

VILNIUS GEDIMINAS TECHNICAL UNIVERSITY

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**RESEARCH OF POLLUTION BY VOLATILE
ORGANIC COMPOUNDS IN AMBIENT AIR
AND ITS REDUCTION IN OIL TERMINALS**

Summary of Doctoral Dissertation
Technological Sciences,
Environmental Engineering and Landscape Management (04T)

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VILNIAUS GEDIMINO TECHNIKOS UNIVERSITETAS

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**ORO TARŠOS LAKIAISIAIS ORGANINIAIS
JUNGINIAIS TYRIMAS IR JOS MAŽINIMAS
NAFTOS TERMINALUOSE**

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1. General characteristic of the dissertation

Topicality of the problem

This day environment pollution research and modern environment protection technology installation became a prior aspect not only in our country, but also in the whole world. The intensification and development of the industrial processes has a negative impact on human's health and environment. As a result, it increases waste products accumulation. It also has a disbalance of natural processes and reckless waste of natural resources. All of the above can cause greenhouse effect formation. Because of intensive expansion of energy, in industrial and transportation sectors, there is significant increase in atmosphere pollution in last decade.

The West part of Lithuania is one most polluted area by volatile organic compounds (VOCs), because there is a location of oil production and refinery industry, as well as intensive development of oil terminals. The problem is becoming more serious and relevant when these objects are located near urban areas.

Topicality of the work

VOCs emission from stationary pollution sources increased in Lithuania approximately 4 times – from 5.952 to 22.208 thousand t in last years (1998–2006). Meanwhile ambient air pollution by VOCs in Klaipėda increased approximately 6 times – from 0.564 to 3.551 thousand t (1998–2006). That's why the major attention should be paid to this environmental problem of Klaipėda and its sea port. The presence of unpredictable meteorological conditions in sea port area creates the recently of modern scientific research evaluation of ambient air pollution by VOCs.

It's important not only to determine VOCs concentration in its emission spots, but also to evaluate its transfer in lower atmospheric boundary layer. The solution of this problem requires complex systematic research on VOCs concentration, meteorological conditions, products loading indicator in oil terminals and nearby.

It's necessary to create numerical model of VOCs transfer and to suggest the optimal technological solution for VOCs emission prevention in order to evaluate precisely VOCs transfer in this region. Also this complex research allows us to determine optimal distance from pollution objects to urban area, as well as new industrial objects location in towns and new projects of urban areas near already existing industrial objects.

Aim and tasks of the work

Aim of the work – to evaluate the atmosphere pollution by VOCs in oil terminals, to determine meteorological conditions and the impact of products loading indicator on VOCs transfer in lower atmospheric boundary layer, as well as to create numerical model of VOCs transfer and to prepare scientific recommendations for VOCs pollution reduction.

Tasks of the work

1. To identify the main VOCs locations in oil terminals and investigate the concentration of pollutant.
2. To perform research of VOCs concentration transfer in lower atmospheric boundary layer during the seasons around oil terminals, which depends on meteorological conditions (air temperature, atmosphere pressure, wind speed and direction, relative humidity) and loading indicator.
3. To create the numerical model, that can predict VOCs transfer from already existing and reconstructed oil terminals in sea port area.
4. To suggest technological solutions that can reduce or eliminate VOCs emission in oil terminals during loading-unloading operations according to scientific research results and it's analysis.

Scientific novelty

Preparing this dissertation the following new research results of environment engineering were created:

1. Innovation of products loading indicator that helps to determine VOCs concentration variation in lower atmospheric boundary layer. Determination of VOCs concentration dependence on loading indicator.
2. Innovation of complex research of VOCs concentration, meteorological conditions and loading indicator in oil terminals and nearby during the seasons.
3. Determination of VOCs concentration dependence on wind speed (1–5 m/s) in sea port area.
4. Creation of numerical model that helps to predict VOCs transfer in lower atmospheric boundary layer depending on meteorological conditions and loading indicator in oil terminals and nearby.
5. Innovation of new construction technological solution that helps to reduce VOCs emission – loading-unloading cover of railroad tanker cars.

