes with low winds, stable stratification and suspended photochemical removal) during usual activity and emergency situations.

The Practical Value. The particular recommendations of VOC control improvement for petrol stations.

The Structure. The research project is divided into four parts: theoretical, research, analytical and modelling. The first part with related literature reviewed submits environmental context of VOCs from petrol stations. Literature review includes more than 80 science articles. The second part concerns research approach and method detail. The third part acquaints with analytical research results evaluation, discusses research results experimentally obtained in two petrol stations of typical technology layout in Vilnius city under similar meteorological conditions during winter season. The final part provides mathematical model’s description, operation and simulation results of VOCs transport from petrol station, using the “ALOHA” software. Conclusions and recommendations sum up the project. The 90 pages project is tabulated by 13 tables and illustrated by 32 figures. The research project presentation is added to the appendixes.

1. THEORETICAL PART

1.1. CLARIFYING ISSUES OF AIR POLLUTION WITH VOCs

The biggest emission of VOC to the environment is related to atmospheric pollution (Paliulis and Baltrėnas 2007). Volatile organic compounds (VOCs) are centrally important to a wide range of health and environmental issues because their atmospheric reactions lead to the formation of major pollutants – ozone (O_3), particulate matter (PM), persistent organic nitrates, and regional haze.

VOCs are of interest in air-quality management for at least three reasons:

- some individual compounds are toxic, carcinogenic, mutagenic, teratogenic, or bioaccumulative (Moran *et al.* 2003);
- VOCs are involved in the formation of ground-level ozone (directly) like O_3 precursors and acid rain (indirectly);
- VOCs contribute both directly and indirectly to the formation of organic particulate matter (PM) like PM precursors.

Air pollution with VOCs issues range explains migration process of organic compounds in environment. Figure 1.1 illustrates organic compounds' atmospheric formation through atmospheric degradation pathways and transport of persistent organic pollutants (POPs) in the global atmosphere.

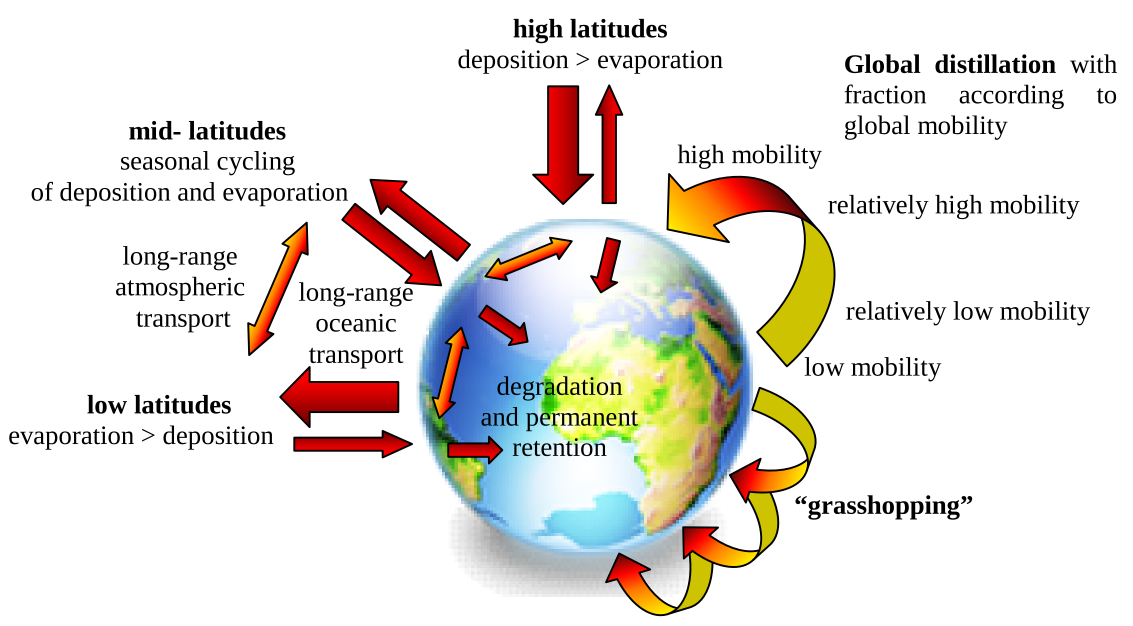


Figure 1.1. Migration of persistent organic pollutants in the global atmosphere

POPs after introduction to the environment undergo long-range transport (Ballschmiter *et al.* 2002) primarily by air. The physico-chemical properties of these compounds are such that they favour sufficiently high atmospheric concentrations that result in global redistribution by evaporation and atmospheric transport. Many of them undergo atmospheric transformation into reaction products that may pose more of a risk or hazard than the released compounds themselves. The atmospheric formation of ozone from released NO_x and VOCs in the urban environment is an obvious example.

VOCs are under increasing international scrutiny due to their potential for long-range transport and because of their possible impacts on the global environment. Ability to determine the fate of VOCs and their local to global influence by examining atmospheric degradation pathways is important for VOCs environmental impacts understanding. A fundamentally important characteristic of released volatile organic compounds is their atmospheric lifetime, which can range from hours (or even less) to years. The *lifetime of a VOC*, τ, is the time required for the concentration of the VOC to decrease to 1/e (37 %) of its original concentration (Atkinson *et al.* 2006). The overall lifetime of a chemical due to the various removal and/or transformation reactions is given by formula:

$$1/\tau_{\text{overall}} = 1/\tau_{\text{OH}} + 1/\tau_{\text{NO}_3} + 1/\tau_{\text{O}_3} + 1/\tau_{\text{photolysis}} + 1/\tau_{\text{wet deposition}} + 1/\tau_{\text{dry deposition}} \qquad (1.1.)$$

and depends on the concentrations of the reactive species OH, NO_3 and O_3, light intensity, and, via their influence on wet and dry deposition rates and lifetimes, precipitation, atmospheric turbulence and nature of the ground surface (Atkinson *et al.* 2006). The principal sources of VOCs are combustion processes including motor vehicle engines and evaporation of fuels, in particular of petrol fuel. Table 1.1 gives tropospheric lifetimes of selected petrol constituents for ambient concentrations of OH radicals, NO_3 radicals and O_3.

Table 1.1. Lifetimes of VOCs due to gas-phase reactions

VOC	Lifetime due to reaction with		
	OH radicals	NO_3 radicals	O_3
Benzene	9,4 d	> 4 yr	> 4,5 yr
1,3-Butadiene	2,1 h	5,6 h	2,6 d
n-Octane	1,3 d	240 d	> 4500 yr
Toluene	1,9 d	1,9 yr	> 4,5 yr
1,2,4-Trimethylbenzene	4,3 h	26 d	> 4,5 yr
m-Xylene	5,9 h	200 d	> 4,5 yr

Today, scientists clearly recognize that processes like ozone and particulate matter (PM) formation, degradation of VOCs, deposition of nitrogen and sulphur, depletion of stratospheric ozone are closely interlinked in atmosphere, i.e. local, regional and global atmospheric issues cannot be fully separated. Figure 1.2 illustrates interactions of air pollution issues caused by VOCs. VOCs issues are very significant, because at different temporal and spatial scales in atmosphere are conduct from personal exposure to global issues like ozone formation issue and climate change, that could lead to some irreversible environmental impacts. The main reason of climate temperature rising – is gas causing climate change (Baltrėnas 2007). VOCs in atmosphere are acting as indirect greenhouse gases.

Scales	**Issues of air pollution with VOCs**
Personal	Exposure
ô	
Local to regional	Exposure, air toxics, ozone (smog) formation, particulate formation
ô	
Remote troposphere	Exposure, free troposphere ozone formation, climate change
ô	
Stratosphere	Ozone depletion, climate change

Figure 1. 2. VOCs issues at different temporal and spatial scales in atmosphere

Many impacts of global warming are already detected. Indeed, average global temperatures have risen considerably. Since the mid-1970s the rate of increase in temperature rises has tripled (Koneswaran and Nierenberg 2008). Climate changes can cause large and even catastrophic results for economics, community, nature and environment quality of many countries (Baltrėnas *et al.* 2003; Baltrėnas 2007). After all air pollution never respects international boundaries (Reuther 2000). VOCs and their degradation products can move from their point of emission to more remote areas of the atmosphere causing transboundary air pollution. Amplitude of climate changes increased and systems of climate mechanisms disarrayed because of human activity (Baltrėnas *et al.* 2003, 2007). Transboundary air pollution is likely to increase as developing countries in Asia rapidly industrialize and raise their emissions and ambient pollutant levels (Yienger *et al.* 2000). Emissions of non-methane volatile organic compounds (NMVOC) are growing in Asia as countries extract and use petroleum products in increasing amounts (Streets *et al.* 2000). To effectively manage a transboundary pollution issue, the source-receptor relationship is an important one to elucidate (DiGiovanni and Fellin 2006). It means that global air pollution issues in case of atmospheric pollution with petrol-related VOCs should be properly managed at local level as air pollution in microenvironments leads to global atmosphere pollution.

1.1.1. THE MAGNITUDE OF HEALTH IMPACTS ASSOCIATED WITH VOCs FROM

PETROL

The health effects of air pollution have always been one of the major reasons for focusing on air quality management. Petrol-related VOCs are some of the most dangerous and widely distributed environmental contaminants known today. Harmful VOCs include petroleum distillates, i.e. petroleum products produced from crude oil after reforming and blending processes such as petrol fuel (light distillate). The production, distribution, storage, and use of petrol results in harmful VOCs release into the atmosphere. The lifetime of a particular petrol constituent is an important factor in determining exposure potential, since longer residence in the atmosphere results in a greater likelihood that people will be exposed (Atkinson *et al.* 2006). Environmentally caused VOC levels are at least one order of magnitude lower compared to occupational limit values in biological material (Heinrich-Ramm *et al.* 2000).

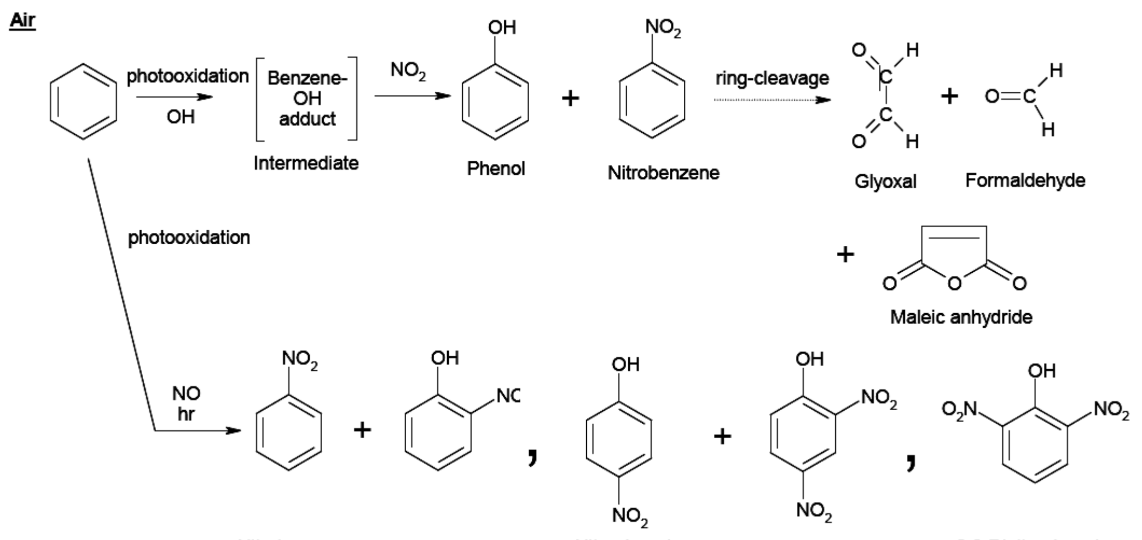
The magnitude of health impact associated with petrol-related VOCs can be obtained from a material safety data sheet (MSDS) of typical petrol fuel (see appendix A for MSDS of petrol from “Mazeikiu Nafta” – oil refinery and oil-processing plant in Lithuania). Human exposure to VOCs from petrol occurs mainly through inhalation. Some *short-term exposure* health effects from overexposure to VOCs are dizziness, headaches, and nausea. *Long-term exposure* to certain VOC, such as benzene (C_6H_6) – a natural component of petroleum and most important from a toxicological point of view, and polycyclic aromatic hydrocarbons (PAHs) has been shown to cause cancer (Huff 2007). There is an apparent correlation between butadiene exposure and a higher risk of cancer. Exposure limits (short-term exposure limit (STEL, 15 min) and time weighted average (TWA, 8 h) for all grades petrol are listed in table 1.2.

Table 1.2. Petrol, all grades exposure limits

Component	CAS No.	Source	Exposure limits		
			TWA, ppm	STEL, ppm	Note
Gasoline	86290-81-5	ACGIH	300	500	A3
Benzene	71-43-2	OSHA ACGIH USCG	1 0,5 1	5 2,5 5	Carcinogen A1, skin
n-Butane	106-97-8	ACGIH	1000	-	Aliphatic Hydrocarbon Gases Alkane (C1-C4)
Ethyl Alcohol (ethanol)	64-17-5	OSHA ACGIH	1000 1000	- -	A4
Ethyl benzene	100-41-4	OSHA ACGIH	100 100	- 125	A3
n-Hexane	110-54-3	OSHA ACGIH	500 50	- -	Skin
Proceed to the next page Table 1.1. continuation					
Methyl-tertiary butyl	1634-04-4	ACGIH	50		A3

ether (MTBE)					
Tertiary-amyl methyl ether (TAME)	994-05-8				None established
Toluene	108-88-3	OSHA ACGIH	200 20	-	Ceiling: 300 ppm; Peak: 500 ppm (10 min.) A4
1,2,4-Trimethylbenzene	95-63-6	ACGIH	25	-	None established
Xylene, mixed isomers	1330-20-7	OSHA ACGIH	100 100	- 150	A4

European cities experience high levels of benzene. In urban areas the main source of benzene is traffic. From additional sources the most significant are the petrol stations (Spyros *et al.* 2007). The general population is exposed by inhaling contaminated air particularly in areas with heavy motor vehicle traffic and around filling stations. Study of individual exposures and blood concentrations of benzene showed significantly higher benzene exposure levels among service station attendants (median 330 µg/m^3) as compared to street vendors (median 62 µg/m^3) and office workers (median 44 µg/m^3) (Romieu *et al.* 1999). Environmental benzene transformation product in air is shown by figure 1.3.



(Nojima *et al.* 1975; Bandow *et al.* 1985)

Figure 1.3. Environmental benzene transformation product in air

Evaporative benzene emission due to environmental transformation produces a number of potentially toxic compounds. Formaldehyde is originally not found in evaporative emissions. Thus due to benzene reactivity the air pollution with VOCs is extremely multiplies.

Exposure assessment studies have indicated petrol service stations – are important microenvironments for benzene exposure, and automobile refueling represents the major source of benzene exposure among the nonsmoking public (Egeghy *et al.* 2000). Although the results obtained in latest studies demonstrated that the exposure levels of service station attendants to benzene have diminished (Periago and Prado 2005). Obviously this is consequence of petrol vapour recovery solutions implementation in stations.

There are few studies that outline the contribution of petrol stations to the benzene concentrations in their wider vicinity. The results of risk assessment evaluation, attempted in terms of increased cancer risk due to the presence of the petrol stations in an area, show an additive concentration ranging from 3 μgm^3 to 6 μgm^3 and remarkable increase of the population risks in the vicinity, ranging from 3 % to 21 % in comparison to the population in the rest of the town (Spyros *et al.* 2007). The toxic chemicals common for all petrol grades are listed in table 1.3.

Table 1.3. Petrol, all grades toxic content

Ingredient name	CAS No.	Concentration wt. percent
Benzene	71-43-2	0,1 to 1,3 for reformulated petrol
Ethyl benzene	100-41-4	< 3
n-Hexane	110-54-3	0,5 to 4
Methyl-tertiary butyl ether (MTBE)	1634-04-4	0 to 15,0
Toluene	108-88-3	1 to 15
1,2,4- Trimethylbenzene	95-63-6	< 6
Xylene, mixed isomers	1330-20-7	1 to 15

The petrol manufactured in “Mazeikiu Nafta” contains MTBE. According to much of the literature, MTBE poses no severe human health threats at the exposure levels anticipated for the general population. Animal and human health effects studies indicate that MTBE may cause eye, skin, and respiratory tract irritation, central nervous system depression and neurotoxicity. MTBE has demonstrated some evidence of developmental toxicity in animal models and classified as an animal carcinogen (A3) by the ACGIH (table 1.1). For ethanol blended petrol research on levels of ethanol in the blood of mice following exposure to several doses of inhaled ethanol suggested that the levels of ethanol likely to be inhaled during typical refuelling would not result in toxic effects to humans (Pastino *et al.* 1997).

Petrol exposure limits and toxic ingredients confirm the importance of ambient pollution with VOCs to population exposures when outdoor pollution levels are high and underline the necessity of petrol-related VOCs’ emission control.

1.1.2. TROPOSPHERIC OZONE ISSUE

In the troposphere, ozone is an air pollutant, referred to as *ground-level ozone* are primary ingredient in photochemical smog and has detrimental effects on human health and the environment. Ozone pollution on a regional to global scale is becoming recognized as an issue of comparable importance to urban air pollution and climate warming.

Chemical formation of ozone driven by VOCs. Ozone exists in the atmosphere in a dynamic equilibrium with NO and NO_2, its imbalance in the lower atmosphere cause VOC emissions, acting as "fuel" in the ozone formation process (Ito *et al.* 2007), whereas NO functions more or less as a catalyst. The relation between O_3, NO_x and VOC is driven by complex nonlinear photochemistry (Konovalov 2003; Stednum 2004), see in figure 1.4. The main consumption reactions are with OH and NO_3 (Beck *et al.* 1998).

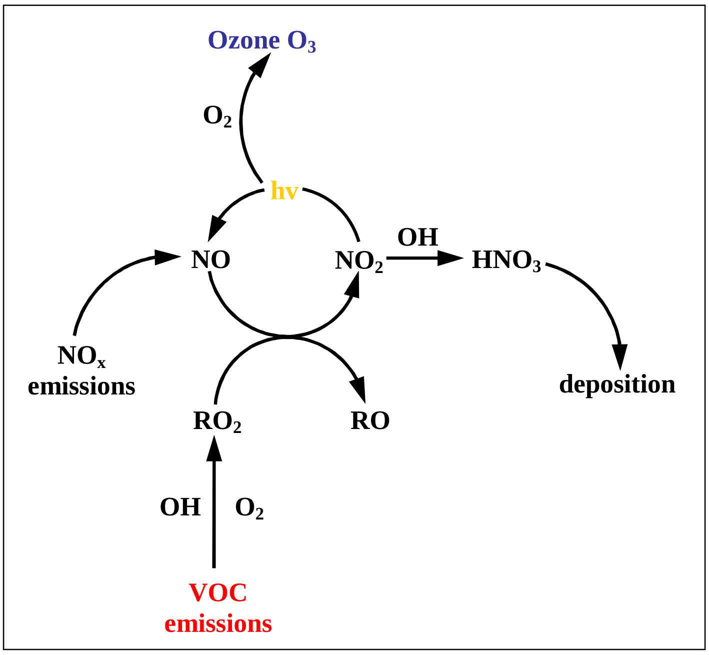


Figure 1.4. Schematic ozone photochemistry driven by VOCs

$$VOC + OH + O_2 \rightarrow RO_2 + H_2O; \tag{1.2}$$

$$RO_2 + NO + O_2 \rightarrow NO_2 + HO_2 + CARB; \tag{1.3}$$

$$HO_2 + NO \rightarrow NO_2 + OH; \tag{1.4}$$

$$NO_2 + hv + O_2 \rightarrow NO + O_3; \tag{1.5}$$

$$(NO_x + OH +)\ VOC + 4O_2 \rightarrow 2O_3 + CARB + H_2O\ (+ NO_x + OH). \tag{1.6}$$

Here RO_2 stands for peroxy radicals, *CARB* – for carbonyl compounds, which play the role of hydrocarbons in further oxidation steps, *hv* indicates that reaction requires the high solar radiation. Pollution events with high ozone concentrations are usually associated with temperatures above 30 °C (Sillman 2003).

VOCs' photochemical potential. Ozone formation is strongly correlated with VOC/NO_x rates. Generally higher VOC concentrations lead to more ozone formation, increasing NO_x for a given VOC concentration may increase or decrease ozone, depending on the prevailing VOC-to-NO_x ratio (Sillman 2003):

- $VOC/NO_2 > 5,5$
  OH reacts mainly with VOCs, potentially producing more radicals and increasing O_3 in the presence of NO.
- $VOC/NO_2 < 5,5$
  More OH reacts with NO_2 than with VOCs, thus reducing the ozone formation efficiency.
- $VOCs >> NO_x$
  NO_x is so low that RO_2 and HO_2 radicals are not propagated efficiently. These radicals react with each other and water soluble peroxides are formed.

In the *VOC- sensitive regime* (NO_x-saturated) O_3 decreases with increasing NO_x and increases with increasing VOC (Sillman and He 2002). Decreasing VOCs for a fixed NO_x always decreases O_3. Decreasing NO_x at a fixed VOC does not always decrease O_3. Typically, VOC reductions are effective and NO reductions ineffective where ozone production is VOC-limited. Analyses of ambient measurements indicated that ozone formation in the largest urban areas generally VOC-limited (Sillman 1999). Calculation of the O_3 production sensitivity to changes in the concentrations of the precursor compounds based on an Observation based model demonstrates the production of O_3 throughout much of the city area limitation by VOC (Zhang *et al.* 2007). Thus the primary regulatory strategy for urban ozone management should respond to VOCs emission reductions.

Reactivity of VOC is one measure of the ozone-forming potential of a VOC species. Over the past decade, studies have been performed to assess the reactivity of organics. Experimental (Kelly and Chang 1999) and modeling based approaches have shown a wide range of VOCs reactivities. The effective range of a reactivity scale is the range of reactivity values generated between the most reactive VOC and an unreactive VOC such as ethane (Derwent 2004) (figure 1.5). VOCs from petrol usage with high ozone forming potentials (Latella *et al.* 2005) include ethene, propene, xylenes, 1,3-butadiene, and formaldehyde (Volkamer 2001; Atkinson *et al.* 2006). As seen from ozone yields diagram (figure 1.6) the olefins and aromatics are very reactive in generating higher amounts of ozone in the atmosphere.

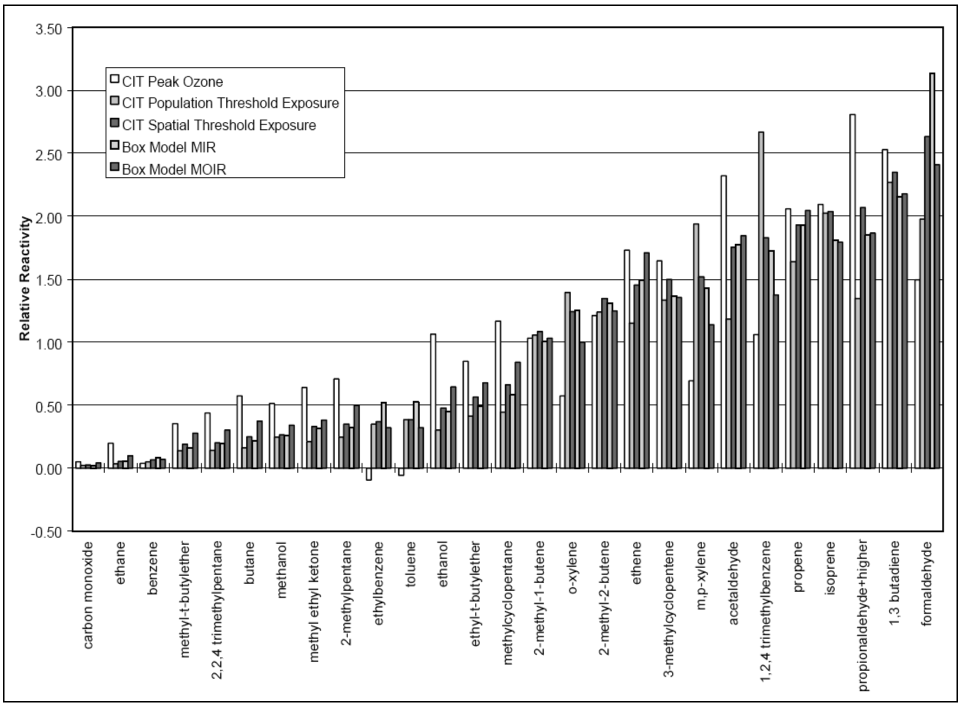


Figure 1.5. Modelled VOCs relative reactivity (VOC reactivity… 1999)

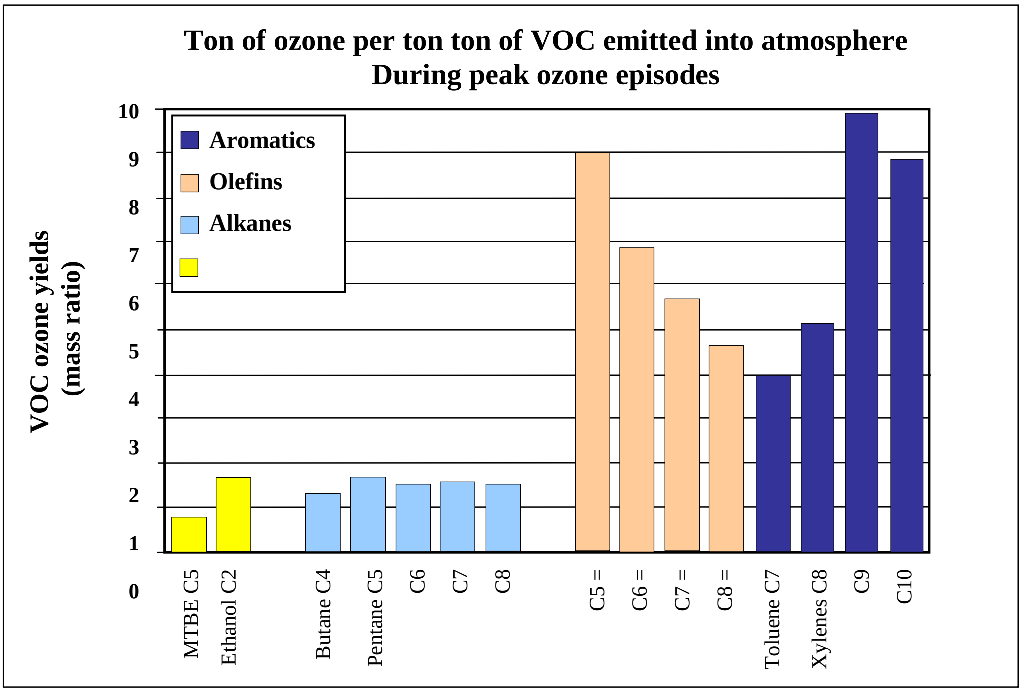


Figure 1.6. Ozone yields of individual petrol VOCs in the atmosphere

Examination of speciated VOCs shows that among petrol-related VOCs the reactive aromatics dominate, in particular xylenes and toluene. However, on longer time frames (e.g. 96-h), the slowly reacting alkanes become increasingly important (Beck *et al.* 1998). VOC with lower reactivity at the urban scale could increase ozone formation in the remote troposphere or it could thin the ozone layer in the stratosphere, contributing to climate change.

1.1.3. PM FORMATION ISSUE

VOC may undergo oxidation reactions to form substances with lower vapour pressures, which subsequently condense to form *secondary organic aerosol* (SOA) (Hoyle *et al.* 2007) – an important component that can significantly contribute to the fine particulate ($PM_{2,5}$) burden (Fine *et al.* 2008), especially during severe urban smog episodes. However VOC chemistry is a primary emissions of $PM_{2,5}$. VOC oxidation leads to the formation of secondary organic aerosol via gas-to-particle conversion (Odum *et al.* 1997), aqueous phase chemistry (Ervens *et al.* 2004), and/or oligomerization (Kalberer *et al.* 2004). SOA generally formed only from the oxidation of VOCs comprised of six or more carbon atoms. This is because oxidation products must have vapor pressures that are sufficiently low to enable them to partition into the aerosol phase (VOC reactivity… 1999). Petrol-related VOCs such as toluene, xylene, and other aromatics are the most important anthropogenic SOA precursors. Chemical links between VOC, ozone, PM formation processes are delineated on figure 1.7, the major precursors are marked in red squares.

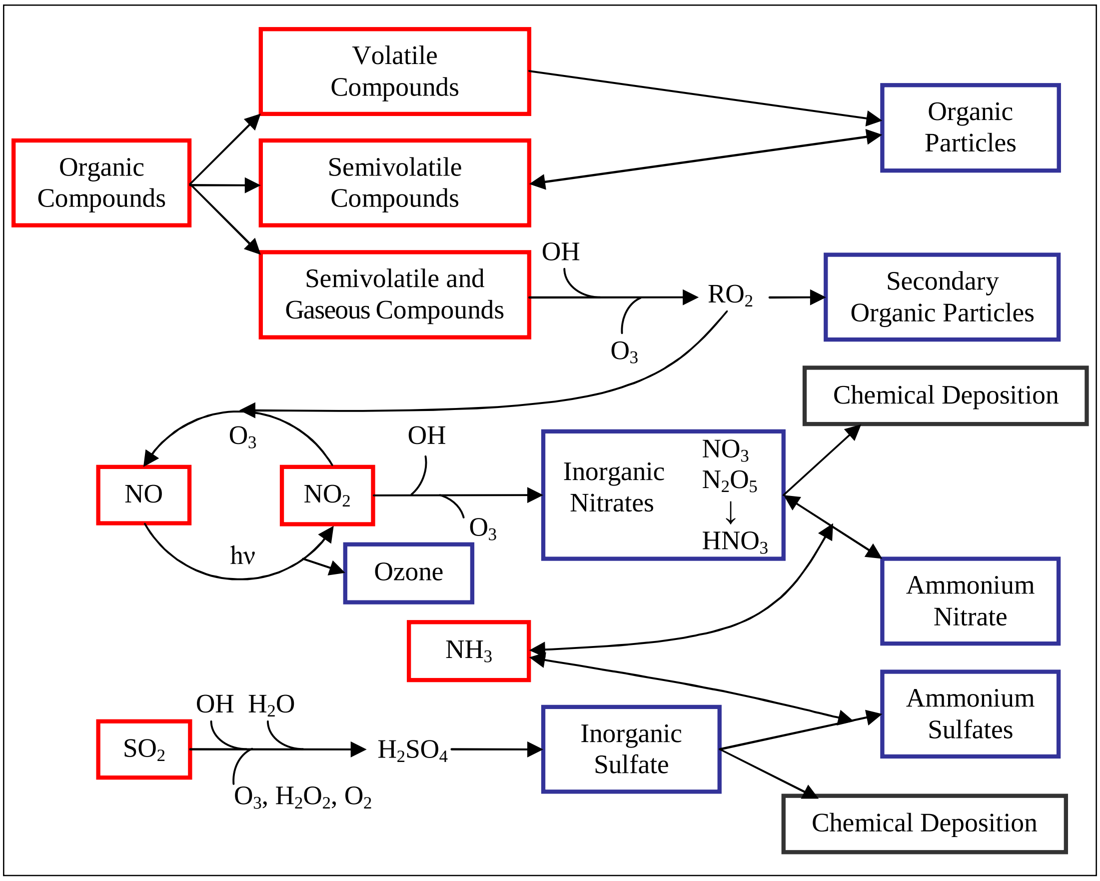


Figure 1.7. Chemical links between the VOC, ozone and PM formation processes

The total source of VOCs emitted into the atmosphere must be removed through one of three possible pathways like schematically showed on figure 1.8 (arrows indicate fluxes).