Methodology of research

Analytical and statistical evaluation methods were used in this work. As well as oil products VOCs concentration analysis method was used. Model of VOCs transfer was performed with the PHOENICS 3.5 software package, which depends on numerical methods of differential equations solution.

Practical value

1. Scientific research of VOCs concentration allows to determine the influence of meteorological conditions and loading indicator to VOCs emission and its transfer in lower atmospheric boundary layer during the season.
2. Evaluation of VOCs concentration research, meteorological conditions and loading indicator that allows to create numerical model VOCs transfer in lower atmospheric boundary layer and to predict VOCs concentration around oil terminals not using expensive control analysis.
3. Creation of practical recommendations for VOCs emission reduction in oil terminals after technical modification in railroad tanker cars loading-unloading system.

Defended propositions

1. VOCs concentration variation in oil terminals depends on air temperature, wind speed and products loading indicator. Relative humidity and atmosphere pressure have marginally influence on atmosphere pollution by VOCs.
2. The highest VOCs concentration in oil terminals is in railway trestles.
3. Numerical VOCs transfer model can be used for calculating the highest permitted VOCs concentration overdose, determining the possibility of increase capacity of loading products in oil terminals and for choosing safe distance from oil terminals to urban area as well as for VOCs recuperation and burning systems installation and rational usage.

The scope of the scientific work

The scientific work consists of the general characteristic of the dissertation, 7 chapters, list of literature and list of publications. The total scope of the dissertation – 130 pages, 79 pictures and 31 tables.

Approval of the results

The research findings of the following 8 papers are published: 1 scientific article in magazine with the Thomson ISI citation index, 1 paper in the scientific periodical publication included in Springer Link international databases of reviewed scientific periodical publication, 1 paper in foreign review publication, 5 papers in other Lithuanian scientific publications. Application to get the Lithuanian patent was preferred.

2. Consistent pattern of volatile organic compounds evaporation and transfer

The second chapter is analyzing the major elements of oil terminals and VOCs evaporation zones. As well as prevention technique that helps to reduce VOCs emission in pollution objects. The chapter talks about meteorological conditions (air temperature, relative humidity, wind speed and direction, atmosphere pressure) influence on VOCs variation and its transfer in lower atmospheric boundary layer.

3. Methodology of experimental research

Research of VOCs concentration was done in Klaipėda University Environmental research laboratory using SHIMADZU GC-2010 gas chromatograph equipped with flame ionization detector (FID). At every observation post, air samples were sampling into Teflon bags. A silicon capillary column, 0.5 m long with internal diameter of 0.52 mm was used for the quantitative analysis of VOCs concentration. Temperature mode: evaporator – 125 °C; column – 125 °C; detector – 150 °C. Gas rate: helium – 30 ml/min, air – 400 ml/min, hydrogen – 40 ml/min. Values of meteorological conditions prevailing at the time when the air samples were taken from the Klaipėda meteorological station.

4. The results of experimental research and analysis

Research of VOCs concentration around oil terminals territory

The highest intensity of products loading indicator (showing the type and amount of loading operations carried out in the oil terminals) was achieved in summer – even up to 56 % (Figure 1). The loading indicator was lower and was up to 40 % in spring and winter, at the moment of VOCs concentration analysis, while in autumn it was the lowest and was up to 19 %. Thus we can see that

variation of VOCs concentration in the atmospheric boundary layer depends not only on the intensity of loading operations in the oil terminals, but also on meteorological conditions.