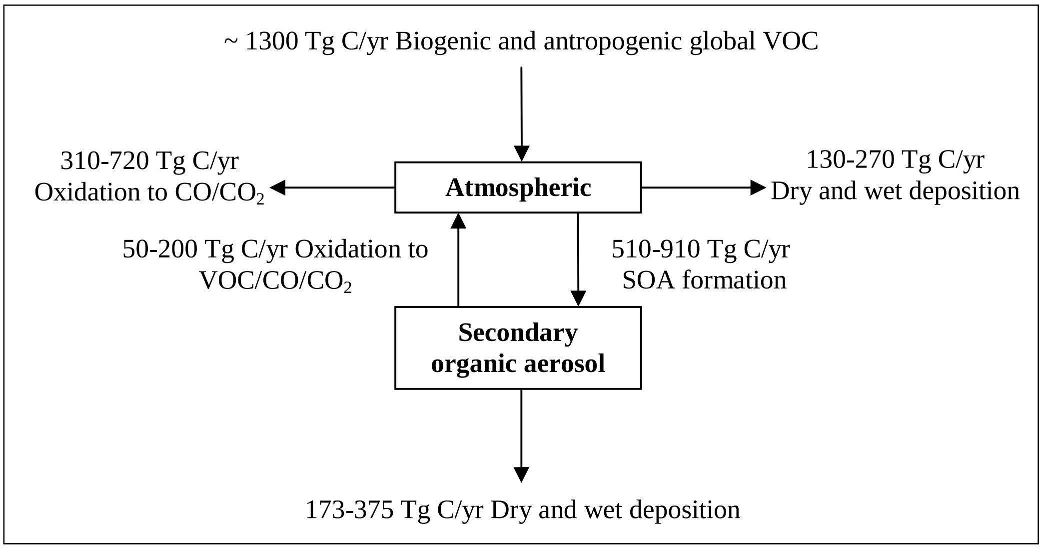


Figure 1.8. Mass-balance-based estimate of the global budget for atmospheric VOCs

Estimates of the global anthropogenic VOC emission range is between 56 and 98 Tg C yr (Li *et al.* 2008). Mass balance of the VOC budget requires that SOA production from about half of the VOC emissions to the atmosphere must account for removal of the remaining VOCs.

Oxidation of SOAs to volatile compounds provides another sink for aerosol organic carbon from the atmosphere, with a volatilization lifetime that is similar to the wet-deposition lifetime (Goldstein 2007). The wet deposition of the gas-phase aerosol precursors depends on their solubility in cloud droplets according to their Henry's law coefficients (H). When the parent VOC is poorly soluble and has low Henry's law constants, their wet deposition negligible (Tsigaridis and Kanakidou, 2003), see figure1.9.

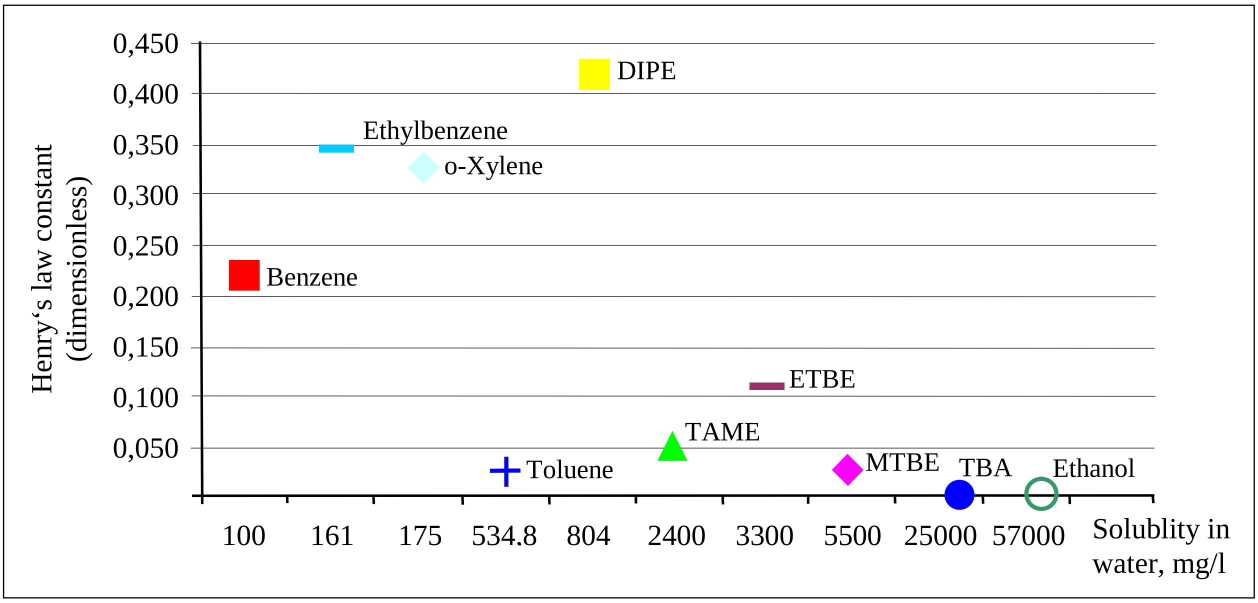


Figure 1.9. Relative solubility and Henry's law constants for selected VOCs and fuel oxygenates

PM impacts of VOCs are much less well understood and quantified than is the case for O_3 impacts. Many of the suspected SOA formation reactions have been reproduced in smog chamber experiments, designed to measure reaction rates and aerosol yields for input into air quality models. Currently is not possible to determine the aerosol formation potential of individual VOCs strictly on the basis of atmospheric chemical reaction mechanisms. Qualitative features of the relationships between airborne PM and VOC are found to depend on temperature. It is argued that the most significant features of the PM-VOC-NO_x relationships in the high-temperature mode are closely associated with the similar features of the OH-VOC-NO_x relationships, whereas the behavior of aerosol in the low temperature mode is strongly perturbed by specific features of the processes of condensation of primary and secondary semi-volatile compounds (Konovalov 2003).

Under certain conditions, SOA may form the majority of the organic aerosol (Tsigaridis and Kanakidou 2003; Pun *et al.* 2003; Zhang *et al.* 2005; Volkamer *et al*. 2006; Robinson *et al.* 2007). The role aerosols play in forming toxic compounds from VOCs through heterogeneous and liquid phase reactions is equally important. Apart from the health effects of SOA, effects upon climat may also be significant as black carbon aerosol absorbs solar radiation and generally leads to a warming of the Earth’s atmosphere (Schulz *et al.* 2006). This may occur through aerosol either causing a modification in the temperature profile of the atmosphere (Ackerman *et al.* 2000), or serving as cloud condensation nuclei and influencing the number, size, lifetimes of cloud particles, having thus an indirect climatic effect by modification of cloud properties (Hoyle *et al.* 2007). Besides, VOCs are generally much shorter-lived in the atmosphere than the hydrochlorofluorocarbons (HCFCs), therefore the indirect radiative forcing is important alike the direct radiative forcing.

1.2. VOC EMISSIONS DEPENDENCE ON PETROL COMPOSITION

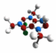
The process of refining fuels and the use, spillage, and incomplete combustion in vehicles is major source of VOCs. Petrol contains over 500 hydrocarbons (HC). Hydrocarbons in ambient air are mainly emitted as a result of petrol evaporation. Petrol-related evaporative emissions include benzene, toluene, ethylbenzene, and xylenes. Petrol evaporation may well be one of the sources that lead to extremely high toluene concentration (Ho *et al.* 2004). The impact of petrol on the environment is directly related to its fuel properties and contents. The formation of air pollution with VOCs from petrol filling station is a dynamic multi-step kinetic process that is highly dependent upon the VOC rate of volatilization from petrol fuel, which nature and composition stipulates the overall rate of VOC emissions in ambient air.

1.2.1. PETROL NATURE

Petrol (aka gasoline) is a complex mixture of hydrocarbons obtained from crude oil distillation and processing. Petrol is a complex blend of petroleum-derived normal and branched-chain alkane, cycloalkane, alkene, and aromatic hydrocarbons, contains antioxidant and multifunctional additives. The main components are paraffinic, naphthenic and aromatic hydrocarbons. For petrol fuel hydrocarbons range C_6-C_{10}. The typical composition of gasoline hydrocarbons (% volume) is as follows:

- alkanes 4-8 %;
- alkenes 2-5 %;
- isoalkanes 25-40 %;
- cycloalkanes 3-7 % cycloalkanes;
- cycloalkenes l-4% cycloalkenes;
- total aromatics 20-50 %
- benzene 0,5-2,5.

Petrol composition, chemical structure is following.

 Saturated hydrocarbons (aka paraffins, alkanes):

- stable, the major component of leaded petrol;
- tend to burn in air with a clean flame;
- octane ratings depend on branching and number of carbon atoms.

Unsaturated Hydrocarbons:

- unstable, are the remaining component of petrol;
- tend to burn in air with a smoky flame.

Alkenes (aka olefins, have carbon double bonds):

- these are unstable, and are usually limited to a few percent;
- tend to be reactive and toxic, but have desirable octane ratings.

```
                          C
                          |                       C5H10
2-methyl-2-butene       C-C=C-C
```

Alkynes (aka acetylenes, have carbon-carbon triple bonds):

- these are even more unstable, are only present in
- trace amounts, and only in some poorly-refined petrol.

```
                         _
Acetylene               C=C                      C2H2
```

Arenes (aka aromatics)

- used to be up to 40 %, gradually being reduced worldwide;
- tend to be more toxic, but have desirable octane ratings.

```
                    C                        C
                  // \                     // \
                 C    C                 C-C    C
 Benzene         |    ||      Toluene     |    ||
                 C    C                   C    C
                  \\ /                     \\ /
                    C                        C

                  C6H6                     C7H8
```

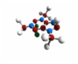
Polynuclear Aromatics (aka PNAs or PAHs)

- these are high boiling, and are only present in small amounts in petrol;
- contain benzene rings joined together.

Modern petrol is a heavily processed product that can also contain various synthetic components, added to improve its performance and meet the demands of today’s advanced engine technology and even more important – strong requirements of environmental policy. The emission reduction requirements have been achieved by petrol reformulation.

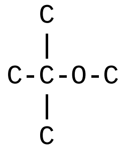
Octane rating is important characteristic of petrol, is a measure of petrol's resistance to auto-ignition in uncontrolled combustion known as detonation. Octane rating is measured relative to a mixture of 2,2,4-trimethylpentane (an isomer of octane) and n-heptane. There are three main groups of octane-raising substances the oil companies use instead of lead:

1) aromatics-organic compounds based on the benzene ring, a 6-carbon ring with 3 delocalised double bonds, e.g., benzene, toluene, xylene, etc;
2) olefines-organic compounds which have double bonds. After combustion, one critical by-product is 1,3-butadiene;
3) oxygenates-organic compounds containing oxygen molecules such as methane, ethane or MTBE (methyl-tertiary-butyl ether).


Oxygenates:

- are just preused hydrocarbons;
- contain oxygen, which can not provide energy, but their structure provides a reasonable antiknock value, thus they are good substitutes for aromatics.

Most oxygenates used in petrol fuels are either alcohols (C_x-O-H) or ethers (C_x-O-C_y), and contain 1 to 6 carbons. The resulting fuel is often known as oxygenated petrol or reformulated petrol (RFG).

Ethanol	C-C-O-H	C2H5OH
Methyl tertiary butyl ether (aka tertiary butyl methyl ether)	 $C-\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}-O-C$	C4H9OCH3

Aromatic hydrocarbons contribute to strong, characteristic aromatic hydrocarbon odour. Oxygenated petrol with MTBE (Cozzarellia and Baehr, 2003) is detectable at a lower concentration than non-oxygenated petrol. Petrol is normally colourless and a dye is added (usually at the refinery) to provide any required colour. Generally, colours are used to differentiate between grades during distribution, in particular between leaded and unleaded petrols.

1.2.2. FACTORS OF PETROL VOC EMISSIONS

Petrol is product classed as dangerous for the environment by distributing organic material over a *volatility* basis. The *evaporative emissions* – discharged petrol vapours, are a result of fuel volatility. Petrol volatility is an indication of how fast the fuel evaporates. Volatile organic compounds have low boiling points (table 1.4) and vaporize easily. Not without reason VOC definition according to Directive 1999/13/EC is based on volatility property, i.e. VOC is any organic compound having at 293,15 K a vapour pressure of 0,01 kPa or more, or having a corresponding volatility under the particular conditions of use.

Table 1.4. Basic chemical-physical properties of petrol

Appearance	Clear pale yellow liquid (may be dyed to various colours)
Odour threshold	Pungent petroleum odour
Odor detection	Non-oxygenated petrol: 0,5 - 0,6 ppm Petrol with 15 % MTBE: 0,2 - 0,3 ppm Petrol with 15 % TAME: 0,1 ppm
Odor recogniton	Non-oxygenated petrol: 0,8 - 1,1 ppm Petrol with 15 % MTBE: 0,4 - 0,7 ppm Petrol with 15 % TAME: 0,2 ppm
Specific gravity at 15,6 °C	0,70 g/ml minimum
pH	Not applicable
Reid Vapour Pressure at (ASTM-D-323)	Less than 0,69 Bar
Vapour density (AIR = 1)	> 1
Boiling point	30-220 °C
Flash point	-40 °C
Solubility (H_2O)	Non-oxygenated petrol – negligible < 0,1 % Petrol with 15 % MTBE slightly soluble = 0,01 g/liter at 20 °C
Evaporation rate (n-butyl acetate = l)	10-11
Percent volatiles	100 %

Certain petrol properties and ingredients affect VOCs emission. These properties and ingredients are:

- aromatics;
- olefins;
- sulphur;
- Reid Vapor Pressure (RVP);
- benzene;
- oxygenates and oxygene;
- distillation points.

In order to reduce evaporative VOC emissions during petrol storage and distribution through petrol filling stations, and also resulting hydrocarbon emissions from vehicles, have been moves to regulate chemical-physical petrol properties modifying traditional petrol content (petrol reformulation) to allowable more eco-friendly petrol profile.

Aromatics. The main source of aromatics, e.g. benzene, toluene, xylene, ethyl benzene, and 1,3 butadiene in petrol is reformate – high octane, low sulfur blending component. While these are desirable characteristics, reformate, with its high aromatics content, also has some undesirable emissions characteristics among them VOC increase with increasing petrol aromatics content. Regulatory limits on aromatics content and identifies aromatics content reduction as the primary factor for toxics performance improvement, and as the secondary factor for VOC improvement. Under related petrol quality directive 98/70/EC aromatics are limited till 35 percent of volume.

Reid Vapour Pressure (RVP). Petrol volatility characteristics are most important because primary affecting evaporative VOC emissions affect. RVP reduction was the only feasible way to meet the VOC petrol fuel performance. The vapour pressure relates principally to the lighter components in the fuel such as butane (figure 1.10). Higher RVP values mean that the fuel is more volatile and more fuel will evaporate at a given temperature (Lyons and Delaney 2000).

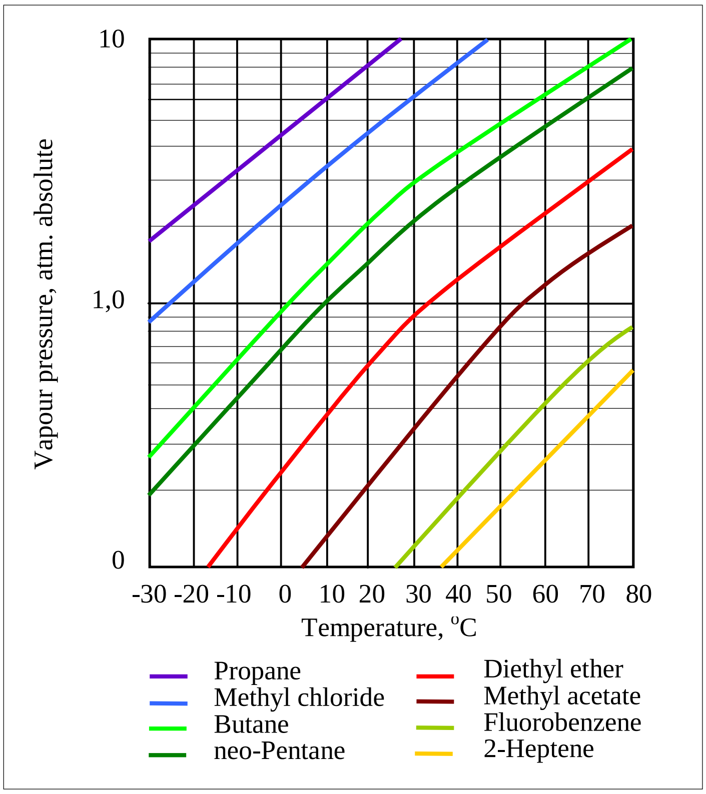


Figure 1.10. Vapour pressure chart

Therefore the RVP is usually controlled during refining by adjusting the proportion of butane, the most volatile component, in the final blend. The heavier compounds in petrol are with the highest energy content and density, so their reduction will tend to reduce the energy content, increasing fuel consumption. Directive 98/70/EC limits RVP till 60,0/70,0 kPa.

Benzene. According to data compiled by CONCAWE, petrol-powered engines account for approximately 80 % of benzene emissions in urban areas. Petrol benzene content has a direct effect on exhaust and evaporative benzene emissions. Reformulated petrol can contain a maximum of 1,0 vol %, max (Directive 98/70/EC). Benzene reduction accounts for much of the air toxics emission reductions in reformulated petrol.

Olefins. Olefins are desirable petrol constituents because of their octane characteristics. The exhaust toxics emissions, NO_x increase with olefin content, but exhaust VOCs will decrease as olefin content increases (Fuel trends... 2008). Under related petrol quality directive 98/70/EC olefins limit is 18 vol %, max.

Sulphur. Sulphur in petrol originates in the crude oil used to produce the fuel. Reductions in petrol sulphur content can reduce exhaust VOC emissions. Under directive 98/70/EC sulphur limit is 10 ppm, max.

Oxygenates and Oxygen. RVP fuels primarily reduce only the evaporative VOC emissions, while oxygenates reduces both evaporative VOCs and “exhaust” VOCs. Oxygenates have been blended into petrol in order to comply with regulatory requirements intended to reduce air pollutant emissions from petrol vehicles. Specifically MTBE decrease the overall reactivity of the VOC mixtures associated with petrol evaporative emissions. Oxygenates are also used in petrol blending for reasons unrelated to emission reduction. The US Environmental Protection Agency emissions reduction data show that the use of oxygenates in petrol provides up to 67 % of total toxics reductions, up to 23 % of all VOCs reductions, the secondary aerosol emissions produced by aromatics reduced by more than 20 %. The relative advantages of oxygenates as environmentally-friendly octane-enhancers are still being researched. Directive 98/70/EC regulatory limit for oxygen is 2,7 wt %, max and for MTBE – 15 % of volume.

Distillation parameters. The relationship between temperature and percent of volume evaporated is referred to as a distillation curve or profile. The higher boiling fractions of the gasoline have significant effects on the emission levels of undesirable hydrocarbons and aldehydes, and a reduction of 40 ^{o}C in the final boiling point will reduce the levels of benzene, butadiene, formaldehyde and acetaldehyde by 25 %, and will reduce HC emissions by 20 % (Schuetzle *et al.* 1994).

1.3. TYPICAL PETROL FILLING STATION

The petrol filling station should be safe in relation to the components of an environment, conditions of residing and health of the population. Today petrol filling station must meet wide range of technical requirements to achieve certain environmental performance and targets for VOCs emission from fuellling operations.

1.3.1. ENVIRONMENTAL LEGISLATION FOR PETROL STATION

The long-term environmental problems are caused when technological processes of petrol stations are not carried and managed properly. The petrol station's technological layout incorporates a wide range of technical considerations, controlled by legislation which lays down allowable limits of VOCs and puts specific duties on petrol filling station's environmental performance.

Directive 94/63/EC aims to prevent emissions to the atmosphere of VOCs during the storage of petrol at terminals and its subsequent distribution to service stations. Prime requirement of the document is reduction of annual petrol evaporative emissions (losses of petrol) resulting from loading into storage installations at stations so that they did not exceed value of 0,01 % (weight by weight) of petrol throughput. Restrictions on the VOC emission into the ambient air for new installations used for storage, loading and transport of petrol at national environmental protection level puts LAND 35-2000. The normative document LAND 1-2003 relates filling stations design, construction, and exploitation. The VOCs emission calculation methodology for proposed filling station in the frames of environmental impact assessment (EIA) formulates the LAND 31-2007/M-11 since such planned economic activity is in the List of proposed economic activities that shall be subjected for obligatory EIA.

The economic activity of filling stations should not affect local living or recreational environment. Thus stations should have a minimum 50 m sanitary protection zone to nearest receptors for VOC dilution. So, the main environmental attitude of environmental legislation applied for petrol filling stations is is to eliminate VOC from human environment.

The petrol filling station for environmental requirements' achievement should be provided with modern, in other words with the best available technology (BAT). The implementation of petrol vapour recovery system (PVR) is considered best management practice for VOC emission reduction from petrol stations.

1.3.2. TYPICAL PETROL STATION’S TECHNOLOGY LAYOUT

The filling station’s (aka dispensing facility) main purpose is retail sells of fuel for motor vehicles in 24 hour operating mode. The retail sell of fuel includes most common petrol brands: 95, 98. Petrol station should be zoned specifically for the purpose (main area) and subdivision (supplementary area – car wash, sells of essential commodities and etc.).

Key components of typical filling station’s installation are following (figure 1.11):

1) operational building;
2) canopy;
3) filling point;
4) underground horizontal double walled steel fuel tank;
5) mounted on island multifuel double-side dispenser.

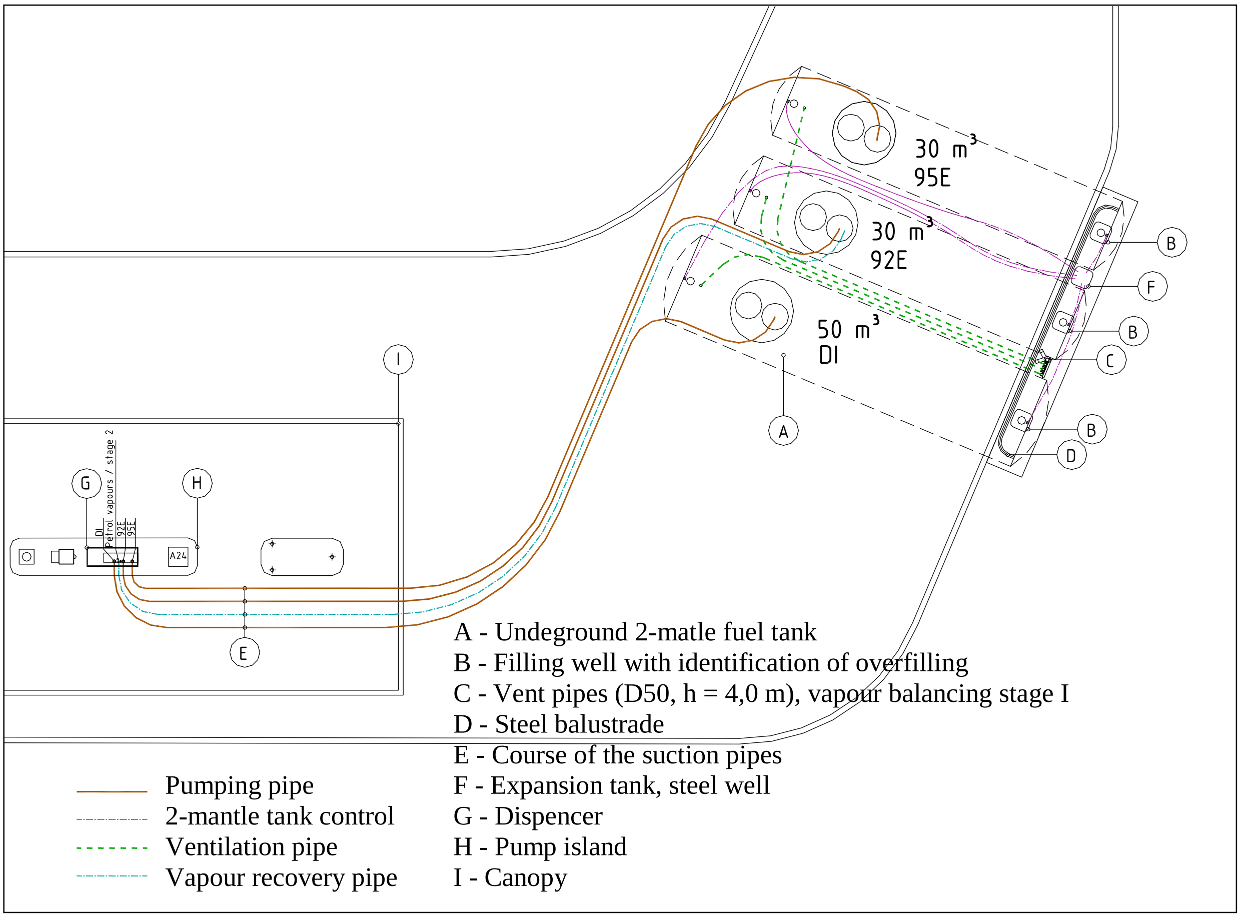


Figure 1.11. Typical petrol filling station’s technology layout

Modern petrol filling station in environmental context is the complex engineering system connecting underground fuel storage tank, dispensers, fuel account, and multiplex environmental protection installation.

Vapour recovery solutions. Tools for implementing environmental purpose are available in advanced technologies that can signally reduce losses of vaporisation in petrol distribution system and recuperating collected vapours (Gulbinas *et a.l* 2002; Kulagin and Korshak 2002). Techniques for preventing VOCs from the core activity of the filling stations enter to ambient air are vapour recovery (VR) Stage 1 and Stage 2. In both cases additional piping is needed for the vapour transfer.

Stage 1 petrol vapour recovery (PVR1) controls emissions while the storage tank are being filled from road tanker. When a road tanker off-loads petrol, the vapour in tank is displaced by the incoming petrol and a vapour space is created in the tanker compartment. As the volume of vapours displaced is roughly balanced by the volume of product discharged, the concept is known as vapour balancing. Vapour recovery system ensure that the amount of vapour recovered is in proportion to the amount of fuel dispensed:

$$Q_{vapour} \approx Q_{petrol}. \tag{1.7}$$

Stage 2 petrol vapour recovery (PVR2) collects petrol vapour released during refuelling, allowing the displaced vapours to be channelled back into underground storage tanks through a separate vapour line connected to the nozzle that feeds the petrol into the vehicle fuel tanks. There are active (open) and passive (closed or balance) systems (Baltrėnas 2001). In the active system a vapour pump assists return vapour flow. The passive system requires a good seal on the nozzle to prevent vapour from escaping to atmosphere. In consequence passive systems have not been installed as extensively in Europe as the active systems.

Besides PVR Stage 1 and Stage 2 the add-on control device (processor) can be used (see appendix B). More preferable measure for petrol vapour emissions into atmosphere reduction are systems of light fraction capturing: adsorbtion, absorbtion, condensation with refrigeration technique, also combined methods (Kulagin 2003). The system, using refrigeration technique to produce liquid condensate at the petrol filling station, is progressive. The system captures the displaced vapour in the same way but has a heat exchanger, which condenses the petrol vapours, and a tank in which water is separated and the recovered petrol stored. The recovered petrol is then passed to the dispenser during refilling. Figure 1.12 provides a schematic view of the petrol vapour recovery system. VOC emissions from fuel tanks and lines into atmosphere can also be reduced by membrane separator (typical systems are small, containing a single 1-2 m^2 membrane module, designed to exhibit selective permeability to either the air or hydro-carbon with a large pressure drop across the membrane forces for permeating compounds to migrate through the membrane pores (Koch 2001; Baker 2002), or VOC absorbing composite materials as reactive barriers to permeation in fuel tank and supply line design (Solovyov *et al.* 2006).

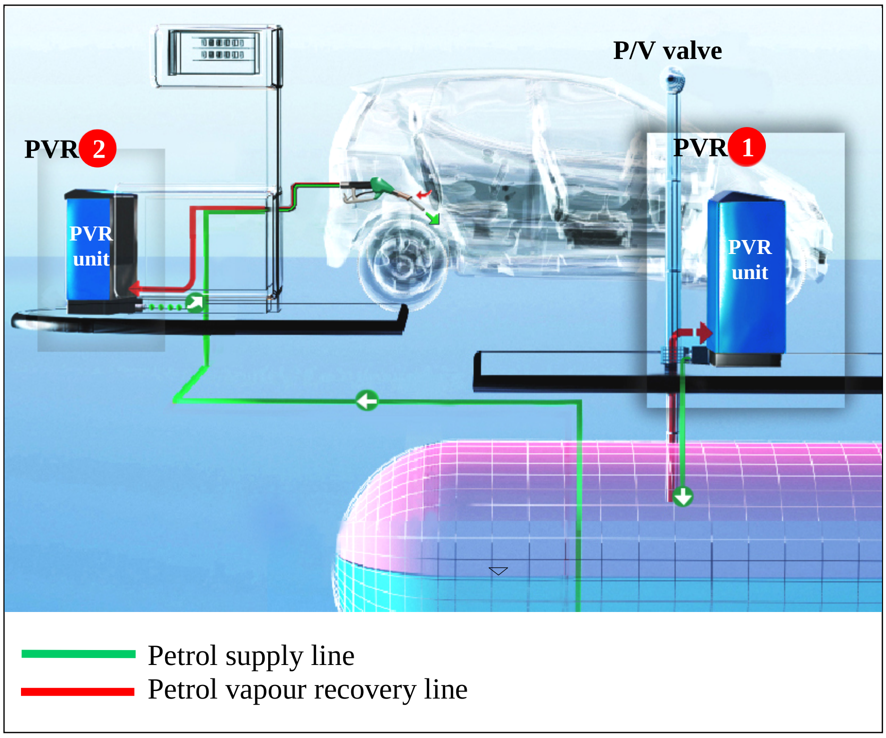


Figure 1.12. Vapour recovery system with refrigeration technique

However, even the best of vapor recovery systems helping to significantly reduce escaping petrol vapours and cut risks to public health and the environment, still allow air pollution with VOC. A number of studies found that typical efficiencies (η) achieved in site are range from 80 % for PVR2 to 90 % for PVR1. From petrol vapour back to liquid petrol system 95 % removal and recovery is appearing.

The safety and efficiency of vapour recovery system is primarily dependent on the correct design, and installation of the system. Furthermore, consultation with an equipment supplier (Tokheim) indicates that one of factor of lower Stage 2 efficiency is traditional fuel dispensers with a high rate of fuel delivery – over 40 l/min, whereas around 38 l/min is optimal for vapour recovery. In Germany, the requirement of the legislation has meant that automatic monitoring installations constantly check the operation of vapour recovery systems (Vapour recovery... 2004). Automatic monitoring systems currently in use include a flow sensor that is based on a calorimetric measuring principle, measuring differences in temperature as vapours pass through. The site is fitted with a “continuous monitoring system,” which is armed to detect leaks with groundwater monitoring wells. If filling station like complex engineering system is proper designed, soil and water pollution will no occur, air pollution will meet hygienic and environmental requirements. It is clear that only good management and a good maintenance programme can guarantee the lowest VOC emissions from petrol stations. Reporting and reviewing *environmental performance of proposed filling station* should be a regular process.

1.3.3. VOC EMISSIONS FROM PETROL STATION

VOC emissions are result of petrol station's core activity, which incorporates technological operations:

- petrol filling into underground tank(s) (tank up);
- petrol storage in underground tank(s);
- petrol dispensing into vehicles and portable containers (refuelling).

VOC emissions from petrol as organic liquids in storage process occur due to evaporative loss of the liquid during its storage and as a result of changes in the liquid level, i.e. during tank loading and unloading. VOCs which evaporate inside the fuel tank fill the air space above the liquid. VOCs generation increase with petrol temperature, and the maximum generation occur at the filled volume rate of 50 % in tank. So VOCs emission is increased as the surface of liquid phase was increased.

Hydrocarbon emissions which are mostly fugitive in nature are emitted not only from petrol station's technological operations, but also from periodic accidental releases such as equipment leaks ("leaking" equipment – valves, seals, connectors/flanges, including leaking car fuel tanks) or spills, especially during customer refuelling and overfilling of portable containers. Petrol vapours escape during refueling adding pollutants like benzene, toluene, ethylbenzene and xylene to ambient air. Fugitive emissions from retail distribution center in urban area constitute a major source (Srivastava *et al.* 2005). Fugitive VOC emissions – all emissions that are released as leakage from equipment are part of diffuse emissions. Estimation of these *diffuse VOC emissions* is more difficult and complex than estimating by stack measurement. It should be realised that the methods that are developed within EU member state are often based on the EPA guidelines.

Loss of product containment from potential sources of VOC emissions during normal station's operations depends on annual petrol throughput. For Lithuania typical service station's a petrol annual throughput of 2000 m^3 - 3000 m^3. The refuelling losses depend on the ambient temperature and the time of refueling process. The filling process is less influenced by temperature factor as temperature in underground environment is stable low. Therefore loss of petrol vapours are less depend on diurnal and seasonal temperature changes, but more on temperature of petrol input from petrol delivery tank. During off-loading process vapour can arise from the turbulence caused by fuel and air entering the tank, and by relatively wanner from the mixing with cooler fuel in the underground storage tank.

EPA's emission factors of petrol vapour and benzene emission from a typical service station are listed in table 1.5.

Table 1.5. Factors of petrol vapour and benzene emission for a typical petrol station

Emission Source	Petrol vapour emission factor, mg/l (%)	Benzene emission factor, mg/l
Underground storage tank, filling losses (submerged fill, Stage 1)	40 (11)	0,4
Underground storage tank, storage losses	120 (32)	1,1
Vehicle, refuelling losses (Stage 2)	132 (35)	1,2
Vehicle, spillage losses	84 (22)	0,76

Typical petrol station's technology assumes the installed petrol vapour control equipment Stage 1 plus Stage 2 of non less than 90 % control efficiency, underground storage tank with submerged fill and pressure/vacuum (P/V) valve on vent pipe. The VOC emissions are identified from petrol's filling losses, storage losses, refuelling losses and spillage losses. The VOC emission from filling process occur due to great breaths of underground tank and from refuelling process due to small breaths of undeground tank. According to EPA's emission factors the most part of VOCs are emitted during vehicle refuelling process, due to petrol displacement losesses.

Calculation of VOC emissions from a proposed typical petrol station with 2000 m^3 annual petrol throughput (Q_p) based on LAND 31-2007 are following.

The VOC emission from filling process is calculated by formula:

$$N_P = 0{,}001 \cdot E_P \cdot Q_P, \tag{1.8}$$

here Q_P – volume of petrol loaded per calculated period, $Q_P = 2000\ m^3$;

E_P – VOC emission factor from filling process, when average annual soil temperature 1,6 m under ground is 7,5 ^oC, $E_P = 70\ g/m^3$.

$$N_P = 0{,}001 \cdot 70 \cdot 2000 = 140 \text{ kg/year.}$$

The VOC emission from storage process calculated according to formula:

$$N_L = 0{,}001 \cdot E_L \cdot Q_P, \tag{1.9}$$

here E_L – VOC emission factor from storage process, $E_L = 120\ g/m^3$.

$$N_L = 0{,}001 \cdot 120 \cdot 2000 = 240 \text{ kg/metus.}$$

The VOC emission from refuelling process calculated according to formula:

$$N_P = E_{tp} \cdot Q, \tag{1.10}$$

here Q – voluem of petrol reffueled to vechicle tanko r portale containers, m^3;

E_{tp} – VOC emission factor from refuelling:

- summer season (V-IX) $E_{tp} = E_{tpV} = 0{,}18\ kg/m^3$;

- transitional season (III, IV, X ir XI) $E_{tp} = E_{tpP} = 0{,}13$ kg/m^3;
- winter season (XII, I ir II) $E_{tp} = E_{tpŽ} = 0{,}10$ kg/m^3.

$$N_{PV} = 0{,}18 \cdot (5 \cdot 166{,}7) = 150 \text{ kg;}$$

$$N_{PP} = 0{,}13 \cdot (4 \cdot 166{,}7) = 86{,}7 \text{ kg;}$$

$$N_{PŽ} = 0{,}10 \cdot (3 \cdot 166{,}7) = 50 \text{ kg.}$$

$$N_P = 150 + 86{,}7 + 50 = 286{,}7 \text{ kg.}$$

The VOC emission from spillage:

$$N_{ISL} = E_{ISL} \cdot Q, \tag{1.11}$$

here E_{ISL} – VOC emission factor, $E_{ISL} = 0{,}08$ kg/m^3;
Q – spilled petrol volume, $Q = 1$ m^3.

$$N_{ISL} = 0{,}08 \cdot 1 = 0{,}08 \text{ kg.}$$

Calculation results reported in table 1.6.

Table 1.6. VOC emissions from typical petrol station with annual 2000 m^3 petrol throughput

Emission Source	VOC emission, t/year (%)
Filling losses	0,14 (21)
Storage losses	0,24 (36)
Refuelling losses	0,29 (43)
Spillage losses	0,0001 (0)

As can be seen from this table, emission from refuelling of vehicles is the largest source of VOC at typical petrol station. Calculation results are corresponding EPA’s petrol vapour emission factors for a typical petrol station as VOC emissions from storage and refuelling processes are predominant. Annual VOC emission from petrol loading is 0,14 ton per year and makes 0,00952 % of station’s annual petrol throughput. This means, that the restricted VOC emission from loading process, i.e. 0,01 % of petrol weight will be not exceeded.

Research of VOCs from petrol filling stations in Lithuania shows, that VOCs concentration is very much depend on petrol station’s constructive design style and equipment arrangement. Propensity to higher VOC concentration is noticed at parallel fuel islands arrangement (Baltrėnas 2001).

1.4. VOCs’ ESTIMATION METHODS

1.4.1. TOTAL VOC APPROACH

VOCs are organic chemical compounds that have high enough vapour pressures under normal conditions to significantly vaporize and enter the atmosphere. In any given airshed, it is common to find hundreds of different VOC species, each with its own unique chemistry. Therefore VOCs present a particularly unique testing dilemma since there are a large number of different compounds defined as VOCs (Pjetraj 1996). Emissions of VOCs are reported in most criteria-air-contaminant emission inventories as a total value, that is, as the sum of all individual VOC species (Moran *et al.* 2003) emitted from a particular source, i.e. total volatile organic compounds (TVOC). Sampling giving a dynamic mixture of many hundreds individual compounds with wide range of volatility and lifetime. The difficulty with emission inventories of VOCs is that they total together from a wide range of emission processes. The total emission can be broken down into the individual emissions of up to 600 identifiable VOC species. As a result the analysis of VOCs is complicated by the extreme complexity of the mixtures and time-consuming.

1.4.2. TRENDS IN VOCs CONCENTRATIONS IN EUROPE

The regular measurements of VOC within the co-operative program for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP) the procedures for light hydrocarbons sampling is collection in stainless steel canisters and chemical analyses by high resolution gas chromatography. The measurements are reported annually, and officially made public by the Steering Body of EMEP.

Europe experienced extreme weather conditions in the summer half year of 2003 with several heat waves, the most pronounced in August (Solberg 2005). The measured concentrations of the VOCs, however, don’t indicate anomalous concentration in either direction. Figure 1.13 shows VOCs’, termed as non methane (NMVOC), emissions from petrol evaporation and from fuel as fugitive emissions in Europe for 2005.

Accuracy and temporal consistency of data series are essential for trend assessment. Emission inventories for VOCs should have a margin of error in total national emissions no greater than 10 % (Strategy for… 2000). Although the number of sites obviously is too low (14 VOC measurement sites) to give a clear picture of the regional background distribution of hydrocarbons in Europe.

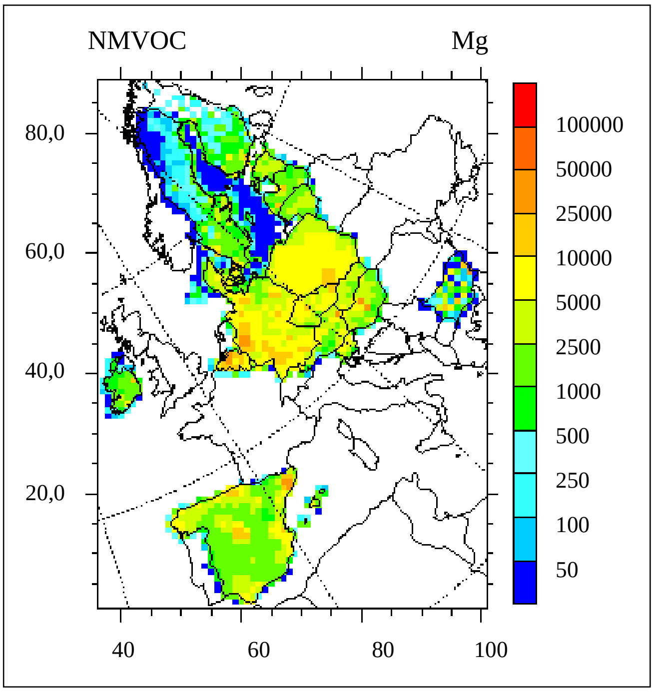


Figure 1.13. Annual VOC emissions in Europe (EMEP area) from petrol evaporation and fuel as fugitive emissions, 2005

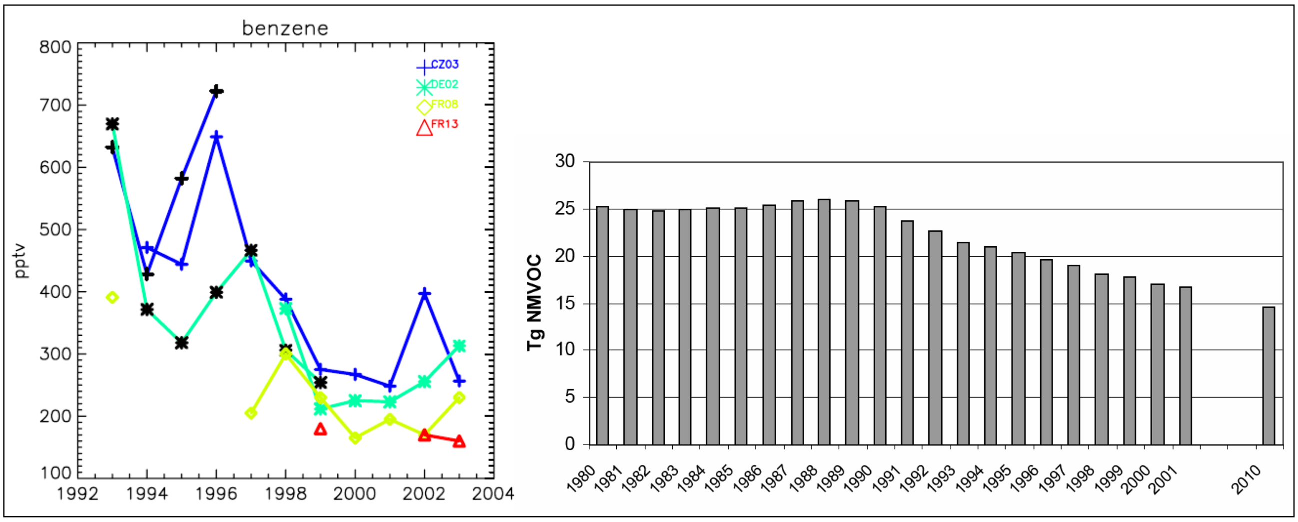


Figure 1.14. Benzene and NMVOC long-term trend in EMEP area (Solberg 2005)

The long-term changes (figure 1.14) in the concentrations of hydrocarbons in Europe indicate stable decrease since nineties. Particularly strong reductions are indicated for benzene. Prognosis for 2010 predicts further VOCs reduction. This means that the European Union has established a comprehensive legislative framework that allows moving towards sustainable air quality. However only in certain areas of Europe are the monitoring time series long enough to detect long-term trends with sufficient significance. The need for more information on VOC concentrations close to the emission sources for modelling purposes is raised.

1.4.3. SEASONAL, DIURNAL VARIATION AND URBAN IMPLICATION OF VOCs

The contribution made by any individual VOC to air pollution depends crucially on environmental conditions. The first studies conducted by Carter in 1994 showed that there that the absolute amount of ozone formed per mass of VOC emissions differed significantly depending upon ambient conditions. The variables that may affect the contaminant concentrations are the atmospheric stability (temperature-height profile), turbulence, wind speed and direction, solar radiation, precipitation, topography, emission rates, chemical reaction rates for their formation and decomposition, and the physical and chemical properties of the contaminant. The studies of seasonal and diurnal VOCs variations (Ho *et al.* 2004; Yang *et al.* 2005; Takegawa *et al.* 2006) showed solidarity in that diurnal and seasonal fluctuations of measured VOC concentrations depended on variations in the strength of sources (anthropogenic activity), meteorological conditions (atmospheric pressure, air temperature, air humidity and wind speed) (Laškova and Vaitiekūnas 2005) and on photochemical activity (solar radiation).

Seasonal variation. At different research sites the annual cycle for total VOC concentrations seasonally proved to be the most dominant pattern. The variables associated with seasonal as well diurnal patterns of VOC emissions variation given most strongly correlation with temperature. Temperature, compare with other meteorological factors at most (till 48 %) have influence on VOCs emission from petroleum products (Laškova *et al.* 2007). It is for reason of petrol vaporization phenomenon: the value of the VOC evaporative emission concentration is varies as a function of temperature (figure 1.15).

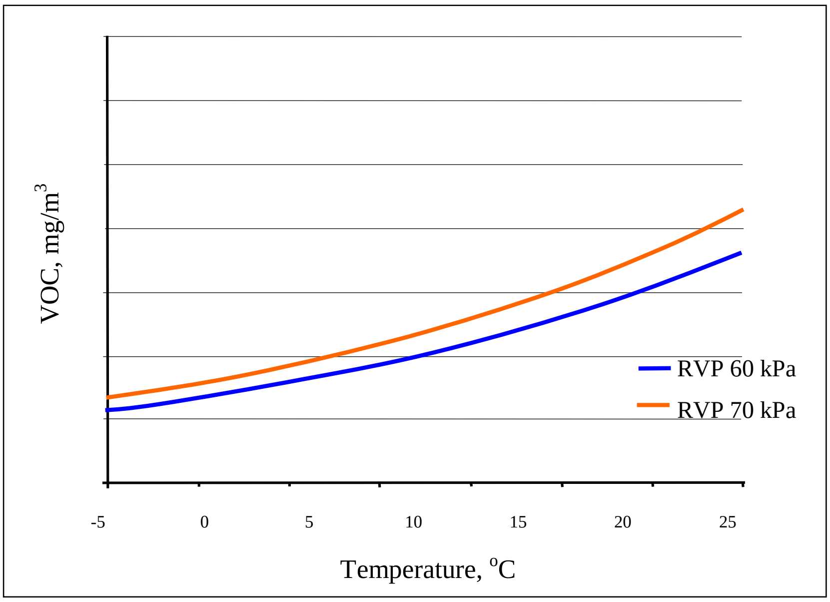


Figure 1.15. Petrol-related VOC emission dependence on ambient temperature

At small temperature fluctuations most influence to VOC concentration has wind speed, little bit less – humidity of an environment, and the least – atmospheric pressure (Laškova *et al.* 2007). VOC dispersion in atmospheric boundary level determines wind direction and speed, humidity of environment, vertical air turbulence, relief singularities (Laškova *et al.* 2007). Secondary formation occurs due to chemical reaction in the atmosphere generally downwind (Hung *et al*. 2005) some distance from the original emission source. Wind speed directly determines whether VOC species are contained locally or are transported downwind. There is a decrease in concentrations in most VOCs when mixing depth, photochemical destruction, and wind speed increased (Filella and Penuelas 2006a). Thus VOC concentration peaks ocurrs in periods with dew formation and no wind. High VOCs concentrations there are always at stagnant air, as low wind speeds lead to the buildup of high local pollutant concentrations. High winds tend to dilute VOCs concentrations locally near sources, dilution effect caused by an increase in the mixing depth (Yang *et al.* 2005). The different compounds also differ in their wind sector dependence. Benzene, show a more homogeneous wind sector distribution (Nemitz *et al.* 2007).

The lower concentration of VOCs in the summer found in many studies (Guo *et al.* 2004; Filella and Penuelas 2006). The authors suggested that this could be from rapid removal of VOCs in summer season. VOC chemical removal, especially by OH radicals, is faster in summer than in winter as more sunlight and higher temperatures produce higher chemical removal reaction rates. Therefore the winter VOC concentrations were higher than those in the summer (Ho *et al.* 2004). Thus the chemical removal of VOCs is another important determinant of the final shape of measured concentrations (Warneke *et al.* 2004). The amplitudes of the seasonal variability, the time of the occurrence of the maxima, and the relative steepness of the temporal gradients show a systematic dependence on OH reactivity (Gautrois *et al.* 2003; Das and Aneja 2003).

Diurnal variation. VOC daily distributions mainly influence by dispersion conditions and respective lifetime of the VOC species. Series of studies revealed that the diurnal VOCs pattern largely influenced by road traffic intensity (Velasco *et al.* 2005). These studies found two peaks of VOC concentrations associated with traffic density and vehicle type (Ho *et al.* 2004). The higher levels of emissions from traffic during the morning and evening rush-hours thus explain the daily concentration peaks of these compounds. The midday decrease could be explained by photochemical destruction (Atkinson 2000; Warneke *et al.* 2004). Diurnal variations of benzene and toluene concentrations also were found. Higher concentrations were recorded in the morning and evening and lower ones at midday and in the afternoon on working days.

Urban implication. VOC concentrations are implicated of urban landscape. There are variations of VOCs levels in different streets configurations, i.e. microenvironments. Because the implication of urban settlements produces different kinds of microclimates inside the city. The urban features, influencing the atmospheric flow, turbulence regime, temperature regime (heat island) and, consequently, the transport, dispersion, and deposition of VOCs within urban areas, are (San Jose *et al.* 2006):

- local-scale non-homogeneities, sharp changes of roughness and heat fluxes;
- the building effect reducing wind velocity;
- redistribution of eddies, from large to small, due to buildings;
- trapping of radiation in street canyons;
- anthropogenic heat fluxes, including the urban heat island effect;
- urban internal boundary layers and the urban mixing height.

The highly significant difference between concentrations results from the geometry of streets. There is typically an exponential decrease in air pollutant concentration with height in urban. The urban effect is more strongly influenced by the local surroundings of the site. Buildings of old urban streets are typically close to each other. These conditions make a kind of box where VOC emissions are more concentrated and such areas are hot spots of urban air quality. Concentrations of most VOC species lower outside such close urban areas due to a dilution effect. Dispersion of pollution from urban street canyons is governed by a complex wind flow structure (Berkowicz 1997). Results indicate that the distribution of pollutant concentration in the street canyons during each period of continuous emission and nonemission can be largely explained in terms of the vortex circulation (Baik and Kim 1999). Air pollutants disperse more easily out of a street canyon that has a lower height-to-width ratio (H/W - ratio of the building height to the width between buildings). As the street H/W aspect ratio increases, the number of vortices increases. In the upper-canyon region, the downward motion near the downwind building is stronger than the upward motion near the upwind building, and the turbulent kinetic energy is higher near the downwind building than near the upwind building because of stronger wind shears near the downwind building. The horizontal advection and diffusion are found to play a crucial role in splitting the vortex into two or more. This highlights the need for improved design of buildings or town plans from air quality viewpoint.

1.4.4. METHODS FOR VOCs MEASUREMENT

Methods for VOCs measurement in ambient air include the procedures for VOCs sampling and chemical analyses. Ensuring that air samples are collected properly is an important step in acquiring meaningful analytical results. A variety of different sampling strategies methods have been developed to address different research and monitoring requirements. The diverse properties of organic pollutants such as VOCs, means that there is no single standard method applicable to their identification and measurement in ambient air.

Key *VOCs' sampling methods* are:

- on-line, semi-continuous sampling of air/gas streams;
- grab sampling into evacuated canisters (passive collection);
- pumped sampling (active collection) into containers (canisters, special bags, etc.);
- pumped sampling into single or multi-bed sorbent tubes;
- diffusive sampling into sorbent tubes or cartridges.

Key *VOCs' analyzing methods* are:

- gas chromatography with flame ionization detector (GC-FID);
- gas chromatography with photoionization detector (GC-PID);
- gas chromatography with mass spectrometry (GC-MS);

The common technique for measurement of VOCs is collections of grab samples followed by analysis using gas chromatography (GC). Each mentioned sampling and analyzing method has advantages and disadvantages relative to the other methods. Due to the strong differences in abundance between components, a large number of components with relatively lower mixing ratios may be completely masked by the enhanced baseline, so that they are not visible on the conventional chromatograms (Lewis *et al.* 2000). The choice of measurement and reporting techniques depends on the purpose that the data will serve.

Passive samplers have been widely used as a cost-effective and reliable technique in measuring ambient VOC concentrations. VOC collection in stainless steel canisters and analyses by high resolution gas chromatography recommended for the detection of light hydrocarbons by EMEP Workshop. In air pollution analysis, gas chromatography is often used in the laboratory to quantify volatile compounds that have been collected. Compact, portable GC-FID and GC-PID instruments are now available for making measurements directly in the field (on-site measurement) and in on-line mode. Automatic site-based systems can take sequential samples to enable continuous monitoring thereby providing time resolution that would be impractical to obtain with canister-based sampling. The onsite analysis enhances the efficiency of environmental monitoring and experimental data sufficiency. For example, in the UK Automatic

Hydrocarbon Network, C_2 to C_8 hydrocarbons in ambient air are collected in a cryogenic trap and then thermally desorbed into the chromatograph (GC-FID) at half-hourly intervals.

Offering a combination of concentration, separation, quantification and identification the most powerful and versatile analytical technology available for VOCs in air is thermal desorption (TD) combined with GC-MS (Warneke *et al.* 2003). TD-GC-MS is compatible with all the main air sampling methods. Just over a decade ago, the novel technique of comprehensive two-dimensional gas chromatography (GC×GC) has been developed to separate and analyze complex samples, such as petrol-related VOCs. This technique employs two coupled columns of different selectivity and subjects the entire sample to a two-dimensional separation (Xu *et al.* 2003). The potential of GC×GC to ambient air measurements was first demonstrated by Lewis *et al.* (2000). Advantages of GC × GC include enhanced sensitivity due to analyte refocusing, true background around resolved peaks, more reliable identification due to two retention times and due to well ordered bands of compound groups (Beens *et al.* 2000; Bertsch 2000). However even with multiple techniques as result no “total” VOCs. Generally, methodologies for the VOCs measurements in ambient air are needed to be improved.

Standard, generally accepted methods, samplers and monitors are used almost exclusively in most VOCs monitoring networks. These are methods as described e.g. in EU directives, or equivalent. Some countries in Eastern Europe (Albania, Bulgaria, Croatia, Estonia, and Romania) use to some extent non-standard methods. Some countries use advanced methods routinely at some sites, such as Differential Optical Absorption Spectrometer (DOAS) in Finland (Virkkula *et al.* 2003), Norway and Sweden, and on-line compound-specific VOC analysis in the UK.

1.4.5. VOCs MEASUREMENT WORLDWIDE

Different programs and measuring campaigns in a number of different areas of the world have been carried out recently to provide information on VOC concentrations, sources, and behavior.

Germany. During a field campaign at the Meteorological Observatory Hohenpeissenberg in July 2004, VOCs were measured using GC×GC (Bartenbach *et al.* 2007). For the reactive compounds (lifetimes < 2 days), a significant, non-zero dependency of the variability on lifetime was found, indicating that chemistry was playing a role in determining the ambient VOC concentrations. The feasibility of this approach for environments dominated by emissions of shortlived VOCs to estimate ambient levels of radical species was discussed.

Finland. Boundary layer concentrations of several VOC were measured during two campaigns in springs of 2003 and 2006 (Haapanala *et al.* 2007). The measurements were conducted over boreal landscapes near SMEAR II measurement station in Hyytiala, Southern Finland. In 2003 the measuremens were performed using a light aircraft and in 2006 using a hot air balloon. Chemical analysis of light C_2-C_6 hydrocarbons samples was performed using GC-FID. Many anthropogenic compounds such as benzene, xylene and toluene, were observed in high amounts. The highest emissions of anthropogenic compounds were those of p/m xylene.

France. In France, VOC measurements are carried out by air quality monitoring networks (Troussier *et al.* 2005). Continuous hourly measurements of 31 VOC from C_2 to C_9 were performed since 2001 in 3 regional networks (Marseille, Strasbourg and Grenoble). Sampling and chemical analysis method based on: 1-preconcentration of VOC of ambient air sample on a trap filled with a mixture of, followed by a thermal desorption; 2-analysis by GC using a dual capillary columns; 3-detection by FID. Mathematical and descriptive analyses (daily variation and wind roses) show, that between 35 % and 60 % of VOC total emissions result from the sources related to the urban traffic, automobile exhaust source have a clear daily variation, in the summer months, evaporation sources have a great importance (up to 50% of total VOC emission). Receptor model have also been used. The results confirm the substantial prevalence of the urban traffic source among the involved sources.

Spain. Daily, weekly, and seasonal patterns of O_3, NO_x and VOCs and their relationship to meteorological conditions were studied in a semi-urban site 10 km northwest of Barcelona (Catalonia) by means of five-day long campaigns that included weekend and labor days in December, March, June, and October (Filella and Penuelas 2006b). A Proton Transfer Reaction (PTR) MS technique was used. Toluene was found to be one of the most abundant VOCs. The highest toluene concentrations were during desember (1,28 ppbv in weekend and 5,17 ppbv in labour days) as ewwl as for benzene (0,56 ppbv in weekend and 1,24 ppbv in labour days). In this study toluene contribution to ozone formation was found to be likely lower than that of acetaldehyde and, above all, methanol, which seem to have an important biogenic origin in this area.

Lithuania. VOC concentrations in ambient air in 6 sampling point in Klaipėda were sampled during monitoring campaign’2006, using diffusive tubes and passive sorbent method. Results of research show that air pollution is most mentioned by road transport. Found VOC concentrations are relatively not high, benzene levels (0,7-2,7 μg/m^3) not exceeds norm for inhabitants health. In march-april were measured highest toluene (5,5-11,6 μg/m^3) and m-xylene (2,5-4,8 μg/m^3) concentrations. Ethylbenzene concentrations differ in 0,6-4,6 μg/m^3 range. VOC concentrations of winter period are lower than measured in summer period.

United States of America. A chemical mass balance approach was used to determine the relative contributions of evaporative versus tailpipe sources to motor vehicle VOC emissions measured downwind of Sacramento, California, in summer 2001 with source speciation profiles (Rubin *et al.* 2006). A composite liquid fuel speciation profile was determined from petrol samples collected at Sacramento area service stations. Vapour-liquid equilibrium relationships were used to determine the corresponding headspace vapour composition. VOC concentrations measured in a highway tunnel were used to define the composition of running vehicle emissions. Was estimated a 6,5 ± 2,5 % increase in vapour pressure-driven evaporative emissions and at least a 1,3 ± 0,4 % increase in daily total (exhaust plus evaporative) VOC emissions from motor vehicles per degree Celsius increase in maximum temperature.

China. Ambient VOCs samples were collected by multiple daily canister method at seven sites in the Pearl River Delta region of China during the Air Quality Monitoring Campaign spanning 4 October to 3 November 2004 (Liu *et al.* 2008). Up to 134 VOCs species were quantified using a cryogenic pre-concentrator with GC equipped with two columns and two detectors. The total VOC levels varied from 10 ppbv to over 200 ppbv. The toluene/benzene ratio showed that VOCs were affected by emissions from solvent usage, fuel storage, and industrial emission. Analysis of the VOC correlations suggests that the ambient VOCs were influenced by both local emissions and transportation of air mass from upwind areas. Alkanes constituted the largest percentage (> 40%) in mixing ratios of the quantified VOCs at six sites; the exception was one major industrial site that was dominated by aromatics (about 52 %).

Mexico. A wide array of VOC measurements was conducted in the Valley of Mexico during the MCMA-2002 and 2003 field campaigns (Velasco *et al.* 2007). Study sites included locations in the urban core, in a heavily industrial area and at boundary sites in rural landscapes. In addition, a novel mobile-laboratory-based conditional sampling method was used to collect samples dominated by fresh on-road vehicle exhaust to identify those VOCs whose ambient concentrations were primarily due to vehicle emissions. Four distinct analytical techniques were used: whole air canister samples with GC-FID, on-line chemical ionization using a PTR-MS, continuous real-time detection of olefins using a fast olefin sensor, and long path measurements using UV differential optical absorption spectrometers. The VOC burden was dominated by alkanes (60 %), followed by aromatics (15 %) and olefins (5 %). The remaining 20 % was a mix of alkynes, halogenated hydrocarbons, oxygenated species (esters, ethers, etc.) and other unidentified VOCs. Elevated levels of toxic hydrocarbons, such as 1,3-butadiene, benzene, toluene and xylenes, were also observed. Results from these various analytical techniques showed that vehicle exhaust is the main source of VOCs in Mexico City and that diurnal patterns depend on vehicular traffic in addition to meteorological processes.