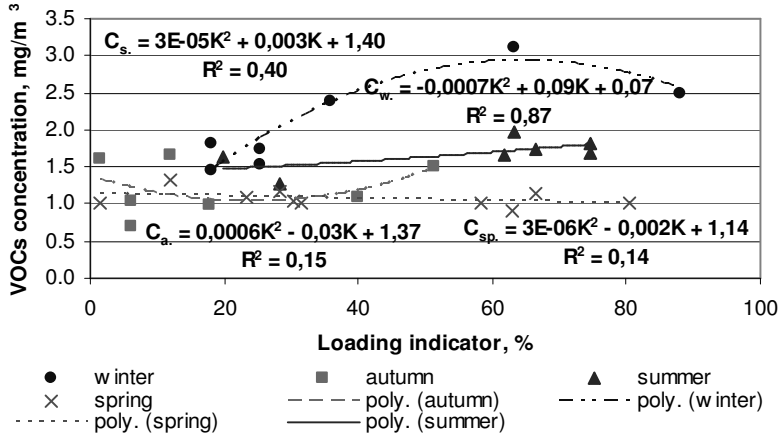


Fig 1. Dependence between VOCs concentration (C) in ambient air and products loading indicator (K) during different seasons

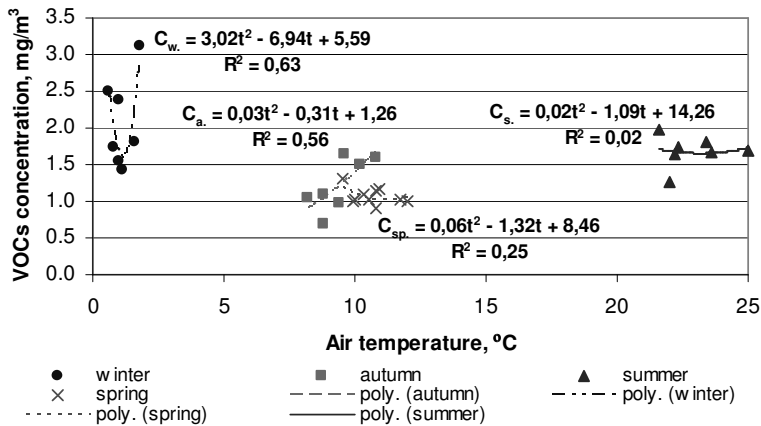


Fig 2. Dependence between VOCs concentration (C) in ambient air and air temperature (t) during different seasons

VOCs concentration during different seasons varied from 0.58 mg/m³ to 3.12 mg/m³ (Figure 2). The highest VOCs concentration levels were recorded in

winter (average 2.08 mg/m³) and in summer (1.68 mg/m³), while the lowest – in autumn (1.23 mg/m³) and in spring (1.09 mg/m³).

Summarizing the information recorded during all the seasons of the year we see that air temperature has no predominant impact on the variation of VOCs concentration in the lower atmospheric boundary layer. This may be related to the fact that other scientific research does not include the assessment of loading operations as an indicator showing the type and amount of loading operations carried out in the oil terminals. The latter factor in the assessment of variation of VOCs concentration is important only in the research objects with fluctuating intensity of loading operations. This is the reason why this factor must be taken into account when analyzing VOCs emission in those terminals, where the intensity of loading operations may vary from 0 to 100 %, while this indicator may be eliminated in oil production plants because of little variation in the intensity of loading operations.

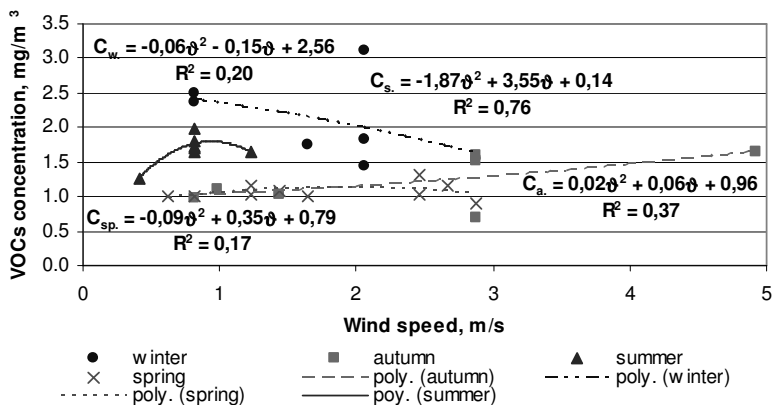


Fig 3. Dependence between VOCs concentration (C) in ambient air and wind speed (v) during different seasons

The highest wind speed in the sample collecting points at 1.5 m height from the surface of the ground on the days of analysis in autumn was 2.40 m/s (Figure 3). The wind speed was almost the same in winter and spring – it was up to 1.76 m/s on average; the lowest wind speed was recorded in summer – only about 0.82 m/s on average. When analyzing the data recorded during different seasons, it was noticed that VOCs concentration tends to decrease with the increase in the wind speed and vice versa. The dependence of VOCs concentration on the wind speed was the most explicitly expressed in winter. When analyzing the results of other seasons, the impact of wind speed on the

VOCs concentration was not dominant. This is related with insignificant variation of wind speed during different seasons of the year.