India. In Bangkok the U.S. EPA receptor model, CMB7 was used to complement the emission inventory by identifying contribution from various sources to ambient VOC concentration (Suwattiga and Limpaseni 2005). Ambient air samplings took place at four air monitoring stations during July 2003 to February 2004 covering the two prevailing wind directions in Thailand, the southwest and northeast monsoon seasons. The air samples collected on sorbent tubes in the morning between 8:00 am – 12:00 pm every 6 days were analyzed by TD-GC-MS. The results from CMB receptor modelling (R^2 = 0,95-1,00) showed that during the southwest monsoon season the average contribution to the ambient VOC concentration for all stations were from the exhaust gas from tailpipes of petrol vehicles 21 %, the exhaust gas from tailpipes of diesel vehicles 5 %, the vapour of petrol 12 %, flue gas from fuel oil boilers 22 %, the vapor of solvent-based paint and thinner 8 %, smoke from biomass burning 19 %, smoke from food barbequing 2 %, air samples from municipal waste disposal 4 % and unexplained sources 7 %. During the northeast monsoon season the average contribution to the ambient VOC concentration were from the exhaust gas from tailpipes of petrol vehicles 50 %, the exhaust gas from tailpipes of diesel vehicles 6 %, the vapor of petrol 12 %, flue gas from fuel oil boilers 2 %, the vapor of solvent-based paint and thinner 3 %, smoke from food barbequing 5 %, air samples from municipal waste disposal 12 % and unexplained sources 10 %.

1.4.6. MODELLING APPROACH

To assess the air quality there may be applied any method allowing measuring, calculating (Petraitis and Vasarevičius 2001) or forecasting (Hjertager *et al.* 1998) the level of air pollution. One of the main methods for the air quality assessment and forecast is mathematical simulation of pollutants (P. Baltrėnas *et al.* 2008) for short-term events and for season and annual time frames. Air quality modeling is an area with a significant progress and interest during the last two decades (San Jose *et al.* 2006). Today modelling approach dominates most environmental research areas.

Air quality models simulate the atmosphere in varying degree of detail by mathematically representing emissions, initial and boundary concentrations, chemical reactions of emitted species and their products and local meteorology. For air pollution modelling, the equations governing air motion are generally assumed to be independent of those describing the chemical pollutant dynamics, meanwhile numerical modelling comprehensible as solution of the whole transport equations system solution (Vaitekūnas 1998). Mathematically, the air pollution phenomenon, can be described by the so called Eulerian approach where the behavior of the species is described relative to a fixed coordinate system or by so called Lagrangian approach where the changes of the concentrations are described relative to the moving fluid (Georgiev 2000).

As was indicated, because a VOC’s impacts on air quality strongly depend on the environment where it is emitted, use of mathematical models provides the only practical means to predict the VOC’s impact in an actual environment and pollution scenario evaluation under different meteorological conditions. There are several models currently available for VOCs simulation and mainly covers long-range VOCs transport impact on regional and local air pollution, VOCs sensitivity analysis, i.e. photochemical models (Carter 1995; Sillman 1999).

One such a two dimensional (2D) long-renge model based on Eulerian approach is the Danish Eulerian Model developed in the National Environmental Research Institute in Roskilde, Denmark (Georgiev 2000). Following the ideas in Marchuk and McRae *et al.* the model is divided in four submodels according to the different processes which are involved in: advection, diffusion, deposition and chemistry. These submodels are discretized using different discretisation algorithms and treated successively at each time-step. The input data for the Danish Eulerian Model may be divided as emission and meteorological input data. The input data are organized in different files and consist of anthropogenic VOC emissions, and the meteorological data about cloud covers, humidity, mixing height, precipitation, temperature, surface temperature, vertical and horizontal components of the wind velocity.

The Regional Air Pollution Information and Simulation (RAINS) model developed by the International Institute for Applied Systems Analysis combines information on air pollution related problems are considered in a multi-pollutant context, quantifying the contributions of VOC, sulphur dioxide (SO_2), nitrogen oxides (NO_x) and etc.

Photochemical models are essential for the development of effective control strategies for reducing photochemical air pollution because they provide the only available scientific basis for making quantitative estimates of changes in air quality (Cartrer 2007) resulting from changes in VOCs emissions as ozone precursor.

To determine the VOC emission rate from diffuse area sources and heterogeneous distributed sources, Schäfer *et al.* (2002) carried out measurements and used inverse modelling to determine emission rates of petrol stations. Results for benzene from refuelling activities show that diffuse emissions have been seriously underestimated in emission inventories: benzene emission's from refuelling with VRS measured value – 2 mg per litre of petrol tanked up (1 up to 9 mg l^{-1}) and modelled – 1,8 mg l^{-1} (1,3 up to 2,3 mg l^{-1}). Difference between measured and modelled values for total measured benzene emission is huge (22 mg l^{-1} versus 2,6 mg l^{-1}). The inverse model for petrol station of Friedrich *et al.* (2002) also mismatches measured values.

About 70 % of the European population leaves in cities. Urban areas present a challenge to atmospheric scientists, both from the experimentalist and modeller point of view as typically urban areas have high roughness elements the main problem in VOCs modelling is the prediction of episodes with high VOCs concentration in urban areas. In these areas most of the well-known methods and models, fail to produce realistically. For proposed petrol filling stations the VARSA software based on OND-86 methodology and two-dimensional Gaussian model is the common VOC' dispersion modelling method for environmental impact assessment procedure in Lithuania. However dispersion of pollution in urban street canyons is governed by a complex wind flow structure, which hardly described by traditional Gaussian models. Therefore in recent years in Lithuania was developed the mathematical model of VOCs dispersion based on "Phoenics" software from CHAM – the mathematical simulation program of the proximity methods of equation solution (P. Baltrėnas *et al.* 2008).

Laškova (2007) formulated and studied reliable mathematical model of VOCs transfer near earth boundary layer. For modelling was used finite volumes method, when the governing equations are solved on discrete control volumes by this integral approach:

$$\frac{\partial}{\partial t}\iiint Q dV + \iint F dA = 0\,, \tag{1.12}$$

where Q – vector of conserved variables;

F – vector of fluxes;

V – cell volume;

A – cell surface area.

For VOCs transfer in atmosthere boundary layer evaluation the system of five equations are solved. Their common form is:

$$div(\rho\vec{V}\Phi - \Gamma_{\Phi} grad\Phi) = S_{\Phi}\,, \tag{1.13}$$

here ρ – dencity, kg/m^3;

Φ – reliant variable, Φ = 1 continuity equation;

$\vec{V}$ – vector of velocity;

Γ_{Φ} – diffusion koeficient of variable Φ;

S_{Φ} – flux member of variable Φ equation.

Γ_{Φ} for motion equations is kinematc viscosity coefficient, for diffusion equations – diffusion coefficient, diffusion Prandtl's number for gaseous substance is 0,56-0,71 (Pr_{air} = 0,7). Main input data are velocity areas, pressure, VOC concentration. Supporting variables such as Prandtl number, air dencity, air viscosity are deduced from algebraic equations and are not differential equations solutions. Aimed to model VOC dispersion at boundary atmosphere layer was formed the scheme of oil terminal and near residential territory with buildings (blocked cell), trees (porous cell) and etc. Whole domain was partitioned in sectors as the partitioning of the computational domain in several subdomains allows solving efficiently the large-scale problems in air pollution modelling. For northwest direction and 2,33 m/s wind speed, 100 mg/m^3 VOC emitted from oil product storage tanks simulation with PHOENICS 3.5 software result showed that VOC concentration behaviour was very similar for Gaussian model, when concentration decrease downwind from source: the 1,5 km plume consistent pattern about was post processed. Sudden concentration decrease (about 23 %) was noted in 50 m distance from pollution sources, in 150 m distance VOC concentration drops slower.

It is important to recognize that uncertainties in model components and in model inputs may have a serious impact on model predictions (Tonnesen *et al.* 1998). Kühlwein *et al.* (2002) analysed uncertainties and errors of modelled emission rates of NMHC result in variation coefficients within 10-50 %. Uncertainties of individual VOCs can be much higher. This fact should to be taken into account when interpreting results of VOC models. Models for urban areas upon which VOC transport modelling is based require further development and testing. In VOCs' modelling case these would be especially important in air pollution episodes with low winds, stable stratification, local air circulations and topographic effects.

CONCLUSIONS

1. VOC conduct to ground-level ozone formation as O_3 precursors, to particulate formation as PM precursors, and take part in climate change perspective as potential for long-range transport.
2. Petrol service stations – are important microenvironments of benzene exposure. Automobile refuelling represents the major source of benzene exposure among the nonsmoking public.
3. The primary regulatory strategy for urban air management should respond to VOCs emission reductions due to VOC-limited ozone formation in the large urban areas.
4. Petrol is product classed as dangerous for the environment by distributing organic material over a volatility basis, and as a result contributing to high VOC concentrations in ambient air. Evaporative VOC emissions can be reduced modifying traditional petrol content (petrol reformulation) to allowable more eco-friendly petrol profile.
5. VOCs concentrations in ambient air are strongly correlated with temperature factor and VOC species reactivity. Among petrol-related VOCs dominate the aromatics, in particular xylenes and toluene. Highest VOC concentrations are always reached at stagnant air and low wind speeds. The chemical removal of VOCs is another important determinant of the final shape of measured concentrations.
6. VOC emissions are result of petrol station's technological operations: petrol filling into underground tank, petrol storage in underground tank, petrol dispensing into vehicles and portable containers. Emission from refuelling is the largest source of VOC at typical petrol station and makes about 40 % of total VOC emission from petrol station.
7. Because a VOC's impacts on air quality strongly depend on the environment where it is emitted, use of air quality models provides the only practical means to predict the VOC's impact in an actual environment and only available scientific basis for making quantitative estimates of changes in air quality.

2. RESEARCH PART

2.1. RESEARCH SITES

Two research sites (RS1, RS2) were intended to measure a representative urban volatile mix of pollutants emitted from petrol stations. The two research sites (RS) with usual activity of service stations supplying petrol to road vehicles in Vilnius city for the estimation of petrol-related VOCs were chosen. Table 2.1 gives brief description of research sites, while accompanying figure 2.1 gives the situation plan.

Table 2.1. Research sites of VOCs' from petrol filling stations in Vilnius

RS No.	Location	Brief description
1	Laisvės prospect 80B	Non-automatic self-service petrol station. Located on the town margins, near Laisves prospectus. In surrounding area high-altitude buildings are prevail.
2	Kauno street 26	Automatic self-servise petrol station (A24). Located not far from the center of town, near crossroad of Kauno street with Shvitrigailos street. In surrounding area buildings are mainly of 2, 4 floors.

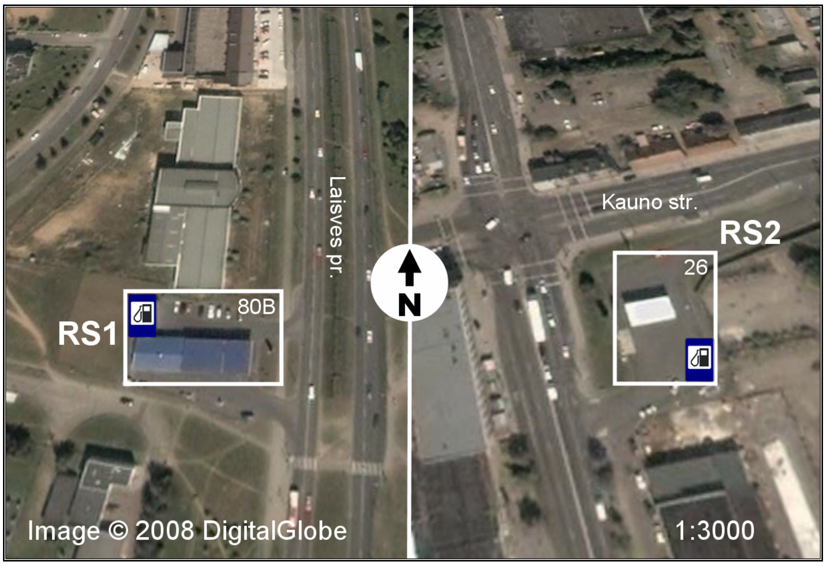


Figure 2.1. Research sites of VOCs' from petrol filling stations in Vilnius

The petrol stations were chosen by equivalent site requirement in a part of the city in which background VOC concentrations are mainly due to traffic and there are no additional VOCs sources. Petrol stations are quite close to the residential buildings, having similar poor greening, meet criteria for high-traffic urban sites and for typical technology layout and installed petrol vapour control equipment (underground storage tank, submerged fill only, pressure/vacuum valve, stage 1 plus stage 2 vapour recovery system).

2.2. SAMPLING

The sampling procedure to collect VOCs from ambient air of petrol filling station involved active collections of samples, pumping air into glass tubes (aka gas pipettes).

Sampling points. The petrol filling station is an area source of VOCs pollution. Therefore the stationary points of VOCs emissions were chosen with reference to hazardous zones of typical petrol filling station. In total there are three hazardous zones, i.e. areas classified as severe or extreme for vapours nonattainment at petrol station. These zones located around controlled VOC emission point-sources at petrol station's territory: zone of 1,5 m radius (R) around aboveground part of petrol storage tank; 3,0 m R zone around P/V valve; 1,0 m R zone around petrol dispensers. With each station's hazardous zone two sampling points were assigned.

Sampling points are listed in table 2.2, their locations at petrol station territory schematically shows figure 2.2.

Table 2.2. Sampling points of VOCs' from petrol filling station

Sampling point No.	Location of sampling point, sampling height above ground (H), m.
I Hazardous area	
1	Near filling point, H = 1,0 m.
2	Near vapour (P/V) vent, H = 1,8 m.
3	Near vapour (P/V) vent, H = 1,0 m.
4	Between dispensers, H = 1,0 m.
5	Near dispenser, H = 1,0 m.
6	Alongside with refueling, H = 1,0 m.
I Non-hazardous area	
7	Near canopy, H = 1,8 m.
8	Near canopy, H = 1,0 m.
9	Near driveway in of the petrol filling station, H = 1,0 m.
10	Near driveway out of the petrol filling station, H = 1,0 m.

Six sampling points (sampling points No. 1-6) include VOCs, measured in hazardous zones, i.e. VOCs samples near filling point, near petrol dispenser, alongside with refuelling were grabbed at 0,6 m height, between petrol dispensers – at 1,0 m, near vapour vent at 1,0 and 1,8 m above ground. Complementary 2 VOC grabs were collected near canopy and 2 VOC grabs near driveways in and out of petrol station. See figure 2.2.

Figure 2.2. Sampling points' location at typical petrol station's territory

Sampling equipment. The sampling equipment includes portable "Zambelli" EGO series sampling pump and glass tubes (aka gas pipette) with plastic plugs (figure 2.3).

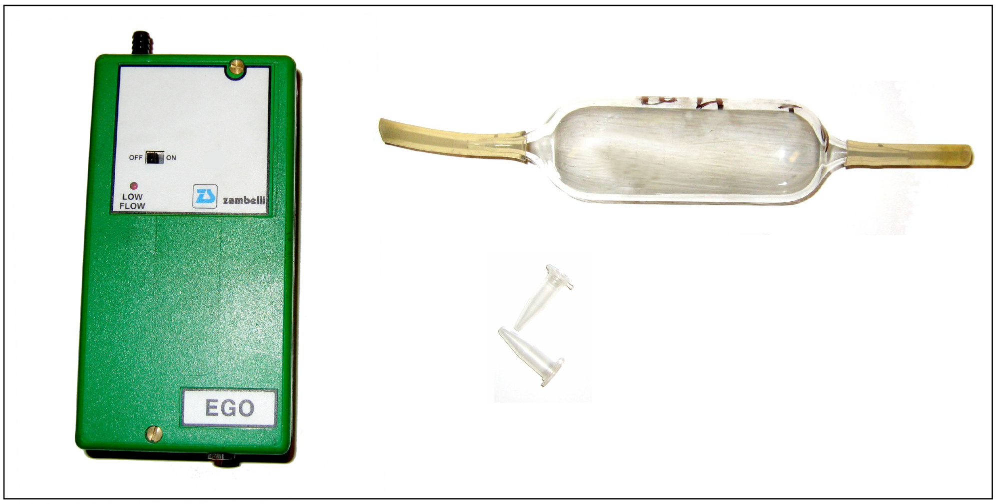


Figure 2.3. Sampling equipment: 1 – sampling pump, 2 - gas pipette, 3 – plugs.

Air sampling – capturing the contaminant (VOCs) from ambient air, was done with air volume aspiration through rubber tube in clean glass gas pipette (d = 5-8 cm, l = 10-30 cm) at 0,25-0,5 l/min velocity. The samples are closed after sampling: aspiration process is cut off and the ends of gas pipette through tubes are sealed with plastic plugs. An identification label is attached to the each glass tube. The sample tubes after sampling procedure are transported to a predetermined laboratory for analysis. The samples holding time is set for analyses within two days.

Sampling period. VOC samples were collected during the cold period of January 2008, 17-18 days (winter season). Sampling was carried out every day and lasted 1 hour while 10 samples were collected for workday 12:00-13:00 h (when the contribution of the road traffic was insignificant) respectively at each petrol station.

Meteorological conditions. It is important to fix meteorological data during sampling as weather conditions strongly influence petrol-related VOCs concentration in ambient air. During VOCs' from petrol filling stations sampling the meteorology conditions: air temperature, atmospheric pressure, air humidity, wind direction and speed, were precisely logged, see table 2.2. The wind rose for Vilnius based on long-term supervisions (figure 2.4) shows, that during winter-season the south and south-eastern winds are dominant.

Table 2.3. Meteorological conditions during sampling (1 h average)

Research sites No.	Location	Sampling timescale	Meteorological conditions
1	Vilnius, Laisvės pr. 80B	2008-01-17 12:00-13:00 h	Overcast 1002,01 hPa + 1,54 ^{o}C SSE 1,32 m/s 82,45 %
2	Vilnius, Kauno str. 26	2008-01-18 12:00-13:00 h	Overcast 989,67 hPa + 1,52 ^{o}C SSE 1,78 m/s 23,96 %

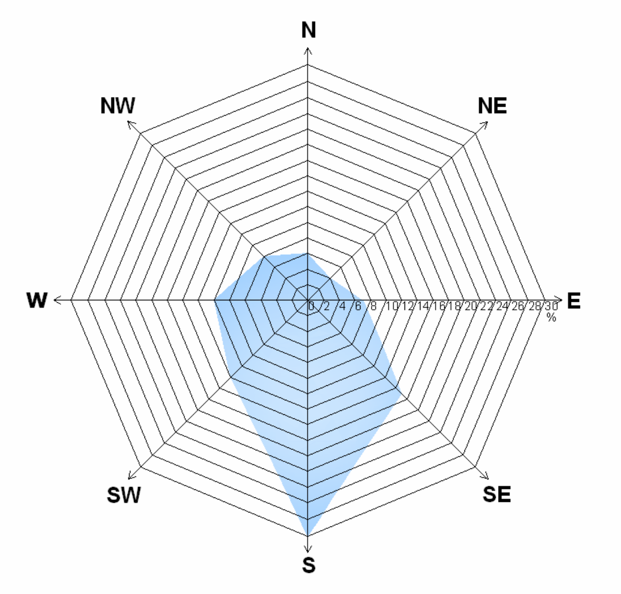


Figure 2.4. Wind Rose for Vilnius, January

Meteorological data of atmospheric conditions is obtained from Vilnius air monitoring service: for RS1 – from Vilnius Lazdynai station (0002), for RS2 – from Vilnius Senamiestis station (0001). Meteorological conditions range during sampling at RS1: air temperature 1,56 ^{o}C -1,52 ^{o}C, atmospheric pressure 1001,88 hPa - 1002,14 hPa, humidity 82,53 % - 82,37 %, wind speed 1,33 m/s - 1,31 m/s, wind direction 158,88^{o} - 166,54^{o}. Meteorological conditions range during sampling at RS2: air temperature 1,49 °C - 1,54 °C, atmospheric pressure 989,67 hPa - 989,67 hPa, humidity 23,81 % - 24,10 %, wind speed 1,79 m/s - 1,77 m/s, wind direction – 169,79° - 168,96°. Meteorological conditions for two sampling days are quite similar, excluding air humidity. The humidity drop for second sampling day is rather sensible. In whole meteorological conditions with slight winds, law temperatures and overcast were not favorable for pollutant dispersion and removal. The wind direction during sampling is in line with long-term wind pattern.

2.3. SUMMARY OF METHOD

2.3.1. SCOPE AND APPLICATION

The type of analysis method is off-site: contaminant capturing from ambient air in the selected sampling points at research sites followed by measuring the result as a concentration during analytical laboratory test. The applicable analyzing method for analyte: petrol-related VOCs (no analyte CAS number assigned) as light petrol range hydrocarbons C_6-C_{10}, is gas chromatography. GC is the approved chromatographic method for thermally stable volatile compounds. Method can provide total VOCs concentration determination and individual VOC species identification.

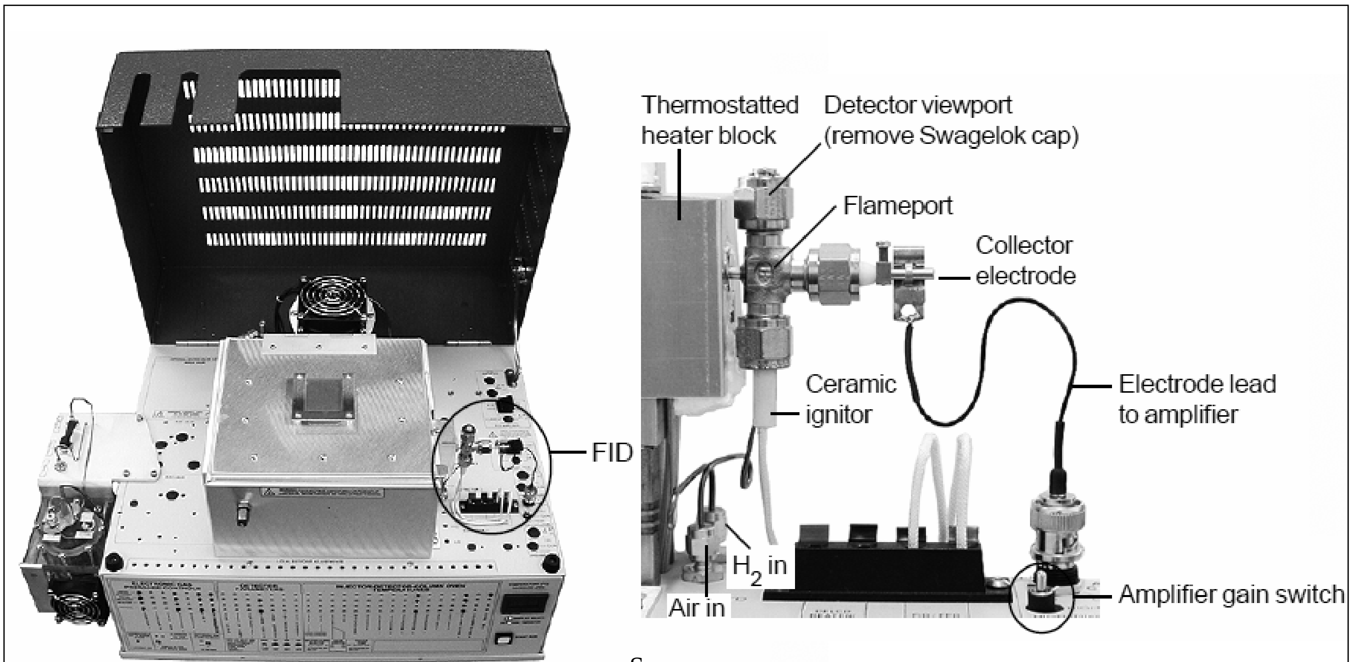
The analytical method involves using a high-resolution gas chromatograph (GC) coupled to one appropriate flame ionization detector (FID) detector. Gas chromatography (GC), in combination with flame ionization detection (FID), has been used in many studies to measure atmospheric VOCs. GC-FID is employed for qualitative identification and quantitative determination of volatile organic compounds. The Flame Ionization Detector is the most commonly used GC detector, responding linearly from its minimum detectable quantity of about 100 picograms to almost 100 %.

2.3.2. EQUIPMENT AND SUPPLIES

Equipment and supplies (instrumental components) are listed below.

1) Aspirator Air Sampling Pump SKC MCS Flite;
2) Gas chromatograph SRI 8610 with a flame ionization detector (FID);
3) Column stainless steel Supelcoport, length - 6,1 m, inner diameter - 0,32 cm, filled with diatomite and 10 % SP-1000 matrix 80/100;
4) Laboratory thermometer;
5) Stop watch;
6) Barometer-aneroid;
7) Ruler;
8) Micro syringes 10, 25 and 50 µl, syringes Agilent 1 ml with teflon piston;
9) Bottle 6,0 l volume;
10) Compressed air (Eime Messer);
11) Nitrogen – especially pure (Eime Messer);
12) Hydrogen 99,999 % cleanness (Eime Messer);
13) Standard material:

n-hexane, ch. clean., d = 0.660 boil. T = 69 °C



Source:

Figure 2.5. SRI capillary FID GC with built-in hydrogen generator

VOCs’ quantitative determination by hexane (n-hexane) and qualitative compounds identification by their corresponding retention time are done using gas chromatograph SRI 8610 with a flame ionization detector (FID) built-in with hydrogen generator.

The gas chromatograph SRI 8610 FID general features:

- type – mass flow;
- support gases – hydrogen and air;
- hydrocarbon selective;
- linear;
- stable.

Ceramic ignitor uses a hydrogen diffusion flame to ionize compounds for analysis. It destroys the sample in the process. This ignitor is positioned perpendicular to the stainless steel detector jet. Opposite this flame is the collector electrode.

The ratio of air to hydrogen in the combustion mixture should be approximately 10:1. On an SRI GC, the hydrogen and air gas flows are controlled using electronic pressure controllers (EPC), which are adjustable via the GC’s front panel.

A thermostatted aluminum heater block maintains a stable detector temperature which is adjustable up to 375 ^{o}C. The air compressor is used to supply the air for the FID.

The carrier chemically inert gas includes nitrogen. In the SRI FID, the carrier gas effluent from the GC column is mixed with hydrogen, and then routed through an unbreakable stainless steel jet. The hydrogen mix supports a diffusion flame at the jet’s tip which ionizes the analyte molecules. Positive and negative ions are produced as each sample component is eluted into the flame. An electrostatic field is generated by the difference in potential between the positively charged collector electrode and the grounded FID jet. Because of the electrostatic field, the negative ions have to flow in the direction of the collector electrode. A collector electrode attracts the negative ions to the electrometer amplifier, producing an analog signal for the data system input.

2.3.3. GAS CHROMATOGRAPH PREPARATION

When the device is turned on, the parameters specified in chromatographic conditions of the analysis are established, a zero line must be checked up. The qualitative zero line means tat device is ready to work.

Chromatographic conditions of analyze:

- nitrogen velocity 30-34 ml/min;
- hydrogen velocity 18 ml/min;
- air velocity 250 ml/min;
- column’s thermostat temperature 90°C.
- vaporizer temperature 90°C.
- detector temperature 90°C.

Combustion ratio may need to be adjusted. Flow is user adjusted through the EPC. Then test chromatograms are generated. The FID temperature must be hot enough so that condensation doesn’t occur anywhere in the system, 150 ^{o}C is sufficient for volatile analytes.

Calibration diagram. To prepare not less than 3 various concentrations of determinate materials compounds with an air static method. The precise volume of a bottle in which compounds are prepared is measured by quantity of the distilled water at a room temperature.

Preparing compounds, volume of a bottle V_T is counted to volume at normal conditions according to the formula:

$$V_0 = \frac{V_T \cdot 273 \cdot p}{(273 + T) \cdot 760}, \tag{2.1}$$

here V_T – bottle volume in which the compound was prepared, l;

T – room temperature, °C;

p – atmospheric pressure, mm inHg.

A few rolls of aluminum foil are put in a bottle to mix standard materials vapour. The 20 mm height rubber plug hermetically stoppered bottle. The rubber plug is wrapped up in foil and pierced with glass 5 mm in diameter tubule. On a glass tubule is strung 30 mm elastic silicone hose, the end of it blocks glass plug. The free end of tubule put out of a rubber plug inside bottle should not exceed 1,5-2 mm. Standard materials in a bottle are dosed out 10-50 ml by micro syringes through free silicone hose.

Proceeding with the GC standard materials is injected into a 6 l bottle. The syringe needle is fully downwards in silicone hose. Then the bottle gently warming up 30 minutes in thermostat, which maintains 40-50 ^{o}C temperature. It is offered to stick almost simultaneously in a silicone hose 1-3 micro syringes with different materials and to sustain 30 minutes at 40-50 ^{o}C temperature. The ready compound is necessary to maintaine 0,5-1 hour, periodically stirring slowly. The calibration begins with smaller concentration.

When through silicone hose micro syringe needle is fully downwards, the micro syringe is swill 5 times with calibrated compound. At sixth time 1 cm^3 calibrated vapour compound is soak up and immediately inject into GC and chromatogram is recorded. The procedure should be repeated 3 times.

TVOCs by hexane concentration is calculated under the following formula:

$$C = \frac{12 \cdot m \cdot n}{M \cdot V_0} \cdot 10^3, \qquad (2.2)$$

here C – VOCs LOJ (total VOCs by hexane) concentration, mg/m;

m – hexane weight, mg;

n – carbon atoms number in hexane molecule;

M – molecular hexane mass;

V_0 – bottle volume counted to volume at normal conditions, l;

10^3 – mg/l to mg/m^3 translation coefficient.

Recorded chromatogram peak area (S) is estimated and the calibration diagram: linear dependence (S) from concentration (C), is drawn.

Absolute calibration coefficient is calculated based on following formula:

$$k = \frac{C \cdot V \cdot 10^{-6}}{S_{vid}}, \qquad (2.3)$$

here k – absolute calibration coefficient, mg;

C – material concentration in a bottle, mg/m^3;

S_{vid} – average peak area;

V – gas sample volume injected into GC, cm^3;

Multiplier 10^{-6} – cm^3 to m^{3}translation.

The calibration diagram should be checked up once a month. Calibration and sample conditions should be identical.

Detectability. The FID responding linearly from its minimum detectable quantity of about 100 picograms to almost 100 %. It is possible to determinate VOCs from 6,74 mg/m^3.

2.3.4. ANALYTICAL PROCEDURE

After GC preparation and calibration the gas pipette with the sample is gently warmed up till 40-50 °C and stored 0,5-1,0 hours. Gas chromatography begins by injecting a very small amount of the sample (1 μl) into the GC Sample injection port (see figure). From gas pipette through silicone hose into clean medical syringe is soaked up 1 cm^3 of analyzed sample and injected into GC vaporizer. This small amount of sample is then volatilized by the heat of the oven and carried into the column by an inert gas. For optimum column efficiency, the sample should be introduced onto the column as a "plug" of vapour, because slow injection of large samples causes band broadening and loss of resolution.

When a sample is introduced, hydrocarbons are combusted and ionized, releasing electrons. A collector with a polarizing voltage located near the flame attracts the free electrons, producing a current that is proportional to the amount of hydrocarbons in the sample. The signal from the flame ionization detector is then amplified and output to a display or external device. At least 3 chromatograms should be recorded. If concentration is too high the air dilution is allowed.

Results calculation. Results calculation is based on formula:

$$C = \frac{S_{vid} \cdot k}{V \cdot K} \cdot 10^6 , \tag{2.4}$$

here C – emitted VOCs concentration , mg/m^3;

S_{vid} – average peak area;

k– absolute calibration coefficient, mg;

V – gas sample volume injected into GC, cm^3;

K – coefficient of determinate concentration translation to normal (standart) conditions;

Multiplier 10^6 – cm^3 to m^3 translation.

K calculation formula:

$$K = \frac{273 \cdot P}{760 \cdot (273 + t)} , \tag{2.5}$$

P – atmospheric pressure, mm inHg;

t – temperature in sample capture place, °C.

Table 2.3. Material‘s suspension time

Nr.	Determinated compound name	Retention time, min
1.	TVOC (sum hydrocarboncs by hexane)	2,466-2,5

Material‘s suspension time is specified in the 2.3 table.

3. ANALYTICAL PART

3.1. EXPERIMENT RESULTS

Twenty VOCs samples from ambient air of petrol filling stations were collected during the 2008-01-17/18 site efforts, sequentially using the same equipment and sampling procedure. Samples are analyzed in a set for each research site respectively. Results obtained from of overall 20 samples VOC analyses by GS-FID method as VOC concentrations are summed in VOC emissions reports for research site No. 1 and research site No. 2. The table 3.1 shows the main results that derive from the analysis.

The VOCs emission report for Research site No. 1 (Vilnius, Laisvės pr. 80B) gives data of five individual volatile organic compounds detected in 6 samples. These identified VOC species include:

- benzene (C_6H_6);
- toluene (also known as methylbenzene $C_7H_8(C_6H_5CH_3)$);
- ethylbenzene (C_8H_{10});
- m,p-xylene (C_8H_{10} ($C_6H_4C_2H_6$));
- ethyl acetate ($CH_3COOC_2H_5$).

The VOCs emission report for Research site No. 2 (Vilnius, Kauno str. 26) gives data of only one individual VOC – benzene. Other VOC species are not detected (ND). Benzene was detected in 6 samples. Most likely it is cause of the longer RS2 samples storage period, than RS1 samples storage. The benzene exclusive identification in RS2 samples explains its ability for long-lasting presence, i.e. lifetime in ambient air.

Concentrations (C) of sum VOCs are indicated in micrograms per cubic meter or mg/m^3 as well as concentrations of speciation of the VOC. As procedure of accuracy quality included GC calibration by n-hexane and laboratory threefold measurements of samples, the concentrations data of the same probe are resulted in average concentration.

Table 3.1. VOC emission report for RS1 and RS2

RS No.	**Research site No. 1**				**Research site No. 2**			
RS location	Vilnius, Laisvės pr. 80B				Vilnius, Kauno str. 26			
	Area A	Koef. K	C, mg/m^3	Average C, mg/m^3	Area A	Koef. K	C, mg/m^3	Average. C, mg/m^3
Sample No. 1								
VOC	1078,39	0,75492	1428,482	1277,897	402,28	0,75492	532,877	525,1504
	932,23	0,75492	1234,873		396,42	0,75492	525,115	
	883,51	0,75492	1170,336		390,64	0,75492	517,459	
Benzene	301,38	49,87034	6,0433	5,405	79,99	49,87034	1,60407	1,4843
	269,75	49,87034	5,4091		73,45	49,87034	1,473	
	238,26	49,87034	4,778		68,62	49,87034	1,376	
Sample No. 2								
VOC	49,78	0,75492	65,9408	60,827	301,9527	0,75492	399,9797	359,154
	44,47	0,75492	58,9062		266,4245	0,75492	352,9175	
	43,51	0,75492	57,635		245,02	0,75492	324,5642	
Ethyl acetate	142,41	8,638425	16,486	15,729				ND
	130,04	8,638425	15,0537					
	135,17	8,638425	15,648					
Ethylbenzene	238,5	26,00244	9,172	10,651				ND
	294,91	26,00244	11,342					
	297,41	26,00244	11,438					
m,p-Xylene	238,5	56,21227	4,243	4,884				ND
	282,06	56,21227	5,0178					
	303,06	56,21227	5,391					
Benzene				ND	63,66	49,87034	1,277	1,143
					57,0	49,87034	1,143	
					50,34	49,87034	1,00942	
Sample No. 3								
VOC	51,63	0,75492	68,391	65,891	316,0	0,75492	418,582	375,0888
	51,08	0,75492	67,656		274,53	0,75492	363,654	
	46,52	0,75492	61,626		258,96	0,75492	343,0297	
Ethyl acetate	95,96	8,638425	11,1082	10,180				ND
	92,46	8,638425	10,7029					
	75,41	8,638425	8,729					
Benzene	64,86	49,87034	1,30057	1,376	53,99	49,87034	1,0826	0,9902
	70,28	49,87034	1,4093		46,295	49,87034	0,928	
	70,67	49,87034	1,417		47,859	49,87034	0,960	
Toluene	64,86	42,77554	1,5163	1,607				ND
	70,67	42,77554	1,652					
	70,67	42,77554	1,652					
Ethylbenzene	281,22	26,00244	10,815	9,913				ND
	257,79	26,00244	9,914					
	234,35	26,00244	9,0126					
m,p-Xylene	257,79	56,21227	4,586	4,308				ND
	234,35	56,21227	4,169					
	234,35	56,21227	4,169					
*ND – not-detected	Proceed to the next page Table 3.1. continuation							
RS No.	**Research site No. 1**				**Research site No. 2**			

	Area A	Koef. K	C, mg/m^3	Average C, mg/m^3	Area A	Koef. K	C, mg/m^3	Average C, mg/m^3
Sample No. 4								
VOC	40,93	0,75492	54,218	56,039	231,73	0,75492	306,960	301,995
	42,31	0,75492	56,0391		241,99	0,75492	320,560	
	43,68	0,75492	57,8604		210,22	0,75492	278,467	
Ethyl acetate	213,21	8,638425	24,682	26,443				ND
	224,52	8,638425	25,991					
	247,56	8,638425	28,658					
Benzene	83,26	49,87034	1,670	1,577	45,72	49,87034	0,917	0,848
	77,08	49,87034	1,546		43,70	49,87034	0,876	
	75,55	49,87034	1,515		37,51	49,87034	0,752	
Toluene	79,45	42,77554	1,857	1,807				ND
	83,26	42,77554	1,946					
	69,11	42,77554	1,616					
Ethylbenzene	155,05	26,00244	5,963	5,212				ND
	135,53	26,00244	5,212					
	116,01	26,00244	4,462					
m,p-Xylene	143,26	56,21227	2,549	2,201				ND
	117,85	56,21227	2,0965					
	110,12	56,21227	1,959					
Sample No. 5								
VOC	726,01	0,75492	961,711	1043,952	186,92	0,75492	247,6047	236,1074
	802,04	0,75492	1062,414		177,17	0,75492	234,687	
	836,25	0,75492	1107,730		170,63	0,75492	226,0304	
Benzene	430,64	49,87034	8,635	7,850	14,62	49,87034	0,293	0,327
	391,49	49,87034	7,8502		16,79	49,87034	0,337	
	352,34	49,87034	7,0651		17,49	49,87034	0,351	
Toluene	528,51	42,77554	12,355	10,983				ND
	489,36	42,77554	11,4402					
	391,49	42,77554	9,152					
Ethylbenzene	565,95	26,00244	21,765	18,742				ND
	471,63	26,00244	18,138					
	424,46	26,00244	16,324					
m,p-Xylene	518,79	56,21227	9,229	8,390				ND
	471,63	56,21227	8,3901					
	424,46	56,21227	7,551					
Sample No. 6								
VOC	1825,75	0,75492	2418,468	2538,570	363,21	0,75492	481,124	445,974
	1742,57	0,75492	2308,282		336,675	0,75492	445,974	
	2180,93	0,75492	2888,9601		310,14	0,75492	410,825	
Benzene	663,29	49,87034	13,30025	11,638	53,10	49,87034	1,0648	0,9408
	552,74	49,87034	11,0835		44,71	49,87034	0,897	
	525,10	49,87034	10,529		42,95	49,87034	0,861	

Proceed to the next page

Table 3.1. continuation

RS No.	**Research site No. 1**	**Research site No. 2**

	Area A	Koef. K	C, mg/m^3	Average C, mg/m^3	Area A	Koef. K	C, mg/m^3	Average C, mg/m^3
Sample No. 6								
Toluene	663,29	42,77554	15,5062	14,860				ND
	690,93	42,77554	16,152					
	552,74	42,77554	12,922					
Ethylbenzene	835,64	26,00244	32,137	29,215				ND
	759,67	26,00244	29,215					
	683,70	26,00244	26,294					
m,p-Xylene	835,64	56,21227	14,866	13,514				ND
	759,67	56,21227	13,514					
	683,70	56,21227	12,163					
Sample No. 7								
VOC	13,68	0,75492	18,121	24,6075	11,79	0,75492	15,618	36,732
	15,27	0,75492	20,227		29,68	0,75492	39,315	
	26,78	0,75492	35,474		41,72	0,75492	55,264	
Sample No. 8								
VOC	17,82	0,75492	23,6051	28,670	28,07	0,75492	37,183	45,144
	22,89	0,75492	30,321		35,02	0,75492	46,389	
	24,22	0,75492	32,0828		39,15	0,75492	51,860	
Sample No. 9								
VOC	75,21	0,75492	99,626	54,942	34,41	0,75492	45,581	43,5101
	17,42	0,75492	23,0753		31,09	0,75492	41,183	
	31,8	0,75492	42,124		33,04	0,75492	43,766	
Sample No. 10								
VOC	31,65	0,75492	41,925	40,0793	39,48	0,75492	52,297	52,893
	22,47	0,75492	29,764		36,37	0,75492	48,177	
	36,65	0,75492	48,548		43,94	0,75492	58,2048	

See next section for experiment results evaluation.

3.2. RESULTS EVALUATION

Experiment results quality assurance. Compounds in ambient air that have similar retention times may co-elute causing inaccurate quantifications as well as misidentification (Standard operating… 2002).There is also a potential for many non-target compounds, in this case non-petrol-related VOCs, presense in samples to interfere and implicate analysis quality. The quality control was conducted for analytical procedure.

The quality control procedure besides procedure of calibration included laboratory samples triple measurements. Triple measurements of samples were analyzed to test the precision of the sampling and analytical techniques, respectively. For results quality assurance the results were evaluated for statistical dispersion. Standard deviation (SD, σ) as the square root of variance, the percent relative standard deviation (RSD, σ %) or coefficient of variation, standard deviation of the mean as a measures of the precision of experimental measurements were computed. The computed results of experiment quality assurance for research site No. 1 and research site No. 2 are listed in table 3.2.

Table 3.2. Experiment results quality assurance data

RS No.	**Research site No. 1**				**Research site No. 2**			
RS location	Vilnius, Laisvės pr. 80B				Vilnius, Kauno str. 26			
	Average C, mg/m^3	SD σ	RSD, %	$\pm\frac{\sqrt{\sigma}}{n}$	Average C, mg/m^3	SD, σ	RSD, %	$\pm\frac{\sqrt{\sigma}}{n}$
Sample No. 1								
VOC	1277,897	109,691	8,584	63,3302	525,1504	6,295	1,199	3,634
Benzene	5,405	0,517	9,552	0,298	1,484	0,0935	6,298	0,0539
Sample No. 2								
VOC	60,827	3,653	6,00506	2,1089	359,154	31,1025	8,660	17,957
Ethyl acetate	15,729	0,587	3,735	0,339	ND			
Ethylbenzene	10,651	1,0461	9,822	0,604	ND			
m,p-Xylene	4,884	0,478	9,793	0,276	ND			
Benzene	ND				1,143	0,10904	9,5401	0,063
Sample No. 3								
VOC	65,891	3,03096	4,600	1,750	375,0888	31,886	8,50099	18,4095
Ethyl acetate	10,180	1,0392	10,2087	0,600	ND			
Benzene	1,376	0,0532	3,866	0,0307	0,9902	0,0666	6,725	0,0384
Toluene	1,607	0,06403	3,985	0,037	ND			
Ethylbenzene	9,913	0,736	7,423	0,425	ND			
m,p-Xylene	4,308	0,197	4,562	0,113	ND			
Sample No. 4								
VOC	56,039	1,487	2,654	0,859	301,995	17,539	5,8078	10,126
Ethyl acetate	26,443	1,655	6,257	0,955	ND			
Benzene	1,577	0,0668	4,237	0,0386	0,848	0,0700083	8,252	0,04042
Proceed to the next page Table 3.2. continuation								
RS No.	**Research site No. 1**				**Research site No. 2**			

	Average C, mg/m^3	SD σ	RSD, %	$\pm\frac{\sqrt{\sigma}}{n}$	Average C, mg/m^3	SD, σ	RSD, %	$\pm\frac{\sqrt{\sigma}}{n}$
Toluene	1,807	0,140	7,736	0,08068	ND			
Ethylbenzene	5,212	0,613	11,758	0,354	ND			
m,p-Xylene	2,201	0,252	11,441	0,145	ND			
Sample No. 5								
VOC	1043,952	61,0247	5,846	35,233	236,1074	8,865	3,755	5,118
Benzene	7,850	0,641	8,165	0,37006	0,327	0,0246	7,515	0,0142
Toluene	10,983	1,347	12,266	0,778	ND			
Ethylbenzene	18,742	2,262	12,0699	1,3061	ND			
m,p-Xylene	8,390	0,685	8,1650	0,396	ND			
Sample No. 6								
VOC	2538,570	251,814	9,920	145,385	445,974	6,435	6,435	16,570
Benzene	11,638	1,197	10,287	0,691	0,9408	0,0888	9,438	0,0513
Toluene	14,860	1,396	9,392	0,8058	ND			
Ethylbenzene	29,215	2,385	8,165	1,377	ND			
m,p-Xylene	13,514	1,1034	8,165	0,637	ND			
Sample No. 7								
VOC	24,6075	7,732	31,4203	4,464	36,732	16,288	44,343	9,4041
Sample No. 8								
VOC	28,670	3,653	12,7406	2,1089	45,144	6,0562	13,415	3,497
Sample No. 9								
VOC	54,942	32,540	59,226	18,787	43,5101	1,8045	4,147	1,0418
Sample No. 10								
VOC	40,0793	7,776	19,408	4,491	52,893	4,115	7,781	2,376

Relative percent differences in air VOCs samples graphically presented in figure 3.1.

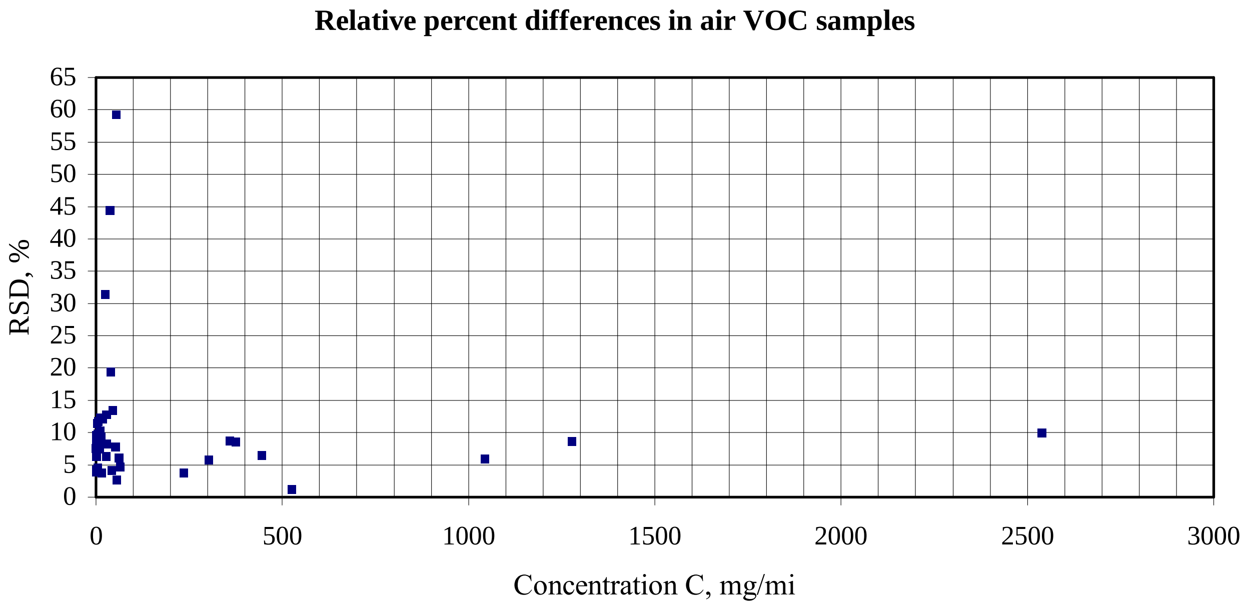


Figure 3.1. Relative percent differences in air VOC samples

As seen from diagram of relative percent difference in air VOC samples the RSD ratios ranged from 3 to 60 %. Nonetheless the RSDs for most of the air VOC samples are less than 10 %. RPDs for individual constituents with concentrations less than 55 mg/m^3 are greater than 20 percent. In consiquence the sample of not so high VOC consentrations obtained from non-hazardous areas of petrol stations (samples No. 7, 8, 9, 10) typically have higher RPDs, when the actual concentrations of air VOC samples collected in main points (samples No. 1, 2, 3, 4, 5, 6) are very close to each other and are within the limits of ten percent.

The great variability of the RPDs (within 25 % - 50 % limits) from air VOC samples analytical methods are often occurs using even multiply analysis teqnuques. Quantitative comparisons indicate that the FID is more subject to error. In either case GC methods, can still cause error incomplex samples especially if, being limited by the separation power of a single colum, because severe peak overlap in single-column chromatography causes difficulties in identification and inaccuracy in quantification. Peak overlapping has another consequence for air analysis (Xu *et al.* 2003).

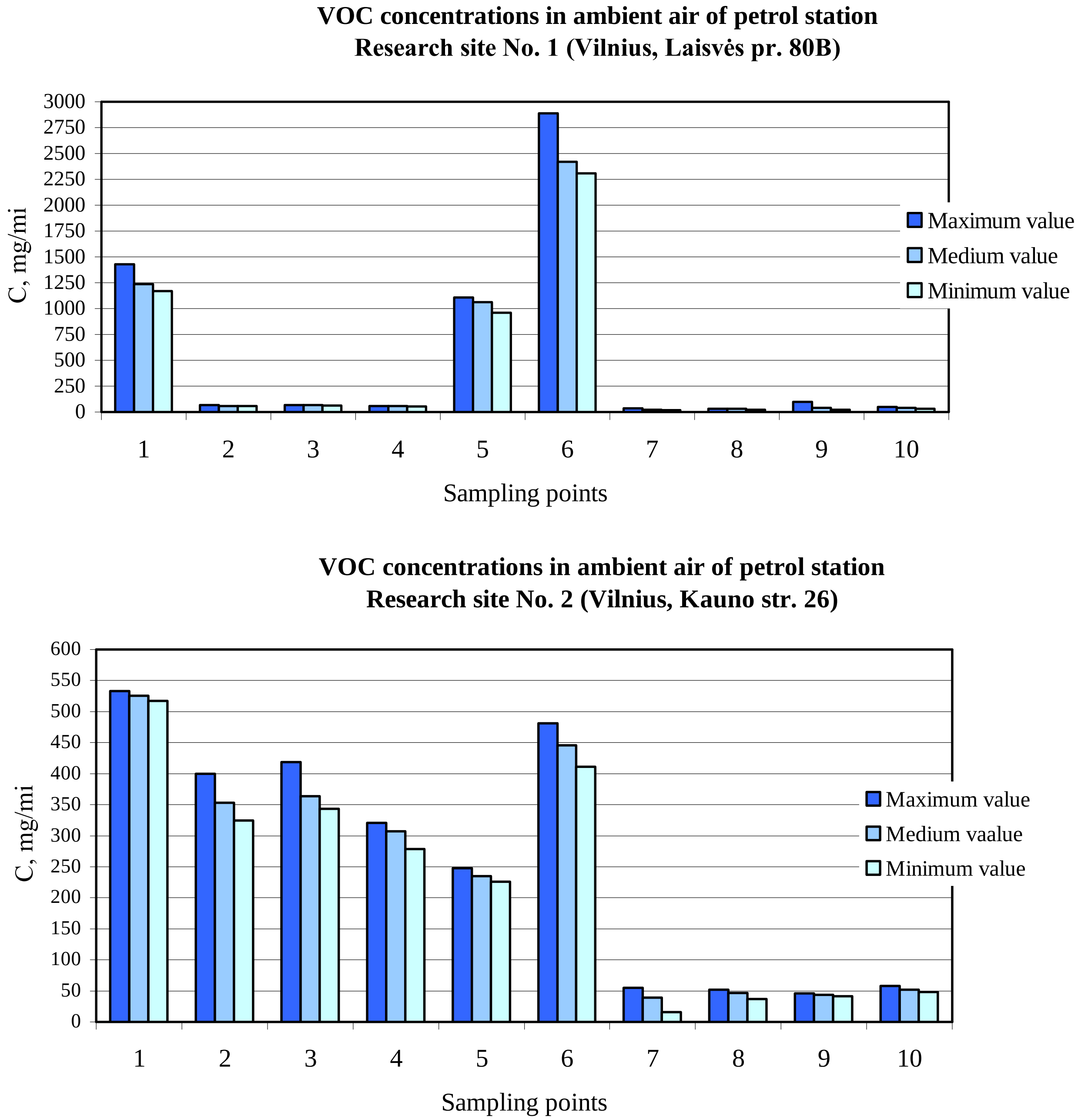
Based on the statistical concentrations ratios evaluation, the data presented in the VOC emission reports for RS1 and RS 2 are of sufficient quality. Whereas in consideration of GC-FID method’s typical complications the quality assurance of experiment results analysis can be considered as acceptable whereas the RSD for most of the air VOC samples are within 10 %.

Graphical results presentation. The results of the experimental research of atmospheric VOCs from petrol filling stations for their better evaluation, comparison and interpretation are presented graphically.

The sampling points conditionally were grouped as main sampling points, selected in hazardous areas of petrol stations (see appendix C), and other or additional saimpling points, selected in non-hazardous areas near canopy and driveways:

- hazardous zones’ sampling points – No. 1, 2, 3, 4, 5, 6;
- non-hazardous zones’ sampling points – No. 7, 8, 9, 10.

The same grouping principle is applicable for experiment results evaluation by tables and diagram means. Histograms presented by figures 3.2, 3.3 visualize experiment results as minimal, medium and maximum VOC concentrations (3.1 table’s data) in main and additional sampling points for research sites respectively. In turn histograms presented by figures 3.4, 3.5, 3.6, 3.7 visualize experiment results as calculated average VOC concentrations in same sampling points (3.2 table’s data) for research sites respectively. These histograms are marked with average 10 % error bar. The sampling point list is attached for each figure, in brackets – sampling altitude H in meters.

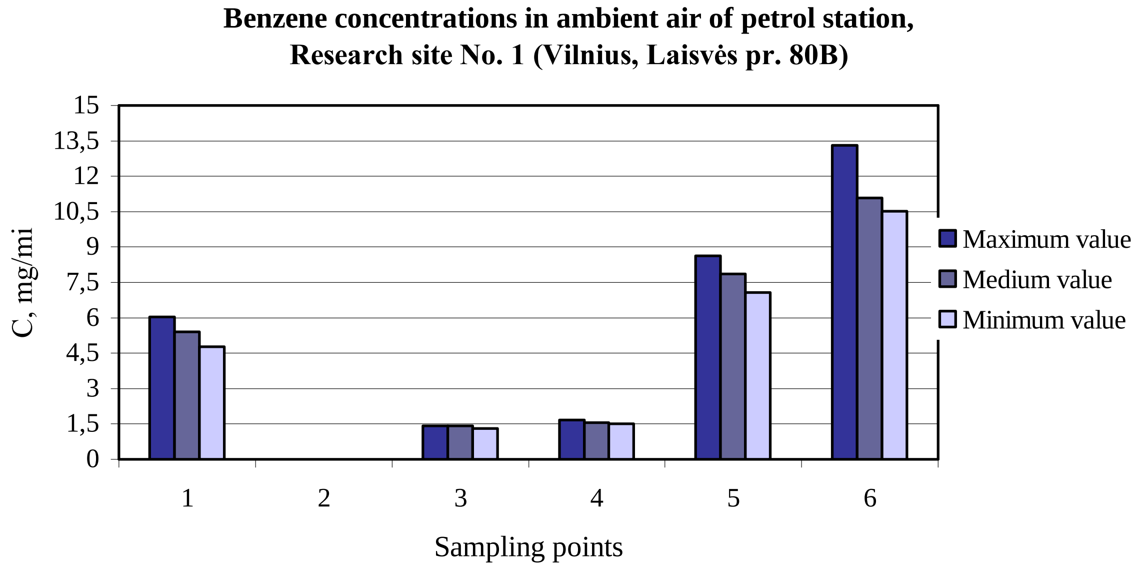


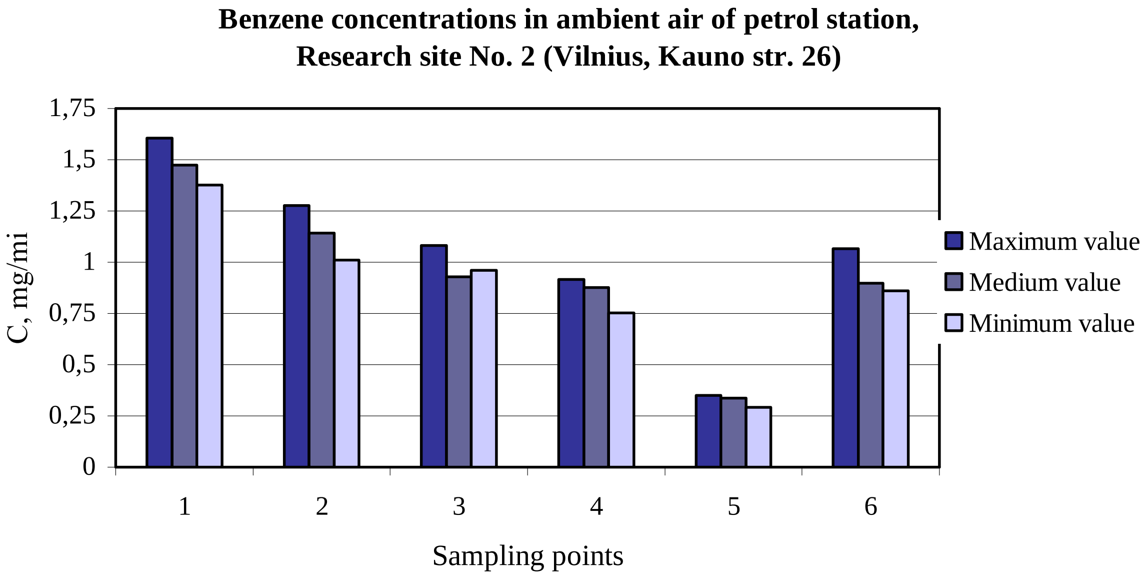
VOC sampling points:

1 - near filling point (H = 1,0 m);	7 - near canopy (H = 1,8 m);
2 - near P/V vent (H = 1,8 m);	8 - near canopy (H = 1,0 m);
3 - near P/V vent (H = 1,0 m);	9 - near driveway in petrol station (H = 1,0 m);
4 - between dispensers (H = 1,0 m);	10 - near driveway out of petrol station (H = 1,0 m).
5 - near dispenser (H = 1,0 m);	
6 - alongside with refuelling (H = 1,0 m);	

Figure 3.2. Maximum, medium and minimum values of VOC concentrations in ambient air of petrol stations

As can be seen from fig. 3.2 the differences in the VOC concentration values are larger for high VOC concentrations and rather smaller for low VOC concentrations. Exceptions are sampling points No. 9 at RS1 and No. 7 at RS2. Both points are pertaining to non-hazardous area of petrol stations.


Benzene concentrations in ambient air of petrol station,
Research site No. 1 (Vilnius, Laisvės pr. 80B)

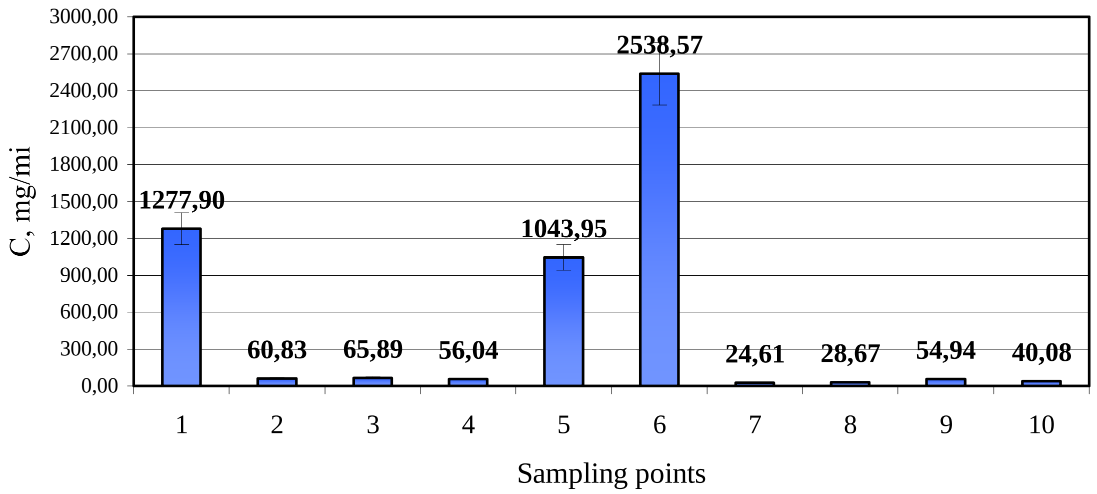

Benzene concentrations in ambient air of petrol station,
Research site No. 2 (Vilnius, Kauno str. 26)

VOC sampling points:

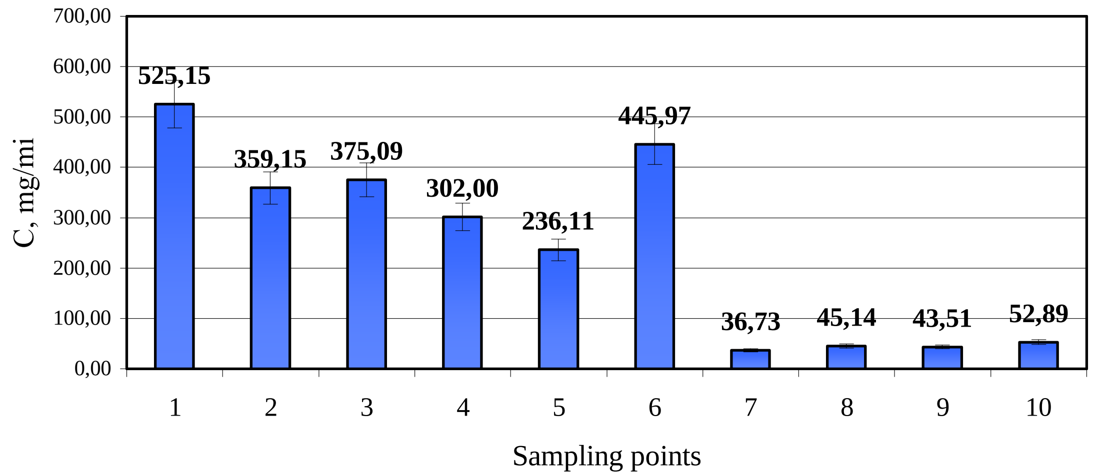
1 - near filling point (H = 1,0 m);	4 - between dispensers (H = 1,0 m);
2 - near P/V vent (H = 1,8 m);	5 - near dispenser (H = 1,0 m);
3 - near P/V vent (H = 1,0 m);	6 - alongside with refuelling (H = 1,0 m).