The impact of relative humidity and ambient air pressure on the variation of VOCs concentration is insignificant, because those two indicators remain almost the same during different seasons of the year.

Statistical data processing was carried out using multifunction transfer analysis method. Such data analysis revealed that the data recorded in spring and autumn may be combined into one group, as there is no statistical significance between the groups – $P > 0.05$ (95 % reliability). It was also determined that VOCs concentration depends on air temperature, when comparing the results of summer-spring (autumn) or winter-spring (autumn) seasons – $P < 0.05$. VOCs concentration depends on wind speed higher that must be higher than 3 m/s (at 1.5 m height from the surface of the ground – 1.64 m/s, $P < 0.05$). The dependence of VOCs concentration on relative humidity and ambient air pressure is statistically insignificant, as P value was $P > 0.05$ in all groups.

Research of VOCs concentration in oil terminals

Having carried out experimental analysis in oil terminals, it was determined that the biggest VOCs concentration is in railway trestles zone is 3778 mg/m³ on average. The biggest amount of oil product is lost due to evaporation, while railroad tanker cars are not connected to the system, i. e. when oil products are not unloaded. However, high VOCs concentrations are instantaneous and are rapidly dashed with ambient air up to 10–15 mg/m³.

Also research of VOCs concentration in storage tank farms and jetty was done. During the analysis of VOCs concentration, the highest concentrations were observed on the sites where refilling operations of tankers and/or storage tanks took place: during refilling of the storage tank capacity of which is 5000 m³ with fuel oil, VOCs concentration at a breather reached approximately 514 mg/m³, and capacity of which is 20 000 m³ – 567 mg/m³; meanwhile, while refilling with light oil products the storage tank capacity of which is 10000 m³ reached 1500 mg/m³ (Table 1).

During refilling of a tanker (capacity 100000 m³) with fuel oil, VOCs concentration at a breather was larger than during refilling of tanks with fuel oil as well as came to as much as 1078.7 mg/m³. This is related to the fact that the storage tanks have a floatable pontoon equipped which reduces the amount of VOCs released from a product above the liquid product, while tankers do not have such pontoons projected.

Table 1. Results of VOCs concentration, mg/m³, research in oil terminal

Air sampling points	Air sampling days								Average
	1	2	3	4	5	6	7	8	
	VOCs concentration, mg/m ³								
Tanker	1078.7								1078.7
LOP -5A		3.7	2.8	2.9					3.1
LOP -5B				2.6					2.6
LOP -10A		4.1	3.6	2.5					3.4
LOP -10B		8.5	41.9	3.3					17.9
LOP-10C					1500.0				1500.0
HOP -5-4								7.9	7.9
HOP -5-5					493.1	638.8			565.9
HOP-5-6								461.7	461.7
HOP-20						509.3		624.3	566.8
HOP -32					5.6	24.9	16.0		31.2

Note: LOP – light oil products, HOP – heavy oil products

In the fleet with heavy oil products (fuel oil) storage tanks, while loading operations were not carried out, VOCs concentration on a tank with 5000 m³ capacity, at a breather reached approximately 7.9 mg/m³. At breathers of the new constructed storage tanks which capacity came to 32250 m³, as the fuel oil was being stored, an average of 30.2 mg/m³ was established. In the fleet with light oil products storage tanks, while loading operations were not carried out, VOCs concentration on a tank with 5000 m³ capacity, at a breather reached approximately 2.9 mg/m³, while on a tank with 10000 m³ – 10.7 mg/m³. Air temperature during air sampling ranges from 2.2 to 13.7 °C, relative humidity ranges from 70 % to 97 % and atmosphere pressure ranges from 755 to 775 mm Hg clm. North-east 2.73 m/s average speed wind was dominated.

4. Numerical modeling of volatile organic compounds transfer in lower atmospheric boundary layer

The system of five equations is being solved in order to establish the VOCs transfer in a lower atmospheric boundary layer (equations of Navier-Stokes, continuity and diffusion), which in generalized form could be as following:

$$\text{div}(\rho \mathbf{V} \Phi - \Gamma_{\Phi} \mathbf{grad} \Phi) = S_{\Phi}, \quad (1)$$

ρ – density, kg/m³; Φ – dependent variable: $\Phi = 1$ for continuity equation, u , v , w – speed components x , y and z by coordinate directions, m/s; C – VOCs concentration, mg/m³; $\mathbf{V}$ – wind speed vector; Γ_{Φ} – diffusion coefficient of variable Φ ; S_{Φ} – source term of variable Φ .

(1) equations system form solving by using final volume method. Diffusion coefficient Γ_Φ consists of two components, which for Navier-Stokes equations expressible by kinematic viscosity is following:

$$\Gamma_\Phi/\rho = \nu + \nu_T, \quad (2)$$

and for diffusion equations:

$$\Gamma_C/\rho = \nu/\text{Pr}_D + \nu_T/\text{Pr}_{D,T} \quad (3)$$

Scalar form of (1) equations system is following:

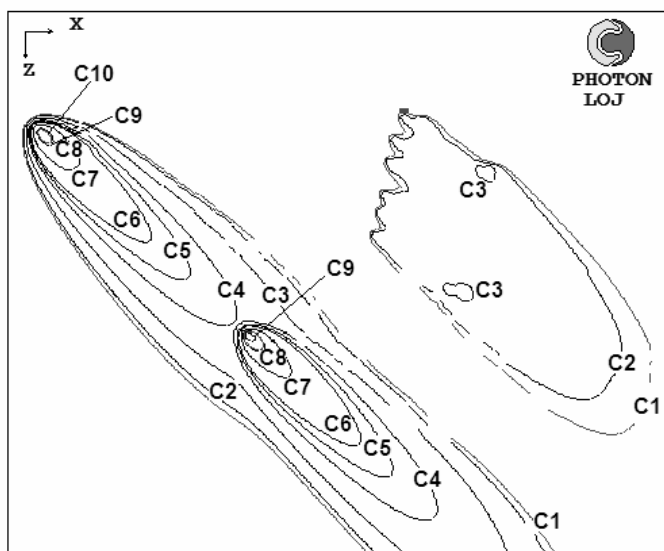
$$\begin{aligned} u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} &= -\frac{1}{\rho} \frac{\partial p}{\partial x} + \frac{\partial}{\partial x} \left((\nu + \nu_T) \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left((\nu + \nu_T) \frac{\partial u}{\partial y} \right) + \\ &+ \frac{\partial}{\partial z} \left((\nu + \nu_T) \frac{\partial u}{\partial z} \right); \\ u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + w \frac{\partial v}{\partial z} &= -\frac{1}{\rho} \frac{\partial p}{\partial y} + \frac{\partial}{\partial x} \left((\nu + \nu_T) \frac{\partial v}{\partial x} \right) + \frac{\partial}{\partial y} \left((\nu + \nu_T) \frac{\partial v}{\partial y} \right) + \\ &+ \frac{\partial}{\partial z} \left((\nu + \nu_T) \frac{\partial v}{\partial z} \right); \\ u \frac{\partial w}{\partial x} + v \frac{\partial w}{\partial y} + w \frac{\partial w}{\partial z} &= -\frac{1}{\rho} \frac{\partial p}{\partial z} + \frac{\partial}{\partial x} \left((\nu + \nu_T) \frac{\partial w}{\partial x} \right) + \frac{\partial}{\partial y} \left((\nu + \nu_T) \frac{\partial w}{\partial y} \right) + \\ &+ \frac{\partial}{\partial z} \left((\nu + \nu_T) \frac{\partial w}{\partial z} \right); \\ \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} &= 0; \\ u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z} &= \frac{\partial}{\partial x} \left((D + D_T) \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left((D + D_T) \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left((D + D_T) \frac{\partial C}{\partial z} \right). \end{aligned} \quad (1a)$$

$D = \nu/\text{Pr}_D$ ir $D_T = \nu_T/\text{Pr}_{D,T}$. Where Pr_D – diffusion Prandtl number ($\text{Pr}_D = 0.65\text{--}0.71$), constant $\text{Pr}_{D,T} = 0.8$.