Figure 3.3. Maximum, medium and minimum values of benzene concentrations in ambient air of petrol stations

As seen from figure 3.3 low benzene concentration samples demonstrate absence of sharp falling from maximum to minimum values. A difference for large concentrations values is similar to VOC concentrations (fig. 3.2) and indicates that they have a larger coefficient of variation. Benzene was detected in all main sampling points at RS2, and in five points at RS1. Can be noticed that, distribution of benzene concentration at RS1 unlike RS2 increases at 1-6 sampling points’ length. The situation for benzene concentration is vice versa for RS2.



VOC concentrations in ambient air of petrol station
Research site No. 1 (Vilnius, Laisvės pr. 80B)



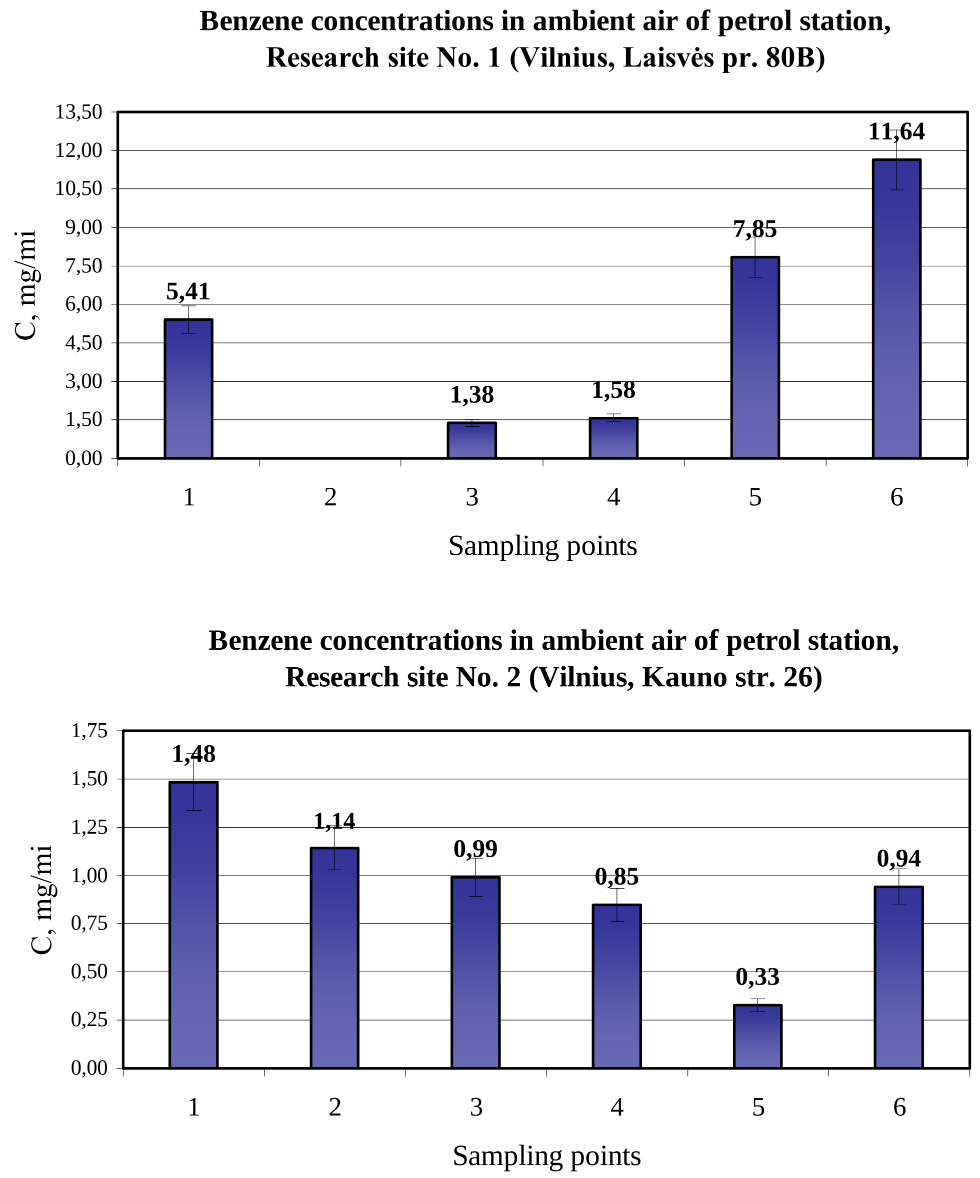
VOC concentrations in ambient air of petrol station
Research site No. 2 (Vilnius, Kauno str. 26)

VOC sampling points:

1 - near filling point (H = 1,0 m);
2 - near P/V vent (H = 1,8 m);
3 - near P/V vent (H = 1,0 m);
4 - between dispensers (H = 1,0 m);
5 - near dispenser (H = 1,0 m);
6 - alongside with refuelling (H = 1,0 m);
7 - near canopy (H = 1,8 m);
8 - near canopy (H = 1,0 m);
9 - near driveway in petrol station (H = 1,0 m);
10 - near driveway out of petrol station (H = 1,0 m).

Figure 3.4. VOC concentrations in ambient air of petrol stations

There are a lot of small VOC concentrations levels at RS1. The VOC concentration is pre-eminent at sampling point 6, i.e. during refuelling operation. The low VOC concentrations bands at RS1 as well as RS2 indicated in the 7, 8, 9 and 10 sampling points, which are in non-hazardous area of the petrol station. Figures 3.5, 3.6 and 3.7 show concentrations of identified individual VOCs.


Benzene concentrations in ambient air of petrol station, Research site No. 1 (Vilnius, Laisvės pr. 80B)

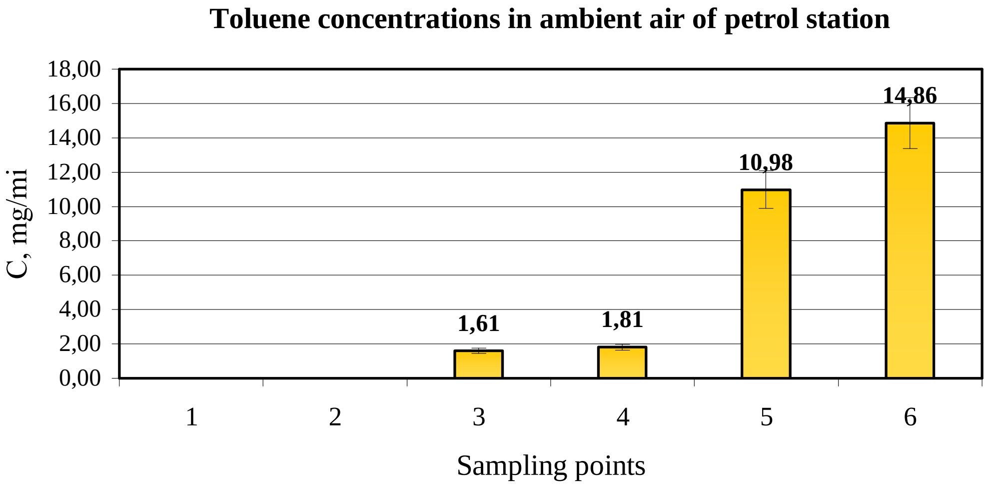
Benzene concentrations in ambient air of petrol station, Research site No. 2 (Vilnius, Kauno str. 26)

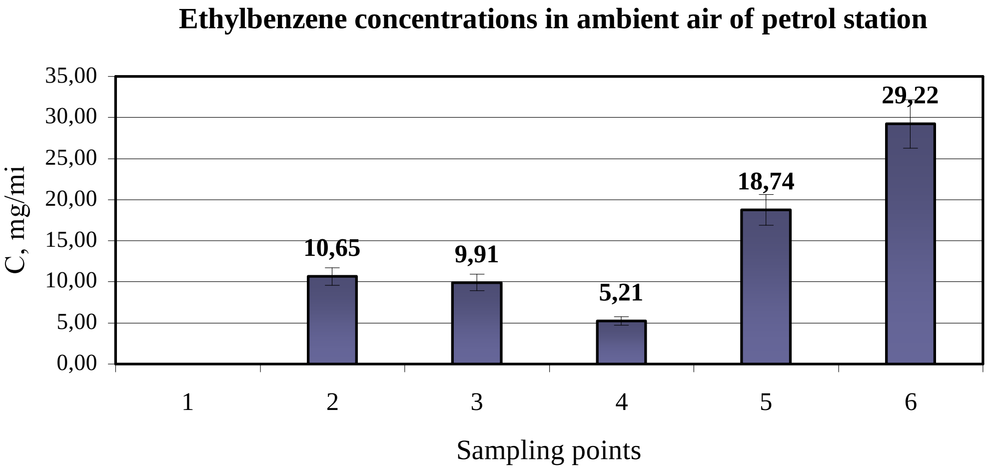
VOC sampling points:

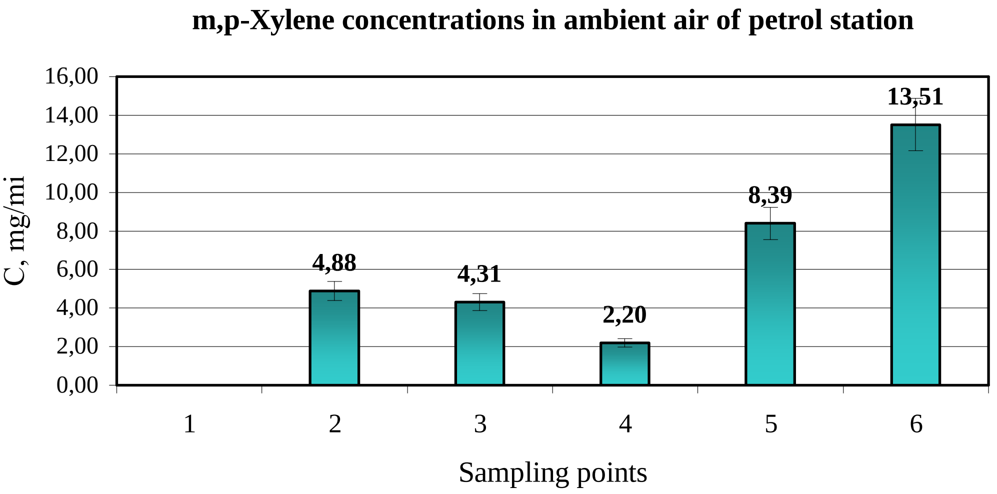
1 - near filling point (H = 1,0 m);
2 - near P/V vent (H = 1,8 m);
3 - near P/V vent (H = 1,0 m);
4 - between dispensers (H = 1,0 m);
5 - near dispenser (H = 1,0 m);
6 - alongside with refuelling (H = 1,0 m).

Figure 3.5. Benzene concentrations in ambient air of petrol stations

VOC measurement in hazardous petrol station's area shows highest benzene concentrations at the RS1, where concentration reaches maximum – 11,64 mg/m^3, during refuelling and minimal – 1,38 mg/m^3, near petrol storage tank vent. Benzene concentration maximum – 1,48 mg/m^3, at R2 is observed near filling point, minimum – 0,33 mg/m^3, near dispenser. As a whole the measured concentrations of benzene at RS1 above in some times of benzene concentrations measured at RS2. For RS2 the benzene concentrations distribution is more uniform, than for RS1. The benzene concentrations maximum-minimum margin at RS1 is 1,55 mg/m^3 versus 10,26 mg/m^3 at RS2.


Toluene concentrations in ambient air of petrol station

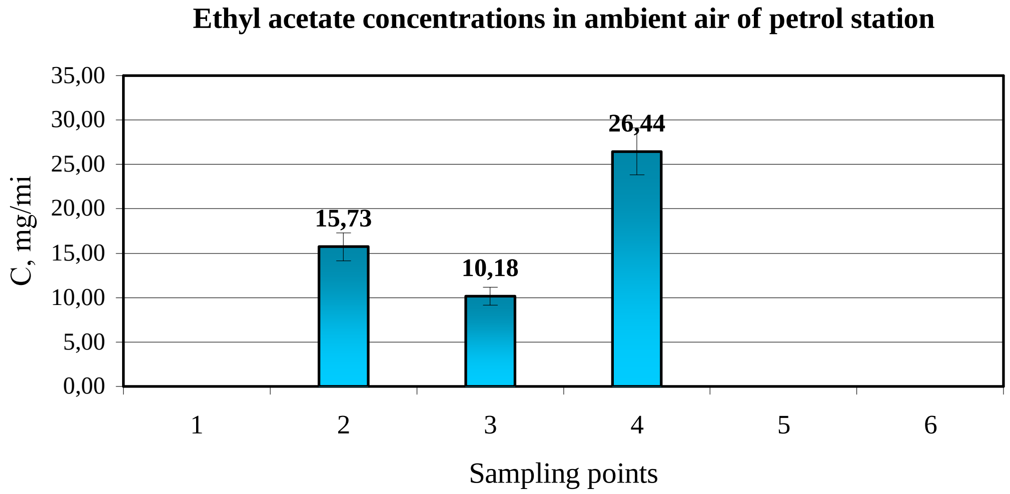

Ethylbenzene concentrations in ambient air of petrol station


m,p-Xylene concentrations in ambient air of petrol station

VOC sampling points:

1 - near filling point (H = 1,0 m);
2 - near P/V vent (H = 1,8 m);
3 - near P/V vent (H = 1,0 m);
4 - between dispensers (H = 1,0 m);
5 - near dispenser (H = 1,0 m);
6 - alongside with refuelling (H = 1,0 m).

Figure 3.6. Toluene, ethylbenzene, m,p-xylene concentrations in ambient air of petrol station, Research site No. 1 (Vilnius, Laisvės pr. 80B)



VOC sampling points:

1 - near filling point (H = 1,0 m);
2 - near P/V vent (H = 1,8 m);
3 - near P/V vent (H = 1,0 m);
4 - between dispensers (H = 1,0 m);
5 - near dispenser (H = 1,0 m);
6 - alongside with refuelling (H = 1,0 m).

Figure 3.7. Ethyl acetate concentrations in ambient air of petrol station, Research site No. 1 (Vilnius, Laisvės pr. 80B)

During the experimental research of VOCs at research site No. 1 toluene was detected in four sampling points, ethylbenzne and m,p-xylene – in five points, ethyl acetate – in three points. Toluene, ethylbenzene, m,p-xylene concentrations reach their maximum in the 6 sampling point, that is the moment of vehicle refuelling. The spatial distribution of ethylbenzene and m,p-xylene is very similar as minimal concentration are stated between dispensers. Situation for ethyl acetate is vice versa, as this individual VOC shows the maximal concentration exactly in the same point. For VOC composition in ambient air of petrol station evaluation the measured at 1,0 altitude concentrations are shown in percentage by figures 3.7 and 3.8.

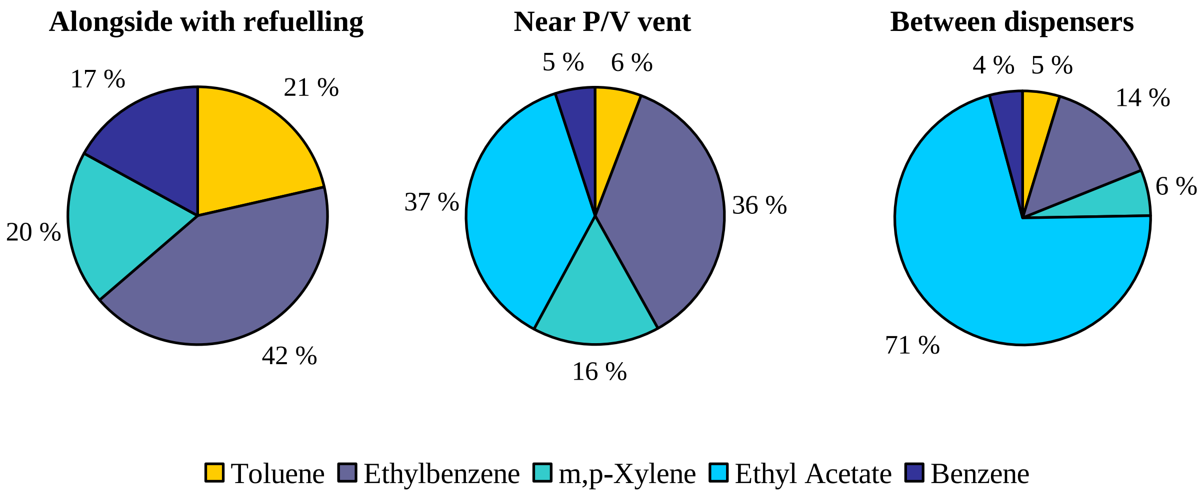


Figure 3.7. VOC composition in sampling points, Research site No. 1

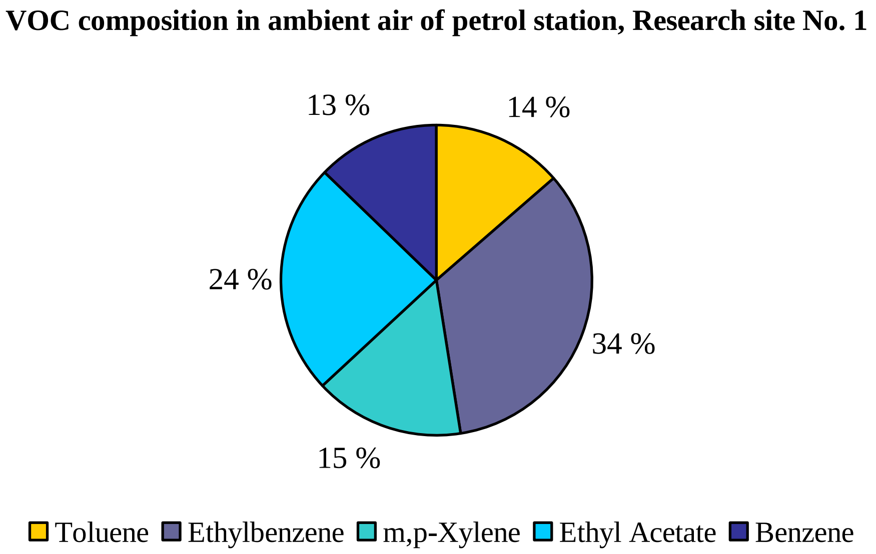


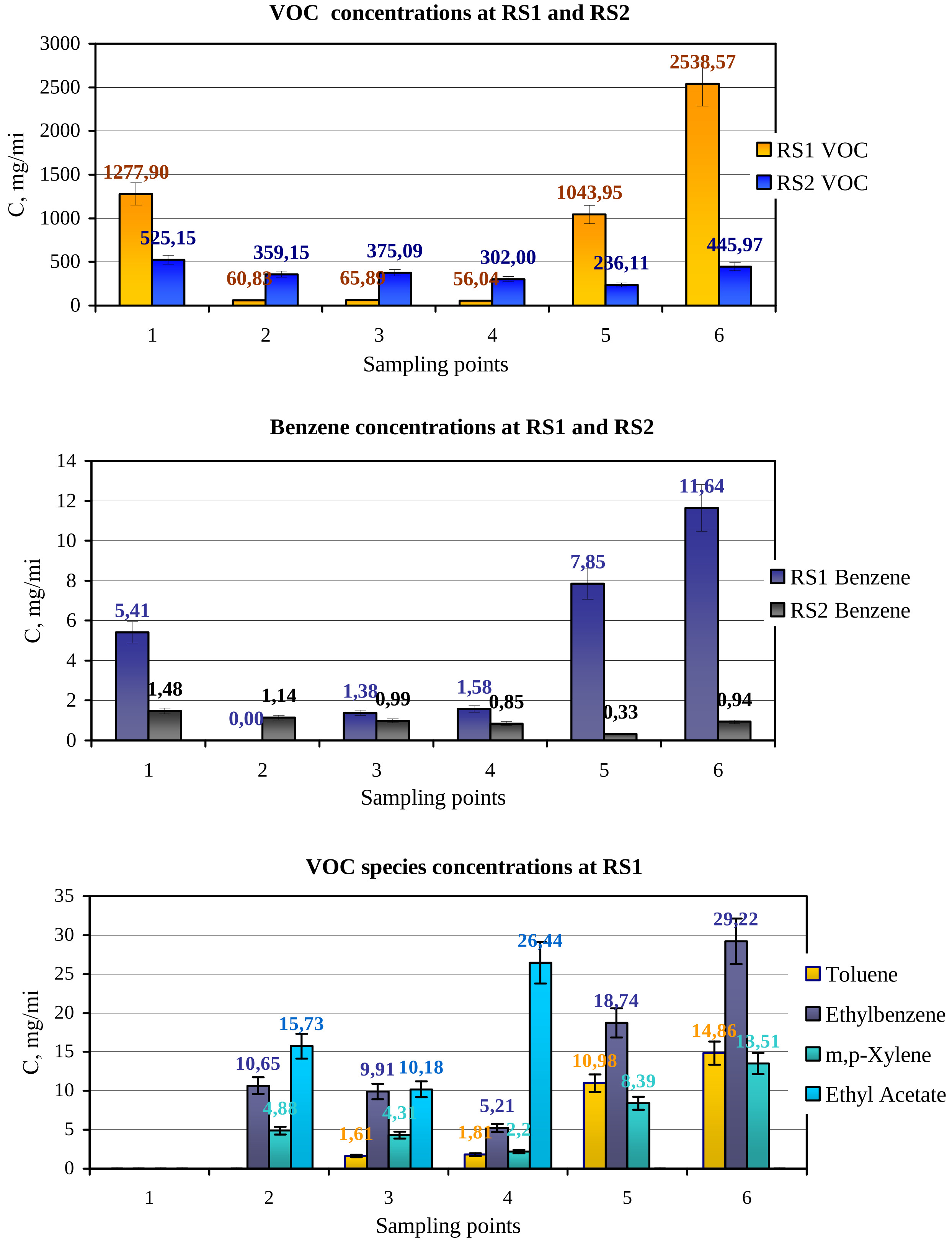
Figure 3.8. VOC composition in ambient air of petrol station, Research site No. 1

The ethylbenzene dominates in VOC composition at refuelling moment, making 42 %, other VOC species – m,p-xylene, toluene, benzene compose about 20 % or or one third of VOC emission. Near P/V vent ethylbenzene and ethyl acetate in VOC emission have practically identical weight – 36 % and 37 % accordingly. Ethyl acetate is major part in VOC emission between dispensers (71 %). Benzene and toluene emissions near P/V vent and between dispensers show analogical tendency, making one twentieth part of whole VOC emission near P/V vent and demonstrating reduction only for 1 percent between dispensers. Overall main component of VOC in ambient air of petrol station (figure 3.8) are ethylbenzene and ethyl acetate, other VOC species make no more than 15 %.

Table 3.3 contains the summarised experiment results with data of accuracy. Figure 3.9 shows histograms, which compare results of experiment between sites. The summarised experiment results will be discussed severally in next section.

Table 3.3. VOC concentrations in petrol stations' ambient air at research sites in Vilnius

VOC,mg/m^3	RS1 sampling points					
	1	2	3	4	5	6
Benzene	5,41 ± 0,30	ND	1,38 ± 0,03	1,58 ± 0,04	7,85 ± 0,37	11,64 ± 0,69
Toluene	ND	ND	1,61 ± 0,04	1,81 ± 0,08	10,98 ± 0,78	14,86 ± 0,81
Ethylbenzene	ND	10,65 ± 0,61	9,91 ± 0,43	5,21 ± 0,35	18,74 ± 1,31	29,22 ± 1,38
m,p-Xylene	ND	4,88 ± 0,28	4,31 ± 0,11	2,20 ± 0,15	8,39 ± 0,40	13,51 ± 0,64
Ethyl Acetate	ND	15,73 ± 0,34	10,18 ± 0,60	26,44 ± 0,96	ND	ND
VOC	1277,90 ± 63,33	60,83 ± 2,11	65,89 ± 1,75	56,04 ± 0,86	1043,95 ± 35,23	2538,57 ± 145,39
VOC, mg/m^3	RS2 sampling points					
	1	2	3	4	5	6
Benzene	1,48 ± 0,05	1,14 ± 0,06	0,99 ± 0,04	0,85 ± 0,04	0,33 ± 0,01	0,94 ± 0,05
VOC	525,15 ± 3,63	359,15 ± 17,96	375,09 ± 18,41	302,0 ± 10,13	236,11 ± 5,12	445,97 ± 16,57



VOC sampling points:

1 - near filling point (H = 1,0 m);
2 - near P/V vent (H = 1,8 m);
3 - near P/V vent (H = 1,0 m);
4 - between dispensers (H = 1,0 m);
5 - near dispenser (H = 1,0 m);
6 - alongside with refuelling (H = 1,0 m).

Figure 3.9. VOC concentrations in ambient air of petrol stations, RS1 and RS2

3.3. RESULTS DISCUSSION

The wide ranges of VOC concentrations in air samples from the sites territory were obtained. The VOC data were analyzed to understand volatile organic compounds concentration and spatial distributions, patterns and composition in the ambient air of typical petrol filling stations in Vilnius city.

A total of 5 VOC species were identified by GC-FID in RS1. The benzene is the most important among aromatic VOC species because of toxicity factor. Only benzene was detected At RS2 in all sampling points. Procedure of accuracy quality included GC calibration by n-hexane and laboratory threefold measurements of samples. The relative standard deviation calculated from laboratory data for VOC compounds collected in petrol stations' hazardous zones is within the limits of 10 %.

Volatile organic compounds detected in the ambient air samples were dominated by aromatic hydrocarbons: benzene (C_6H_6), toluene (also known as methylbenzene $C_7H_8(C_6H_5CH_3)$), ethylbenzene (C_8H_{10}), m&p-xylene (C_8H_{10} ($C_6H_4C_2H_6$)). So in ambient air of petrol station was detected the major aromatic constituents of petrol, collectively known as BTEX compounds (benzene, toluene, ethylbenzene, xylenes). Specific composition of sampled VOCs is explained by reformulated petrol's ingredients, especially marked methyl tertiary butyl ether (MTBE) presence, which is the prevailing petrol's blending ether in Lithuania. The ethyl acetate ($CH_3COOC_2H_5$) was detected in three samples. Ethylbenzene and ethyl acetate comprise a large portion of the total VOCs measured – 34 % and 24 % accordingly, other species m,p-xylene, benzene and toluene are also major components, but only make up to 15 % of VOC emissions from petrol filling station's usual activity.

Maximum permissible concentration of benzene and other identified VOC species in air as professional exposure is regulated by national hygienic norm HN 23:2007. Benzene concentrations at RS2 (Vilnius, Kauno str. 26) not exceed long-term exposure limit (LTEL) for benzene (3,25 mg/m^3), at RS1 (Vilnius, Laisvės pr. 80B) benzene concentration exceeds this limit near filling point and near dispensers, at refuelling moment close to short-term exposure limit (19 mg/m^3). These concentrations still allowable because their occuring as emission of petrol station's operations during short time period (15 min). Toluene, m,p-xylene, ethylbenzene concentrations are far from long-term exposure limit. Measured highest concentration of ethylbenze is 15 times less of permissible long-term limit (442 mg/m^3) also as m,p-xylene (LTEL = 200 mg/m^3). Measured highest concentration of toluene is 13 times less of LTEL (192 mg/m^3). Ethyl acetate also is far from the concentration ceilings that HN 23:2007 prescribes for workers.

Total VOC measured at the RS1 were considerably above of those measured at RS2. More narrow VOCs variation pattern for RS2 (ranged from 236,11 mg/m^3 to 525,15 mg/m^3 range) than for RS1 (56,04 mg/m^3 – 2538,57 mg/m^3) is observed. The same average trend is valid for benzene ratios. Benzene range from 1,38 mg/m^3 to 11,64 mg/m^3 at RS1, and from 0,33 mg/m^3 to 1,48 mg/m^3 at RS2. VOC concentrations near filling point, near petrol dispenser and alongside with petrol car refuelling at RS1 are exceed RS2 VOC concentrations in some times. RS2 samples show more uniform territorial dispersion of VOCs concentration in comparison with RS1. The analogy between concentrations is found in non-hazardous areasof the petrol stations, i.e. near canopy and driveways, where VOC concentrations are equal or less than 55 mg/m^3.

A characteristic petrol odour in sampling points near dispensers was sensible at both research sites, but was more persuasive at RS1. It is entirely due to uncaptured petrol vapour. While an odor threshold for petrol a value of 0,3 ppm (0.00003%). is not absolute since its composition and people’s sensitivity can vary, the concentration of petrol vapors in air at the sites several orders of magnitude greater than the point at which a person will smell petrol.

VOC concentrations changes at 1,0 m and 1,8 m altitudes are noticed. VOC concentrations are slight higher at 1,0 m above ground near P/V vent and near canopy at both sites. The reason for this is petrol vapours density in relation to air ~3:1 (relative density).