Atmosphere instability in a low wind speed 1–5 m/s is estimated by coefficient ν_T expression as follows:

$$\nu_T = (A/\rho) \cdot U_0, \quad (4)$$

A – atmospheric stability coefficient.



VOCs concentrations, mg/m^3 :

C1 - 0.05; C2 - 4; C3 - 10; C4 - 20; C5 - 50; C6 - 100; C7 - 300; C8 - 500; C9 - 1000; C10 - 1500

Fig 4. Isolines of the VOCs transfer modeling in the oil terminal and nearby

Figure 4 provides the numerical modeling results of the VOCs concentration transfer in the lower atmospheric boundary layer. The figure shows that the main pollution sources having impact on the pollution during the analysis of VOCs concentration was a light oil products storage tank of 10000 m^3 capacity – $1500 \text{ mg}/\text{m}^3$ (C10 isoline) and a tanker being filled with fuel oil – $1079 \text{ mg}/\text{m}^3$ (C9 isoline).

Isoline C7 shows the limit of the highest permitted VOCs concentration in the oil terminals, and C2 – outside the territory of the oil terminals. The distance from the pollution source to isoline C2 by fair wind reached 1700 m. It is important to note that on the way of the pollution movement from light oil products storage tank there is one more pollution source, i.e. a tanker. The distance between those sources is 750 m.

Against the wind, from isoline C10, VOCs concentration in radius of 33 m remains higher than $4 \text{ mg}/\text{m}^3$, and perpendicularly to the pollutant movement direction even up to 200 m towards both directions.

In order to decrease the difference of VOCs concentration in the numerical modeling and analysis results, we selected Prandtl number and an ambient air

instability coefficient A . The difference between average VOCs concentration in the analysis and modeling results was 3.45 % – when Prandtl number is 0.71 and 4.33 % – when Prandtl number is 0.56. Thus, we are going to use Prandtl number equal to 0.71 for further numerical modeling of VOCs spread in the lower atmospheric boundary layer.

Table 1. Modeling results of VOCs transfer under different atmosphere instability coefficient A

Sample collecting points	VOCs concentration, mg/m^3					
	Experimental	$A = 1.1$	$A = 1.2$	$A = 1.3$	$A = 1.4$	$A = 1.5$
1	1.97	1.78	1.80	2.01	2.04	2.09
2	1.88	1.71	1.76	1.92	1.98	1.99
3	1.80	1.65	1.70	1.88	1.92	1.94
4	1.69	1.54	1.62	1.77	1.80	1.79
5	1.39	1.25	1.30	1.49	1.53	1.55
6	1.07	0.81	0.93	1.05	1.16	1.19

The best result is when atmosphere stability coefficient $A = 1.3$ (Table 1).

Numerical modeling data differ from the analysis of VOCs concentration in six sample-collecting points by approximately ± 3.6 % (Fig 5).

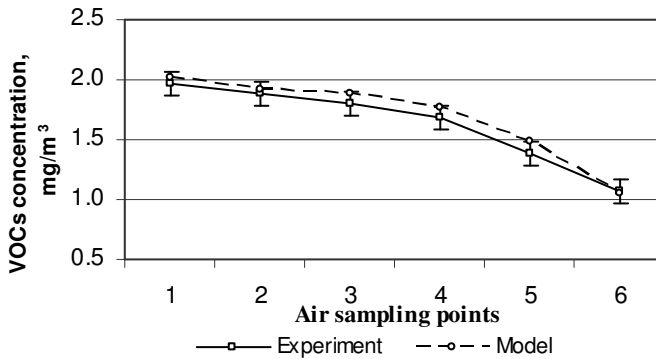


Fig 5. Mathematical model testing in different sample collecting points

Figure 5 provides comparison of the data of natural experiment and numerical modeling. It shows that the modeling results within the limits of a slight error practically reveal the VOCs concentration results obtained during the experiment. It shows that in formula A constant (4) well corresponds to the atmosphere stability of the given solution.