A discovered difference in obtained data depends on a number of factors, but the main cause is in petrol station’s constructive design style, particularly of the dispensing zone canopy and location of fuel islands. RS2 with more open petrol station’s constructive solutions, without restriction by buildings and as a consequence dilution of volatile organic compounds there is less limited. Propensity to higher concentration of speciated VOC as ethylacetate is noticed at RS1 parallel fuel islands arrangement. Measured VOCs at both research sites show concentrations increase near filling point, near dispencer and especially alongside with refuelling, in other words inzones of petrol filling and despencing which ara controlled by appropriate PVR. That is standard situation for typical petrol station as the overall control efficiency for stage 2 vapour recovery system less than for stage 1. The PVR2 of RS1 obuviosly weaker and need for upgrade.

3.4. COMPARATIVE ANALYSIS

Experiment results show a clear influence of the activity of the petrol station on the measured benzene concentrations. The benzene concentrations observed at research sites is significant at refuelling moment. Therefore personal exposure during automobile refuelling represents the major source of benzene exposure as was indicated in Egeghy *et al.* study (2000). In Egeghy *et al.* study benzene exposures during self-service automobile refuelling averaged 2,9 mg/m^3 with a range of < 0,076-36 mg/m^3. Observed benzene concentrations range in ambient air of petrol stations in Vilnius 0,33-11,64 mg/m^3 and fitted in the Egeghy *et al.* study benzene range.

In comparison with Spyros *et al.* study (2007), benzene concentrations in examined environments of urban petrol filling stations show the similar higher values than in surrounding area. In Spyros *et al.* study the active sampling and gas chromatography with flame ionization detector was used, atmospheric stratification varied from stable to slightly unstable as well as in this research project. The highest value of benzene was measured during the refueling process of the station’s tanks. Benzene concentrations caused by the petrol station in the urban location were founded 22-28 mg/m^3 in petrol station area and 12-20 mg/m^3 around station. Measured in Spyros *et al.* study benzene concentrations daily variation shows benzene concentration stable decrease between 11:00 and 13:00 hours in work day. In the current project benzene concentrations values shown in figure 3.9 are lower and seems explained by sampling period and town size in which sampling was taken (chosen for sampling in Spyros *et al.* study medium-sized European town of Ioannina, Greece, known to experience high levels of benzene (Pilidis *et al.* 2005)).

Chiu *et al.* (2006) study analyzed the VOCs in the ambient air around petrol stations during rush hours and assessed their impact on human health. Results from this study clearly indicate that methyl tertiary butyl ether, toluene, and isobutane are the major VOCs emitted from petrol stations. Moreover, the concentrations of MTBE and toluene in the ambient air near petrol stations are remarkably higher than those sampled on surrounding roads. In current project detected VOC also dominated by aromatic hydrocarbons, among which ethylbenzene and ethyl acetate comprised a largest portion, toluene makes up to 15 % of VOC emissions from petrol filling station’s usual activity.

The comparative analyses in VOCs emitted from the petrol station area shows relatively similarity for experiment results compared to other cities worldwide.

CONCLUSIONS

1. Volatile organic compounds detected in ambient air of petrol stations in Vilnius in winter season present the BTEX complex. Composition of VOC samples is driven by reformulated petrol based on oxygenate MTBE. Ethylbenzene and ethyl acetate comprise a large portion of the measured speciated VOCs – 34 % and 24 % accordingly, other species m,p-xylene, benzene and toluene are also major components, but only make up to 15 % of VOCs.
2. Benzene concentrations at Research site No. 2 (Vilnius, Kauno str. 26) not exceed long-term exposure limit (< 3,25 mg/m^3), at Research site No. 1 (Vilnius, Laisvės pr. 80B) benzene concentration exceeds this limit near filling point and near dispensers, at refuelling moment close to short-term exposure limit (19 mg/m^3). Toluene, m,p-xylene, ethylbenzene and ethyl acetate concentrations are lower of permissible long-term limits.
3. VOC at both research sites show concentrations increase in zones of petrol filling and dispensing, which are controlled by appropriate petrol vapour recovery system. The PVR2 is obviously weaker at RS1 and needs for upgrade.
4. Emission factors from the literature are reflecting the real situation. Measured VOC at both research sites show concentrations increase near filling point and alongside with petrol car refuelling. The low VOC concentrations (within 55 mg/m^3 limit) observed in non-hazardous areas (near canopy and driveways) of the petrol stations.
5. Change in VOC concentrations at 1,0 m and 1,8 m altitudes are noticed. VOC concentrations are slight higher at 1,0 m above ground near P/V vent and near canopy at both sites. The reason for this is petrol vapours density in relation to air (> 1).
6. Total VOC measured at the Research site No. 1 (Vilnius, Laisvės pr. 80B) considerably higher of those measured at Research site No. 2 (Vilnius, Kauno str. 26). More narrow VOCs variation pattern for RS2 (236,11 mg/m^3 - 525,15 mg/m^3) than for RS1 (56,04 mg/m^3 – 2538,57 mg/m^3) is observed. The automatic self-service petrol station (RS2) demonstrates lower VOCs concentration due to constructive design and better dilution in hazardous area under canopy. On the other hand valve P/V installed through column of canopy in RS1 shows lower concentration than separately installed valve P/V in RS2.

4. MODELLING PART

The Areal Locations of Hazardous Atmospheres (ALOHA) version 5.4.1, developed by office of emergency management, EPA and Emergency response division NOAA, for the simulation of VOCs releases from typical petrol station is used in this project. ALOHA is an air quality computer program designed for respondents, which activities conduct to regular and accidental chemical releases.

4.1. MODEL DESCRIPTION

Modelling in ALOHA. The program predicts the dispersion of a chemical as a Gaussian or *heavy gas release*. ALOHA heavy gas model DEGADIS estimates the movement and dispersion of heavier than air *chemical gas clouds*, the overpressure values from a vapor cloud explosion, or the flammable vapor cloud. That’s actual for petrol-related VOCs releases to atmosphere. Key hazards of ALOHA air dispersion models are:

a) toxicity;
b) flammability;
c) thermal radiation;
d) overpressure (explosion).

A cloud of gas that is denser or heavier than air as petrol vapours spread downdind, but can also spread upwind to a small extent. When a gas that is heavier than air is released, it initially behaves very differently from a neutrally buoyant gas. The heavy gas will first “slump”, or sink, because it is heavier than the surrounding air. As the gas cloud moves downwind, gravity makes it spread and this can cause some of the vapor to travel upwind of its release point. When a valve causes a break in the petrol stations supply lines cause petrol sudden vaporization and a storage tank contents foam up, filling the tank and ambient air with a gaseous VOCs mixture. When the liquid and gas phases escape together, the two-phase flow release is modelled.

The equations accounting for site topography are not involved in ALOHA models. This feature is useful in some long-range transport dispersion model, when model domain in kilometres, but it not necessary in typical petrol filling station case, where hazardous areas of VOCs releases are under or near canopy and surrounding areas for 50 m distance (under Lithuanian sanitary protection zone rules for petrol station) should be without residential buildings, water bodies, forests or thick vegetation and specific relief elements as petrol stations are located near traffic roads. Furthermore topographic elements require extensive input and computational time, while in typical petrol filling station case as in benzene microenvironment practically local and personal scales air quality issues should be addressed.

Modelling scenarios. Model of VOCs releases from three types of sources: direct, puddle and tank, are simulated. Direct source is fitted for VOCs release during refuelling operation (60 l inject is assumed), puddle for petrol spillage from dispenser supply line (50 l spill puddle is assumed) and tank fro petrol spillage from road tanker during tank up (946 l is assumed). For simulation the Research site No. 1 and ethylbenzene are chosen as at RS 1 it concentration is highest during refuelling and part in total VOCs is largest. Heavy gas model for ethylbenzene runs for multiple scenarios, which besides sources type differs by atmospheric conditions (table 4.1). Scenarios No. 4, 5 are simulated under atmospheric conditions of experiment.

Table 4.1. Simulation scenarios for RS1 (Vilnius, Laisvės pr. 86B)

Scenario No.	Source type and source strenght	Event	Event type	Atmospheric conditions	Pollutant	Model type
1	Tank 946 l	Tank up	Emergency situation	Wind 5 m/s from S Air temperature 2 ^{o}C Cloudy Reliative humidity 50 %	Ethylbenzene	Heavy gas model
2				Wind 5 m/s from S Air temperature 20 ^{o}C Cloudy Reliative humidity 50 %		
3	Puddle 50 l	Dispensing		Wind 5 m/s from S Air temperature 20 ^{o}C Cloudy Reliative humidity 50 %		
4				Wind 2 m/s from S Air temperature 2 ^{o}C Overcat Reliative humidity 70 %		
5	Direct 60 l	Refuelling	Usual activity	Wind 2 m/s from S Air temperature 2 ^{o}C Overcat Reliative humidity 70 %		
6				Wind 2 m/s from S Air temperature 20 ^{o}C Clear sky Reliative humidity 50 %		

Model gives concentrations output in ppm. Graphical results of the ethylbenzene releases simulation shown as source strength, i.e. evaporation rate by figure 4.1, and as toxic threat zone by figure 4.2. Release rate for a direct source remain constant for the duration of the release, therefore to give the graphs for this source type is inexpedient. Graphs follow after results of solving model.

4.2. RESULTS AND GRAPHICAL PICTURES OF SOLVING MODELS

SITE DATA:

Location: VILNIUS, LAISVES PR. 80B, LITHUANIA

Scenario No. 1

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)

Wind: 5 meters/second from S at 10 meters

Ground Roughness: open country	Cloud Cover: 3 tenths
Air Temperature: 2 ° C	Stability Class: E
No Inversion Height	Relative Humidity: 50 %

CHEMICAL DATA:

Chemical Name: ETHYLBENZENE	Molecular Weight: 106,17 g/mol

Ambient Boiling Point: 135,4 ° C

Vapor Pressure at Ambient Temperature: 0,0030 atm

Ambient Saturation Concentration: 3,014 ppm or 0,30 %

SOURCE STRENGTH:

Leak from short pipe or valve in horizontal cylindrical tank

Flammable chemical escaping from tank (not burning)

Tank Diameter: 2,5 feet	Tank Length: 6,8 feet
Tank Volume: 250 gallons	
Tank contains liquid	Internal Temperature: 2° C
Chemical Mass in Tank: 0,63 tons	Tank is 68 % full

Circular Opening Diameter: 0,5 inches

Opening is 1,25 feet from tank bottom

Ground Type: Concrete

Ground Temperature: equal to ambient

Max Puddle Diameter: Unknown

Release Duration: ALOHA limited the duration to 1 hour

Max Average Sustained Release Rate: 204 grams/min
(averaged over a minute or more)

Total Amount Released: 9,79 kilograms

Note: The chemical escaped as a liquid and formed an evaporating puddle.

The puddle spread to a diameter of 6,6 meters.

Scenario No. 2

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)

Wind: 5 meters/second from S at 10 meters

Ground Roughness: open country Cloud Cover: 3 tenths

Air Temperature: 20 ° C Stability Class: E

No Inversion Height Relative Humidity: 50 %

CHEMICAL DATA:

Chemical Name: ETHYLBENZENE Molecular Weight: 106,17 g/mol

Ambient Boiling Point: 135,4 ° C

Vapor Pressure at Ambient Temperature: 0,0094 atm

Ambient Saturation Concentration: 9,601 ppm or 0,96 %

SOURCE STRENGTH:

Leak from short pipe or valve in horizontal cylindrical tank

Flammable chemical escaping from tank (not burning)

Tank Diameter: 2,5 feet (.. m) Tank Length: 6,8 feet (m)

Tank Volume: 250 gallons (m)

Tank contains liquid Internal Temperature: 20° C

Chemical Mass in Tank: 0,63 tons Tank is 70 % full

Circular Opening Diameter: 0,5 inches

Opening is 1,25 feet from tank bottom

Ground Type: Concrete

Ground Temperature: equal to ambient

Max Puddle Diameter: Unknown

Release Duration: ALOHA limited the duration to 1 hour

Max Average Sustained Release Rate: 610 grams/min
(averaged over a minute or more)

Total Amount Released: 29,0 kilograms

Note: The chemical escaped as a liquid and formed an evaporating puddle.

The puddle spread to a diameter of 6,6 meters.

No explosion: no part of the cloud is above the LEL at any time

Scenario No. 3

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)

Wind: 5 meters/second from S at 10 meters

Ground Roughness: open country Cloud Cover: 3 tenths

Air Temperature: 20 ° C Stability Class: E

No Inversion Height Relative Humidity: 50 %

CHEMICAL DATA:

Chemical Name: ETHYLBENZENE Molecular Weight: 106,17 g/mol

Ambient Boiling Point: 135,4 ° C

Vapor Pressure at Ambient Temperature: 0,0094 atm

Ambient Saturation Concentration: 9,601 ppm or 0,96 %

SOURCE STRENGTH:

Evaporating Puddle (Note: chemical is flammable)

Puddle Area: 3 square meters Puddle Volume: 50 liters

Ground Type: Concrete Ground Temperature: 20° C

Initial Puddle Temperature: Ground temperature

Release Duration: ALOHA limited the duration to 1 hour

Max Average Sustained Release Rate: 62.1 grams/min
(averaged over a minute or more)

Total Amount Released: 3,54 kilograms

THREAT AT POINT Scenario:

Concentration Estimates at the point:

Downwind: 10 meters Off Centerline: 1 meters

Max Concentration:

Outdoor: 57,2 ppm

Indoor: 28 ppm

Scenario No. 4

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)

Wind: 2 meters/second from S at 10 meters

Ground Roughness: open country Cloud Cover: 10 tenths
Air Temperature: 2 ° C Stability Class: D
No Inversion Height Relative Humidity: 70 %

CHEMICAL DATA:

Chemical Name: ETHYLBENZENE Molecular Weight: 106,17 g/mol
Ambient Boiling Point: 135,4° C
Vapor Pressure at Ambient Temperature: 0.0030 atm
Ambient Saturation Concentration: 3,014 ppm or 0,30 %

SOURCE STRENGTH:

Evaporating Puddle (Note: chemical is flammable)
Puddle Area: 3 square meters Puddle Volume: 50 liters
Ground Type: Concrete Ground Temperature: 2 ° C
Initial Puddle Temperature: Ground temperature
Release Duration: ALOHA limited the duration to 1 hour
Max Average Sustained Release Rate: 10 grams/min
(averaged over a minute or more)
Total Amount Released: 588 grams

THREAT AT POINT:

Concentration Estimates at the point:
Downwind: 10 meters Off Centerline: 1 meters
Max Concentration:
Outdoor: 7,45 ppm
Indoor: 3,02 ppm

Scenario No. 5

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)

Wind: 2 meters/second from S at 10 meters
Ground Roughness: open country Cloud Cover: 10 tenths

Air Temperature: 2 ° C
Stability Class: D
No Inversion Height
Relative Humidity: 70 %

CHEMICAL DATA:

Chemical Name: ETHYLBENZENE
Molecular Weight: 106.17 g/mol
Ambient Boiling Point: 135,4 ° C
Vapor Pressure at Ambient Temperature: 0.0030 atm
Ambient Saturation Concentration: 3,014 ppm or 0,30 %

SOURCE STRENGTH:

Direct Source: 1 grams
Source Height: 1 meters
Release Duration: 1 minute
Release Rate: 0,0167 grams/sec
Total Amount Released: 1,00 grams

Scenario No. 6

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)

Wind: 2 meters/second from S at 10 meters
Ground Roughness: open country
Cloud Cover: 0 tenths
Air Temperature: 20 ° C
Stability Class: F
No Inversion Height
Relative Humidity: 50 %

CHEMICAL DATA:

Chemical Name: ETHYLBENZENE
Molecular Weight: 106,17 g/mol
Ambient Boiling Point: 135,4° C
Vapor Pressure at Ambient Temperature: 0.0094 atm
Ambient Saturation Concentration: 9,601 ppm or 0,96 %

SOURCE STRENGTH:

Direct Source: 1 grams
Source Height: 1 meters
Release Duration: 1 minute
Release Rate: 0,0167 grams/sec
Total Amount Released: 1,00 grams

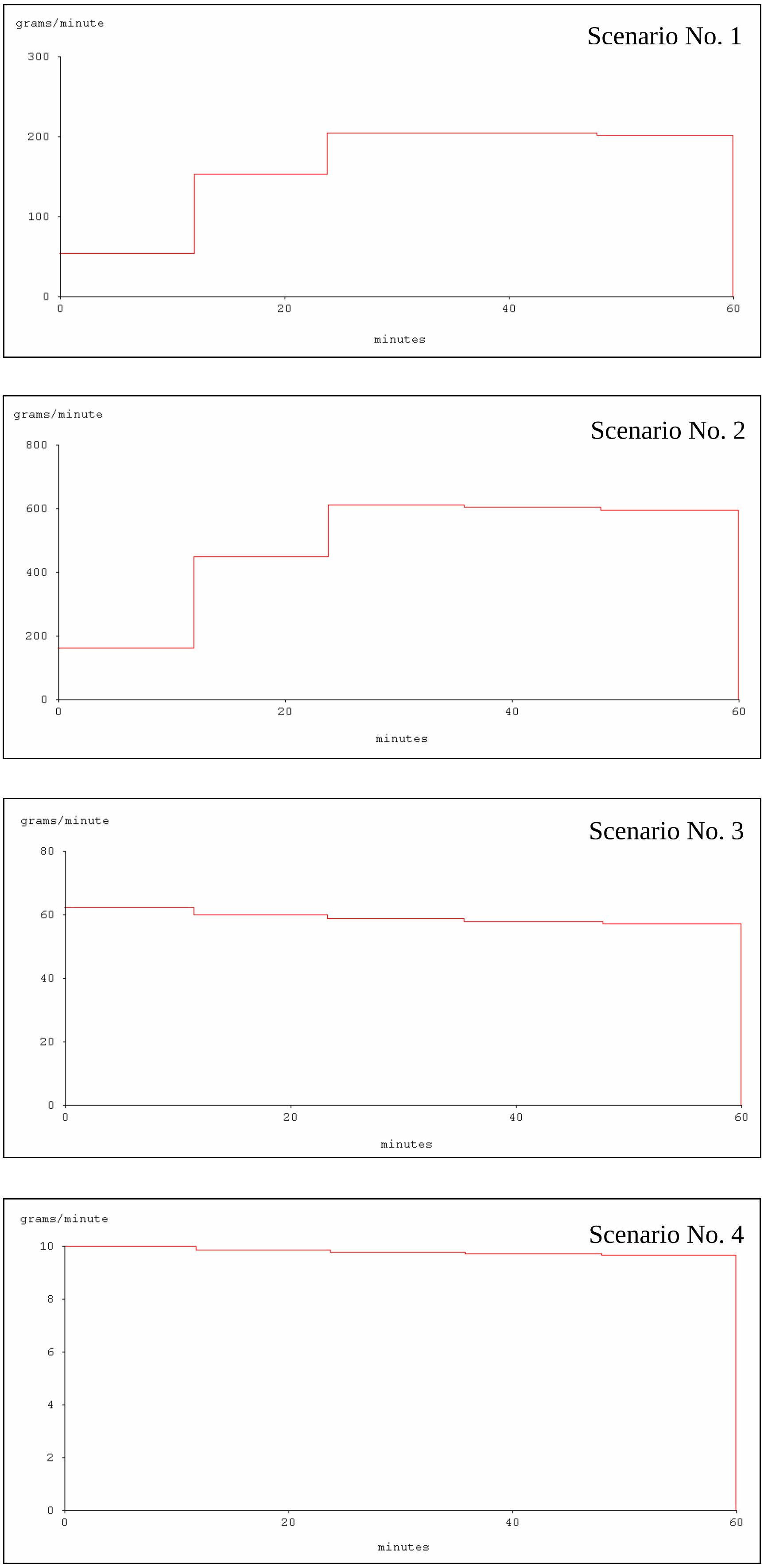


Figure 4.1. Modelled ethylbenzene source strength (evaporation rate)

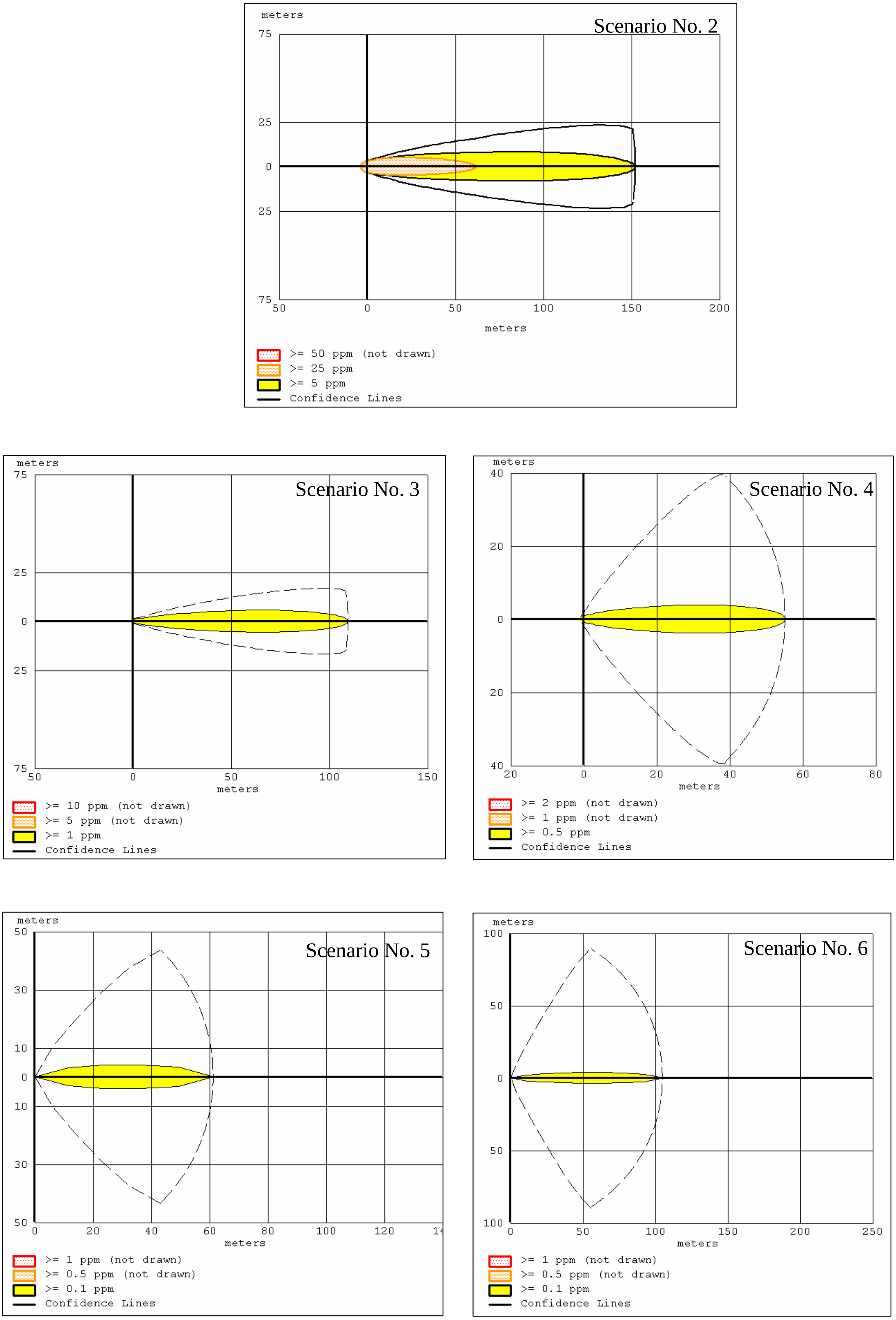


Figure 4.2. Modelled ethylbenzene toxic threat zone

4.3. MODELS OUTPUT INTERPRETATION

Scenario No. 1 and No. 2 for ethylbenzene concentrations prognosis for leak from short pipe or valve in horizontal cylindrical tank event differs only with air temperature. Scenario No. 1 runs under 2 ^{o}C, scenario No. 2 under 20 ^{o}C. From their graphs for source strenght, time since the release started is shown on the horizontal axis (minutes), and release rate is shown on the vertical axis (g/min). ALOHA predicts that release of ethylbenzene from short pipe or valve in horizontal cylindrical tank for scenario No. 2 with higher temperatures is more intensive (610 g/min). The petrol puddle spread to a diameter of 6,6 meters at both scenarios, but total amount of ethylbenzene to ambient air released in scenario No 2 (29,0 kilograms) about three times higher than in scenario No. 1 with 9,79 kilograms of ethylbenzene released. ALOHA predicts absence of overpressure and possible explosion. The strong temperature factor influence to volatile organic compound is demonstrated at these scenarios, as the higher temperature conduct to higher concentration of ethylbenzene. ALOHA for scenario No. 2 predicts ethylbenzene concentration higher or equal to 25 ppm downwind within 62 meters distance, 5 ppm at 152 meters distance from 946 l petrol spillage. The ethylbenzene transport upwind on some meters is observed in this event.

At the similar temperature difference of 18 ^{o}C (20 ^{o}C - 2 ^{o}C) were solved scenarios No. 3 and No. 4 for evaporating puddle event. From source strength graphs are seen that scenario No. 4 with puddle evaporative rate at 2 ^{o}C is submit in six times for evaporative rate of ethylbenzene in ambient air of 20 ^{o}C. 10 ppm ethylbenzene concentration at 11 m, 5 ppm at 16 m, and 1 ppm at 39 meter longway is predicted for scenario No. 3. Possible spread of toxic ethylbenzene cloud is significantly wider in scenario No. 4 with lower wind speed.

Scenarios No. 5 and No. 6 simulate ethylbenzene release during refuelling of vehicle and differs in meteorological parameters input. Scenario No. 5 simulates refuelling under whether conditions from VOC experiment. Scenario No. 6 presents refuelling in sunny summer day. Threat zone for scenario No. 5: 20 meters – 1 ppm, 27 meters – 0,5 ppm, and all-ot dilution (0,1 ppm) at 61 m from dispenser. Threat zone for scenario No. 6: 33 meters – 1 ppm, 48 meters – 0,5 ppm, 105 meters – 0,1 ppm. For ethylbenzene dilution at sunny day the longer distance are require. As temperatures differs in 10 times, distance for ethylbenzene dilution in ambient air of 20 ^{o}C is longer nerly 2 times, however the plume projection is visibly thinner. In scenario No. 6 the ethylbenzene vapors transported for longer distance, however toxic vapours cloud spread more widely in scenario No. 5. According to solved heavy gas model ethylbenzene vapours released at refuelling moment in 20 m distance downwind becomes enough diluted and its density approaches to air density and it begins behaving like a neutrally buoyant gas.

Generated scenarios have some common features as mathematical model of heavy gas predicts atmospheric dispersion characterized by three phases: (1) near field, negative buoyancy-dominated flow regime; (2) intermediate field, stably stratified shear flow regime; and (3) far field, passive turbulent diffusion regime. Model computes pollutant concentrations at ground level, where a dispersing ethylbenzene is most likely to contact people. Produced “footprint” of scenarios represents that average concentrations will be highest near the release point and along the centerline of any pollutant cloud, and will drop off smoothly and gradually in the downwind and crosswind directions. Dashed lines, one along each side of the footprint represent uncertainty in the wind direction. The “uncertainty lines” around the footprint enclose the region within which, the gas cloud is expected to remain. The reviewed scenarios show, that the lower the wind speed, the more the wind changes direction, so as wind speed decreases, the uncertainty lines become farther apart (scenario No. 4, 5, 6). This happens, because, especially near the source of a release, wind eddies push a cloud unpredictably about, causing gas concentrations at any moment to be high in one location and low in another.

Anyway a heavy gas cloud is expected by the model to disperse downwind in a more complex manner than a neutrally-buoyant cloud. Early in a heavy gas release, the dense vapour cloud is expected to slump away from the release point, rapidly becoming increasingly less dense by entraining air, and forming a secondary blanket centred on the release point. Further from the source, the cloud maintains its stable stratification, remaining low to the ground and resisting the effects of air turbulence as it moves downwind. Even further from the source, the cloud is expected to be so diluted by air that its further travel is modelled by ALOHA as passive dispersion. Petrol-related VOCs are affected by gravity and other forces besides wind and turbulence. As they move downwind, they remain much lower to the ground than neutrally-buoyant clouds. Ground-level concentrations within such clouds may reach much higher levels at some locations than the Gaussian model would predict. Therefore the ALOHA heavy gas model use to estimate the affected of petrol vapours areas is more reasonable and preferable. Environmentalists can use ALOHA as a response tool for quick and rather accurate quantify of what petrol-related VOCS impact could be present especially in case of proposed petrol filling stations.

CONCLUSIONS

1. ALOHA predicts that average ethylbenzene concentrations will be highest for petrol spillage from broken pipe or valve in tank up event: downwind on the 50 m threshold the concentration nearly 25 ppm and not exceed long-term exposure limit (<< 100 ppm). So even during 964 l petrol spillage the 50 m distance (petrol station's sanitary protection zone) from release source is enough for ethylbenzene dilution.
2. All modelled events show toxic vapours concentration increase with increasing temperature. The same pollution events at higher temperatures require longer way for pollutant dilution. The possible spread of toxic ethylbenzene cloud is significantly wider in atmospheric conditions with lower wind speed.
3. For small petrol-related VOCs releases model predicts low-level concentrations and ethylbenzene behaviour similar to fugitive emissions. Analogy between model calculations and the experiment data can be noted in ethylbenzene release during refuelling event, when VOC concentration are rather high at source point and becomes rather insignificant on small distance from dispenser. According to solved heavy gas model ethylbenzene vapours released at refuelling moment in 20 m distance downwind becomes enough diluted and its density approaches to air density and it begins behaving like a neutrally buoyant gas.

GENERAL CONCLUSIONS

1. VOCs at different temporal and spatial scales in atmosphere conduct from personal exposure to local issues as $O_{3,}$ PM precursors, and finally result in global issue like climate change, acting as indirect greenhouse gases.
2. Petrol is product classed as dangerous for the environment by distributing organic material over a volatility basis. Highest VOC concentrations are always reached at stagnant air and low wind speeds. The chemical removal of VOCs due to reactivity with OH radicals is important determinant of the final shape of measured concentrations.
3. The VOC emissions are identified from petrol’s filling, storage, refuelling and spillage losses. Automobile refuelling represents the major source of benzene exposure. Therefore petrol service stations can be defined as important microenvironments of benzene exposure.
4. VOCs detected in ambient air of petrol stations in Vilnius in winter season present the BTEX complex. Ethylbenzene and ethyl acetate comprise a large portion of the measured speciated VOCs – 34 % and 24 % accordingly, other species m,p-xylene, benzene and toluene make up to 15 % of VOCs.
5. Benzene concentrations at Research site No. 2 (Vilnius, Kauno str. 26) not exceed long-term exposure limit (< 3,25 mg/m^3), at Research site No. 1 (Vilnius, Laisvės pr. 80B) benzene concentration exceeds this limit near filling point and near dispensers, at refuelling moment close to short-term exposure limit (19 mg/m^3). Toluene, m,p-xylene, ethylbenzene and ethyl acetate concentrations are lower of permissible long-term limits.
6. Total VOC measured at the Research site No. 1 (Vilnius, Laisvės pr. 80B) considerably higher of those measured at Research site No. 2 (Vilnius, Kauno str. 26). More narrow VOCs variation pattern for RS2 (236,11 mg/m^3 - 525,15 mg/m^3) than for RS1 (56,04 mg/m^3 – 2538,57 mg/m^3) is observed. The low VOC concentrations (within 55 mg/m^3 limit) observed in non-hazardous areas (near canopy and driveways) of the petrol stations.
7. VOC at both research sites show concentrations increase in zones of petrol filling and dispensing, which are controlled by appropriate petrol vapour recovery system. The PVR2 is obviously weaker at RS1 and needs for upgrade.
8. The automatic self-service petrol station (RS2) demonstrates lower VOCs concentration due to constructive design and better dilution in hazardous area under canopy. On the other hand valve P/V installed through column of canopy in RS1 shows lower concentration than separately installed valve P/V in RS2.

RECOMMENDATIONS

1. Petrol filling station should be safe in relation to the components of an environment, conditions of residing and health of the population. Petrol toxic ingredients as benzene is significant during refuelling therefore underline the importance of petrol-related VOC emission control, and enforces raise of petrol station’s environmental performance. Besides PVR stage 2 the add-on control devices should be used in petrol supply line. The “Enviro-fill” assist fuel nozzles and refrigeration technique are recommended.
2. VOC emissions reduction can be done by improving the evaporation recovery system stage 2. In PVR stage 1 supplementary systems of light fraction capturing: adsorbtion, absorbtion, membrane separator, also combined methods are desirable.
3. More efforts should be made to maintain VOC emission reduction technologies and to check them to ensure effective operation. Reporting and reviewing environmental performance of filling station should be a regular process.
4. The ALOHA air quality model of VOCs emission can be used as the auxiliary tool for proposed petrol station’s emergency plan preparation to meet the requirements for nearest receptors and can be integrated in procedures of environmental impact assessment.

REFERENCES

1. Ackerman, A. S.; Toon, O. B.; Stevens, D. E.; Heymsfield, A. J.; Ramanathan, V.; Welton, E. J. 2000. Reduction of Tropical Cloudiness by Soot. *Science* 288(5468): 1042-1047.
2. Atkinson, R., 2000. Atmospheric chemistry of VOCs and NO_x. *Atmospheric Environment* 34: 2063-2101.
3. Atkinson, R.; Hoover, S.; Arey, J.; Preston, K. 2006. *Atmospheric chemistry of gasoline-related emissions: formation of pollutants of potential concern*. Oakland: CalEPA. 3 p.
4. Baik, J. J.; Kim, J. J. 1999. A numerical study of flow and pollutant dispersion characteristics in urban street canyons. *Journal of Applied Meteorology* 38: 1576-1589.
5. Baker, R.W. 2002. Future directions of membrane gas separation technology. *Industrial & Eng Chem Research* 41: 1393-1411.
6. Ballschmiter, K. ; Hackenberg, R.; Jarman, W. M.; Looser, R. 2002. Man-made chemicals found in remote areas of the world: the experimental definition for POPs. *Environmental Scncei & Polluiont Research* 9(4): 274-288.
7. Baltrėnas, P. 2001. Vilniaus miesto degalinių tarša. *Mokslas ir gyvenimas* 7-8. Available from internet: <http://ausis.gf.vu.lt/mg/nr/2001/078/07deg.html>.
8. Baltrėnas, P. 2007. Globali klimato kaita: realybė ir prognozė [Global climate change: reality and prognosis]. Iš *Aplinkos apsaugos inžinerija* [Environmental protection engineering]: *10-osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“* [10th Conference of Junior Researchers Science – Future of Lithuania], įvykusios Vilniuje 2007 m. kovo 29 d., pranešimų medžiaga. Vilnius: Technika, 35-43.
9. Baltrėnas, P.; Morkūnienė, J.; Vaitiekūnas, P. 2008. Mathematical simulation of solid particle dispersion in the air of Vilnius city. *Journal of Environmental Engineering and Landscape Management* 16(1): 15-22.
10. Baltrėnas, P.; Špakauskas, V.; Vaiškūnaitė, R. 2003. Experimental study and mathematical modelling of biofiltration of volatile organic compound mixtures by a biofilter. *Journal of Environment Engineering and Landscape Management* 11(3): 87-92
11. Bandow, H.; Washida, N.; Akimoto, H. 1985. Ring-cleavage reactions of aromatic hydrocarbons studied by FT-IR spectroscopy: photooxidation of toluene and benzene in the NO_x-air system. *Bulletin of the Chemical Society of Japan* 58: 2531-2540.
12. Bartenbach S.; Williams, J.; Plass-Dülmer, C.; Berresheim, H.; Lelieveld, J. 2007. In-situ measurement of reactive hydrocarbons at Hohenpeissenberg with comprehensive two-dimensional gas chromatography (GC×GC-FID): use in estimating HO and NO_3. *Atmospheric Chemistry and Physics* 7: 1-14.
13. Beck, J.P.; Krzyzanowski, M.; Koffi, B. 1998. Tropospheric ozone in the European Union. The Consolidated Report. European Environment Agency. Available from internet: <http://reports.eea.europa.eu/TOP08-98/en/page001.html>.
14. Beens, J.; Blomberg, J.; Schoenmakers, P. J. 2000. Proper tuning of comprehensive twodimensional gas chromatography (GC×GC) to optimise the separation of complex oil fractions. *Journal of High Resolution Chromatography* 23: 182–188.
15. Berkowicz, R. 1997. Modelling street canyon pollution: model requirements and expectations. *International Journal of Environment and Pollution* 8,5: 609-619.
16. Bertsch, W. 2000: Two-dimensional gas chromatography. Concepts, instrumentation, and applications – Part 2: Comprehensive two-dimensional gas chromatography. *Journal of High Resolution Chromatography* 23: 167–181.
17. Carter, W. P. L. 1995. Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic Compounds. *Atmospheric Environmnet* 29: 2513-2517.
18. Carter, W. P. L. 2007. *Development of the SAPRC-07 chemical mechanism and updated ozone reactivity*. Final report to the California Air Resources Board. Center for Environmental Research and Technology College of Engineering University of California. 367 p.
19. Carter, W. P. L.; Luo, D.; Malkina, I. L.; Pierce, J. A. 1994. Environmental chamber studies of atmospheric ozone formation from selected biogenic compounds. *Air and Waste Management*

Association 44: 881–899.

20. Chiu, K.; Hsieh, L.; Lo, J.; Sree, U.; Wu, B. 2006. Determination and impact of volatile organics emitted during rush hours in the ambient air around gasoline stations *Journal of the Air & Waste Management Association* 56(9):1342-8.
21. Cozzarellia, I.M.; Baehr, A.L. 2003. Volatile fuel hydrocarbons and MTBE in the environment. *Treatise on Geochemistry* 9: 433-474.
22. Das. M.; Aneja. V.P. 2003. Regional analysis of nonmethane Volatile Organic Compounds in the lower troposphere of the Southeast United States. *Journal of Environmental Engineering* 129(12): 1085-1103.
23. Derwent R. G. 2004. *Evaluation and charakterisation of reactivity metrics*. Report to the United States Environmental Protection Agency. EPA. 17 p. Available from internet: <http://www.narsto.org/files/files/usepa03.pdf>.
24. DiGiovanni, F.; Fellin, P. 2006. *Transboundary Air Pollution*. Oxford: Encyclopedia of Life Support Systems. 30 p. Available from internet: <http://www.eolss.net/ebooks/Sample%20Chapters/C09/E6-38A-03-04.pdf >.
25. Egeghy, P.P., Tornero-Velez, R., Rappaport, S.M.. 2000. Environmental and biological monitoring of benzene during self-service automobile refueling. *Environmental Health Perspectives* 108 (12): 1195.
26. Erdöl, E.; Kohle V. 2004. *Vapour Recovery and Monitoring Systems at Petrol Stations*. Hamburg: Deutsche Wissenschaftliche Gesellschaft. 5 p. Available from internet: <http://www.dgmk.de/downstream/report_550-05_%20englisch.pdf>.
27. Ervens, B.; Feingold, G.; Frost, G. J.; Kreidenweis, S. M. 2004. A modeling study of aqueous production of dicarboxylic acids: Chemical pathways and speciated organic mass production, *Journal of Geophysical Researh* 109: 15205.
28. Filella, I.; Penuelas, J. 2006 Daily, weekly, and seasonal time courses of VOC concentrations in a semi-urban area near Barcelona. *Atmospheric Environment* 40: 7752–7769.
29. Filella, I.; Penuelas, J. 2006. Daily, weekly and seasonal relationships among VOCs, NO_x and O_3 in a semi-urban area near Barcelona. *Journal of Atmoipherie Chemistr*y 54:189-201.
30. Fine, P.M.; Sioutas, C.; Paul, S.A. 2008. Secondary particulate matter in the United States: insights from the particulate matter Supersites Program and related studies. *Journal of the Air & Waste Management Association* 58(02).
31. Friedrich, R.; Wickert, B.; Blank, P.; Emeiss, S.; engewald, W.; Hassel, D.; Hoffman, H.; Michael, H.; Obermeier, A.; Schafer, K.; Schmitz, T.; Sedlmaier, A.; Stockhauses, M.; Theloke, J.; Weber, F.J. 2002. Development of emission models and improvement of emission data for Germany. *Journal of Atmoipherie Chemistry* 42: 179-206
32. Fuel trends report: gasoline 1995-2005. 2008. Compliance and Innovative Strategies Division Office of Transportation and Air Quality U.S. Environmental Protection Agency. 268 p.
33. Gautrois, M.; Brauers, T.; Koppmann, R.; Rohrer, F.; Stein, O.; Rudolph J. 2003. Seasonal variability and trends of volatile organic compounds in the lower polar troposphere. *Journal of Geophysical Research* 108(D13): 4393.
34. Georgiev, K. T. 2000. Two dimensional computer modeling of long range transport of air pollutants. *Journal of international research publication* 01:1311-8978.
35. Goldstein A.H. 2007. Known and unexplored organic constituents in the Earth’s Atmosphere. *Environmental Science & Technology* 41(5): 1515-1521.
36. Gray, K. A.; Finster, M. E. 1998. *The urban heat island, photochemical smog and Chicago: local features of the problem and solution*. Atmospheric Pollution Prevention Division. U.S. Environmental Protection Agency. 146 p. Available from internet: <http://www.epa.gov/heatisland/resources/pdf/post_chicago/chicago_toc_exsum.pdf>.
37. Guo, H.; Lee, S.C.; Louie, P.K.K.; Ho, K.F. 2004. Characterization of hydrocarbons, halocarbons and carbonyls in the atmosphere of Hong Kong. *Chemosphere* 57: 1363-1372.
38. Haapanala, S.; Rinne1, J.; Hakola, H.; Hellen, H.; Laakso, L.; Lihavainen, H.; Janson, R.; O’Dowd, C.; Kulmala, M. 2007. Boundary layer concentrations and landscape scale emissions of

volatile organic compounds in early spring. *Atmospheric Chemistry and Physics* 7: 1869–1878.

39. Heinrich-Ramm, R.; Jakubowski, M.; Heinzow, B.; Molin Christensen, J.; Olsen, E.; Hertel, O. 2000. Biological monitoring for exposure to volatile organic compounds (IUPAC Recommendations 2000). *Pure and Applied Chemistry* 72(3): 385–436.
40. Hjertager, B. H.; Mathiesen, V.; Solberg, T. 1998. Computational analysis of some fluidized systems. *Advanced Technologies for Particle Processing*, in proceedings AIChE. II, 462-468.
41. Ho, K.F.; Lee, S.C.; Guo, H.; Tsa, W.Y. 2004. Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong, *Science of the Total Environment* 322:155–166.
42. Hoyle, C. R., Berntsen, T.; Myhre, G.; Isaksen, I. S A. 2007. Secondary organic aerosol in the global aerosol – chemical transport model Oslo CTM2. *Atmospheric Chemistry and Physic* 7: 5675-5694.
43. Huff J. 2007. Benzene-induced cancers: abridged history and occupational health impact. *International Journal of Occupational and Environmental Health* 13(2): 213-21.
44. Hung, I-F; Deshpande, C.G.; Tsai, C-J.; Huang, S-H. 2005. Spatial and Temporal Distribution of Volatile Organic Compounds around an Industrial Park of Taiwan. *Aerosol and Air Quality Research* , 5(2): 141-153.
45. Ito, A.; Sillman, S.; Penner, J.E. 2007. Effects of additional nonmethane volatile organic compounds, organic nitrates, and direct emissions of oxygenated organic species on global tropospheric chemistry. *Journal of Geophysical Researh* 112(6): 6309.
46. Kalberer, M.; Paulsen, D.; Sax, M. 2004. Identification of polymers as major components of 20 atmospheric organic aerosols. *Science* 303(5664): 1659–1662.
47. Kelly, N. A.; Chang, T. Y. 1999. An experimental investigation of incremental reactivities of volatile organic compounds. *Atmospheric* Environment 33: 2101-2110
48. Koch, W. H. 2001. Developing technology for enhanced vapor recovery. *Petroleum Equipment & Technology*, February/March: 16-22. Available from internet: <http://www.t-r-i.com/gifs/xPET2-01.pdf>.
49. Koneswaran, G.; Nierenberg, D.; 2008. Global farm animal production and global warming: impacting and mitigating climate change. *Environmental Health Perspectives* 116(5): 578-582.
50. Konovalov, I. B. 2003. Nonlinear relationships between atmospheric aerosol and its gaseous precursors: Analysis of long-term air quality monitoring data by means of neural networks. *Atmospheric Chemistry and Physic* 3: 607–621. Available from internet: <www.atmos-chem-phys.org/acp/3/607/>.
51. Kühlwein, J.; Wickert, B.; Trukenmüller, A.; Theloke J.; Friedrich, R. 2002. Emission modelling in high spatial and temporal resolution and calculation of pollutant concentrations for comparisons with measured concentrations *Atmospheric Environment* 36(1): 7-18
52. Laškova, T. 2007 Lakiųjų organinių junginių (LOJ) sklaidos modeliavimas. Iš *Aplinkos apsaugos inžinerija* [Environmental protection engineering]: *10-osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“* [10th Conference of Junior Researchers Science – Future of Lithuania], įvykusios Vilniuje 2007 m. kovo 29 d., pranešimų medžiaga. Vilnius: Technika, 72-78.
53. Laškova, T.; Vaitiekūnas, P. Lakiųjų organinių junginių (LOJ) išsiskyrimo naftos terminaluose analizė. Iš Aplinkos apsaugos inžinerija: *8-osios Lietuvos jaunųjų mokslininkų konferencijos „Lietuva be mokslo – Lietuva be ateities*“, įvykusios Vilniuje 2005 m. kovo 24 d., pranešimų medžiaga. Vilnius: Technika, 227–233.
54. Laškova, T.; Zabukas, V.; Vaitiekūnas, P. 2007. Meteorologinių sąlygų įtaka lakiųjų organinių junginių sklaidai pažemės atmosferos sluoksnyje. *Journal of Environmental Engineering and Landscape Management* 15(3): 135-143.
55. Latella, A.; Stani, G.; Cobelli, L.; Duane, M.; Junninen, H.; Astorga, C.; Larsen, B.R. 2005. Ozone forming potential of C_2-C_9 hydrocarbons in Milan. *Journal of Chromatography* A 1071: 29-39.
56. Lewis, A.C.; Carslaw, N.; Marriott, P. J.; Kinghorn, R. M.; Morrison, P.; Lee, A. L.; Bartle, K.D.; Pilling, M. J. 2000. A larger pool of ozone-forming carbon compounds in urban atmospheres. *Nature* 405: 778–781.

57. Li, D.W.; Shi, Y.; He, X.Y.; Chen, W.; Chen, X. 2008. Volatile organic compound emissions from urban trees in Shenyang, China. *Botanical Studies* 49: 67-72.

58. Liu, Y., Shao, M.; Lu, S.; Chang, C.; Wang, J., Chen, G. 2008. Volatile Organic Compound (VOC) measurements in the Pearl River Delta (PRD) region, China. *Atmospheric Chemistry and Physics*. 8: 1531-1545.

59. Lyons J.M.; Delaney S.S. 2000. Potential evaporative emission impacts associated with the Introduction of ethanol-gasoline. Blends in California. American Methanol Institute. 37 p. Available from internet: <http://www.methanol.org/reformgas/reports/sierra.pdf>.

60. Moran, M.D.; Niemi D.R.; Makar, P.A.; Mah, T. 2003. An alternate approach to VOC speciation: *12th Annual Emission Inventory Conference "Emission inventories – applying new technologies"*, San Diego, California 2003 April 29 - May 1, reporting paper, 1-15. Available from internet: <http://www.epa.gov/ttn/chief/conference/ei12/modeling/moran.pdf >.

61. Nemitz, E.; Langford, B.; House, E.; Phillips, G.; Famulari, D.; Neil Cape, J.; Davison, B.; Hewitt, N. 2007. Micrometeorological measurements of anthropogenic VOC emissions from urban areas. Contribution to the ACCENT Workshop on Volatile Organic Compounds. *Atmospheric Sciences* 68-71.

62. Nojima, K.; Fukaya, K.; Fukui, S.; Kanno, S. 1975. The formation of nitrophenols and nitrobenzene by the photochemical reaction of benzene in the presence of nitrogen monoxide. *Chemosphere* 2: 77–82.

63. Odum, J. R.; Jungkamp, T. P. W.; Griffin, R. J. 1997. The atmospheric aerosol-forming potential of whole gasoline vapour. *Science* 276: 96–99.

64. Paliulis, D.; Baltrėnas, P. 2007. Volatile organic compound emissions to the atmosphere and their reduction. *Ekologija* 53(4): 102-107

65. Pastino, G.M.; Asghanan, B.; Roberts, K.; Medinsky, M.A.; Bond, J.A.; 1997. A Comparison of physiologically based pharmacokinetic model. Predictions and experimental data for inhaled ethanol in male and female B6C3F mice, F344 rats, and humans. *Toxicology and Applied Pharmacology* 145: 147-157.

66. Periago, J.F.; Prado, C. 2005. Evolution of occupational exposure to environmental levels of aromatic hydrocarbons in service tations. Oxford: Oxford University Press. 8 p.

67. Petraitis, E.; Vasarevičius, S. 2001. Numerical modeling of solid particle dispersion in the atmosphere using the programs "Varsa" and "Phoenics". *Aplinkos inžinerija* [*Environmental Engineering*] 9(1): 23–28.

68. Pilidis, G.; Karakitsios, S.; Kassomenos, P., 2005. BTX measurements in a medium sized European city. *Atmospheric Environment* 39(33): 6051-6065.

69. Pjetraj M. 1996. *VOC emissions influence of VOC measurement and reporting methods on regulatory policy and emissions estimations*. NC Division of Air Quality Stationary Source Compliance Branch. 13 p. Available from internet: <http://daq.state.nc.us/enf/sourcetest/voc/VOCweb.pdf>.

70. Pun, B.K.; Wu, S.Y.; Seigneur, C.; Seinfeld, J.H.; Griffin, R. J.; Pandis, S.N. 2003. Uncertainties in modeling secondary organic aerosols: three-dimensional modeling studies in Nashville/Western Tennessee. *Environmental Science & Technology* 37: 3647–3661.

71. Reuther, C.G. 2000. Reducing transboundary air pollutants. *Environmental Health Perspectives* 108 (4): 170-175.

72. Robinson, A. L.; Donahue, N. M.; Shrivastava, M. K.; Weitkamp, E. A.; Sage, A. M.; Grieshop, A. P.; Lane, T. E.; Pierce, J. R.; Pandis, S. N. 2007. Rethinking organic aerosols: semivolatile emissions and photochemical aging. Science 315 (5816): 1259-1262.

73. Romieu, I.; Ramirez, M.; Meneses, F.; Ashley, D.; Lemire, S.; Colome, S.; Fung, K.; Hernandez-Avila, M. 1999. Environmental exposure to volatile organic compounds among workers in Mexico city as assessed by personal monitors and blood concentrations. *Environmental Health Perspectives* 107(7): 511.

74. Rubin, J.I.; Kean, A.I.; Harley, R.A.; Millet, D.B.; Goldstein, A.H. 2006. Temperature dependence of volatile organic compound evaporative emissions from motor vehicles. *Journal of Geophysical Research* 111: D03305.

75. San Jose, R.; Baklanov, A.; Sokhi, R.S.; Karatas, K.; Perez, J.L. 2006. Air quality modelling: state-of-the-art. *3rd Biennial meeting of the International Environmental Modelling and Software Society*, 1-17. Available from internet: <http://www.iemss.org/iemss2006/papers/w17/pp.pdf>.

76. Schäfer, K.; Hoffmann, H.; Dormuth, I.; Jahn, C.; Emeis, S. 2002. VOC emission source strengths of tankers during refuelling activities determined by spectroscopic remote sensing and inverse dispersion modelling. *8th International Symposium on Remote Sensing*, 17-21.09.2000, Toulouse, Proceedings of SPIE 4539, 247-257.

77. Schuetzle, D. ; Siegl, W.O.; Jensen, T.E.; Dearth, M.A.; Kaiser, E.W.; Gorse, R.; Kreucher, W.; Kulik. E. 1994. The Relationship between gasoline composition and vehicle hydrocarbon emissions: A review of current studies and future research needs. *Environmental Health Perspectives* 102(4): 3-12.

78. Schulz, M.; Textor, C.; Kinne, S.; Balkanski, Y.; Bauer, S.; Berntsen, T.; Berglen, T.; Boucher, O.; Dentener, F.; Guibert, S.; Isaksen, I. S. A.; Iversen, T.; Koch, D.; Kirkevag, A.; Liu, X.; Montanaro, V.; Myhre, G.; Penner, J. E.; Pitari, G.; Reddy, S.; Seland, O.; Stier, P.; Takemura, T. 2006. Radiative forcing by aerosols as derived from the AeroCom present-day and pre-industrial simulations. *Atmospheric Chemistry and Physic* 6:5225-5246.

79. Sillman, S. 1999. The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. *Atmospheric Environment* 33: 1821-1845.

80. Sillman, S. 2003. Tropospheric ozone and photochemical smog. *Treatise on Geochemistry* 9:407-431.

81. Sillman, S.; He, D. 2002. Some theoretical results concerning O_3-NO_x-VOC chemistry and NO_x-VOC indicators. *Journal of Geophysical Researh* 107(22): 4659.

82. Solberg, S. 2005. *VOC measurements 2003*. Chemical Co-ordinating Centre of EMEP. Available from internet: 83 p. <http://www.nilu.no/index.cfm?ac=publications&folder_id=4309&publication_id=8064&view=rep>.

83. Solovyov, S. E.; Powers, T. H.; Incorvia, S. A.; Williams, J. A.; Koch, P. E. 2006. Control of moisture and volatile organic compounds by sorbent-loaded composites. *Society of Plastics Engineers Automotive Composites Conference*, 1-7. Available from internet: <http://www.multisorb.com/library/techpapers/SPE%20AACCE-6.pdf>.

84. Spyros, P. K.; Vasileios, K. D.; Pavlos, A. K.; Georgikos, A. P. 2007. Contribution to ambient benzene concentrations in the vicinity of petrol stations: estimation of the associated health risk. *Atmospheric Environment* 41(9): 1889-1902.

85. Srivastava, A.; Joseph, A.E.; More, A.; Patil, S. 2005. Emissions of VOCs at urban petrol retail distribution centres in India (Delhi and Mumbai). *Environmental Monitoring and Assessment* 109(1-3): 227-242.

86. Stednum, D.K. 2004. Photochemical ozone formation, simplified. *Environmental Chenistry* 1:65-66.

87. Streets, D.G.; Bond, T.C.; Carmichael, GR., Fernandes, S.D.; Fu, Q.; He, D.; Klimont, Z.; Nelson, S.M.; Tsai, N.Y.; Wang, M.Q.; Woo, J.-H.; Yarber, K.F. 2003. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. *Journal of Geophysical Researh* 108(D21): 8809.

88. Suwattiga, P.; Limpaseni, W. 2005. Seasonal Source Apportionment of Volatile Organic Compounds in Bangkok Ambient Air. *ScienceAsia* 31: 395-401.

89. Takegawa, N.; Miyakawa, T.; Kondo, Y.; Jimenez, J.L.; Zhang, Q.; Worsnop, D.R.; Fukuda, M. 2006. Seasonal and diurnal variations of submicron organic aerosol in Tokyo observed using the Aerodyne aerosol mass spectrometer. *Journal of Geophysical Researh* 111: D11206.

90. Troussier, F.; Locoge, N.; Galloo, J.C. 2005. Source apportionment of volatile organic compounds in 3 french sites by descriptive analyses and receptor modelling. *Third International Symposium on Air Quality Management at Urban, Regional and Global Scales and 14 th IUAPPA Regional Conference*, 26-30 September Istanbul, proceedings, 4-13.

91. Tsigaridis, K.; Kanakidou, M. 2003. Global modelling of secondary organic aerosol. *Atmospheric Chemistry and Physic* 3: 2879–2929.

92. Vaitiekūnas, P. 1998. *Konvencinio pernešimo skaitinis modeliavimas*. Kaunas: Lietuvos energetikos institutas. 261 p.

93. Velasco E.; Lamb, B.; Westberg, H.; Allwine, E.; Sosa, G.; Arriaga-Colina, J.L.; Jobson, B.T.; Alexander, M. L.; Prazeller, P.; Knighton, W.B.; Rogers, T.M.; Grutter, M.; Herndon, S.C.; Kolb, C. E; Zavala, M.; de Foy, B.; Volkamer, R.; Molina, L. T.; Molina, M. J. 2007. The valley of Mexico during the MCMA 2002 & 2003 field campaigns. *Atmospheric Chemistry and Physics* 7: 329-353.

94. Velasco, E.; Lamb, B.; Pressley, S.; Allwine, E.; Westberg, H.; Jobson, B. T.; Alexander, M.; Prazeller, P.; Molina, L.; Molina, M. 2005. Flux measurements of volatile organic compounds from an urban landscape. *Journal of Geophysical Researh* 32(20): L20802.

95. Virkkula, A.; Teinila, K.; Hillamo, R.; Stohl, A. 2003. A decade of trace gas measurements using DOAS in Finnish Lapland. *Boreal Environment Research* 8: 351-363.

96. *VOC reactivity science assessement: Executive summary*. 1999. NARSTO. 29 p. Available from internet: <http://www.narsto.org/files/files/AssessExSum.pdf>.

97. Volkamer R. 2001. *A DOAS Study on the Oxidation Mechanism of Aromatic Hydrocarbons under Simulated Atmospheric Conditions*. Natural Sciences and for Mathematics of the Rupertus Carola University of Heidelberg. 196 p. Available from internet: <http://archiv.ub.uni-heidelberg.de/volltextserver/volltexte/2002/1939/pdf/Volkamer_R_Dissertation.pdf>.

98. Volkamer, R.; Jimenez, J. L.; San Martini, F.; Dzepina, K.; Zhang, Q.; Salcedo, D.; Molina, L. T.; Worsnop, D. R.; Molina, M. J. 2006. Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected, *Journal of Geophysical Researh* 33: L17811.

99. Warneke, C.; de Gouw, J.A.; Goldan, P.D.; Kuster, W.C.; Williams, E.J.; Lerner, B.M.; Jakoubek, R.; Brown, S.S.; Stark, H.; Aldener, M.; Ravishankara, A.R.; Roberts, J.M.; Marchewka, M.; Bertman, S.; Sueper, D.T.; McKeen, S.A.; Meagher, J.F.; Fehsenfeld, F.C. 2004. Comparison of daytime and nighttime oxidation of biogenic and anthropogenic VOCs along the New England coast in summer during New England. Air Quality Study 2002. *Journal of Geophysical Research* 109: D1309.

100. Warneke, C.; de Gouw, J.A.; Kuster, W.C.; Goldan, P.D.; Fall, R. 2003. Validation of atmospheric VOC measurements by proton-transfer-reaction mass spectrometry using a gaschromatographic preseparation method. *Environmental Science and Technology* 37: 2494–2501.

101. Xu, X.; van Stee, L. L. P.; Williams, J.; Beens, J.; Adahchour, M.; Vreuls, R. J. J.; Brinkman, U. A. Th.; Lelieveld, J. 2003. Comprehensive two-dimensional gas chromatography (GC×GC) measurements of volatile organic compounds in the atmosphere. *Atmospheric Chemistry and Physic* 3: 1139–1181.

102. Yang, K.; Tinga, C.; Wanga, J.; Wingenterb, O.W.; Chan, C. 2005. Diurnal and seasonal cycles of ozone precursors observed from continuous measurement at an urban site in Taiwan. *Atmospheric Environment* 39: 2829-2838.

103. Yienger, J.J.; Galanter, M.K.; Holloway, T.A.; Phadnis, M.J.; Guttikunda, S.K.; Carmichael, G.R.; Moxim, W.J.; Levy H. 2000. The episodic nature of air pollution transport from Asia to North America. *Journal of Geophysical Researh* 105: 26931-26945.

104. Zhang, J.; Wang, T.; Chameides, W. L.; Cardelino, C.; Kwok, J.; Blake, D. R.; Ding, A; So, K. L. 2007. Ozone production and hydrocarbon reactivity in Hong Kong, Southern China. *Atmospheric Chemistry and Physic* 7: 557–573.

105. Zhang, Q.; Worsnop, D. R.; Canagaratna, M. R.; Jimenez, J. L. 2005. Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols. *Atmospheric Chemistry and Physic* 5: 3289-3311.

106. Кулагин А.В. 2003. *Прогнозирование и сокращение потерь бензинов от испарения из горизонтальных подземных резервуаров* АЗС. Уфа: УГНТУ 25 стр. Available from internet: <http://www.oil-info.ru/ngd/trans/Kulagin_3.pdf>.

107. Кулагин, А.В.; Коршак, А.А. 2002. Улавливание паров бензина при его приеме в резервуары автозаправочных станций. *Трубопроводный транспорт нефти и газа*. Материалы Всероссийской научно-технической конференции. Уфа: Изд-во УГНТУ, 128-132.

THE ARTICLES

LIST OF ARTICLES

1. Bikbajeva, Ž. 2007. Lakiųjų organinių junginių garavimas nuo degalinių iš *Aplinkos apsaugos inžinerija: 10-osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“*, įvykusios Vilniuje 2007 m. kovo 29 d., iš pranešimų medžiagos, Vilnius: Technika, 88–93.
2. Bikbajeva, Ž. 2008. Research of VOCs from petrol filling stations from *Environmental protection engineering: 11*th *Conference of Junior Researchers Science – Future of Lithuania*, įvykusios Vilnius 2008-04-03, reporting material.
3. Bikbajeva, Ž.; Girgždys, A. 2008. Benzene in ambient air of petrol filling stations. *Sveikatos Mokslai*.