6. Creation of volatile organic compounds emission reduction device

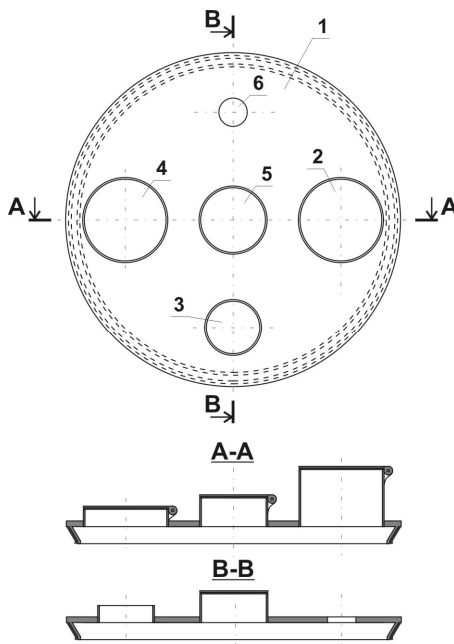


Fig 6. Loading-unloading cap scheme for railroad tanker cars:

1 – conical body; 2 – bottom railroad tanker car valve opening hole for product unloading; 3 – VOCs collect hole; 4 – product level in railroad tanker car measurement hole; 5 – product loading in railroad tanker car hole; 6 – vacuum valve

The product is fed into the tank through loading hole (5), and emitted VOCs are returned to the system through VOCs collection hatch (3), to which a flexible hose is connected during the loading of a tank (Fig 6). Other holes are not used and must be kept sealed during the loading of a tank. Thus, using a cover all the vapours emitted during the loading of oil product are neutralized in recuperative systems or utilized in combustion equipment.

The samples of a product are taken through (5) hatch before the tank unloading operation, while the measurement of the level of the product is carried out through (4) hatch. Hatch (2) is used for the opening of the product unloading valve. The vacuum valve (6) does not allow the pressure to fall to the critical value during the unloading of the product. Other hatches/holes are not used and are kept sealed during the unloading process. The cover of each hatch

is opened at the moment of each specific operation, which allows reducing the highest possible VOCs concentration.

The efficiency of its usage, depending on the type of a tank, can vary from 79 % (the diameter of a hatch – 560 mm) to 81 % (the diameter of a hatch – 590 mm) when unloading the oil product and up to 100 % – when loading the oil product.

7. General conclusions and recommendations

1. The highest VOCs concentrations were recorded in winter and summer periods – 3.12 mg/m^3 and 1.98 mg/m^3 respectively. This can be explained as follows:
 - VOCs concentration increases in winter due to the peculiarities of the fuel production, i. e. fuels used during the cold season are more volatile;
 - the main reason for increase of VOCs concentration in summer is high temperature (up to 25°C);
 - the levels of VOCs concentration are very similar and its different were up to 12 % in spring and autumn due to similar meteorological conditions.
2. It is necessary to introduce one more indicator – the indicator of loading operations – in order to make the measurements of variation of VOCs concentration in the atmospheric boundary layer more precise. VOCs concentration dependence on loading indicator was determined.
3. It was determined that the highest VOCs concentrations in oil terminals are in the following terminals zones:
 - a) the biggest VOCs concentration in oil terminals was determined in the areas of railway trestles during A-92 gasoline unloading operation – 3778 mg/m^3 on average. Such VOCs concentration is instantaneous and depending on the prevailing meteorological conditions with different speeds decrease up to $10\text{--}15 \text{ mg/m}^3$.
 - b) when filling 5000 m^3 capacity storage tank with fuel oil, VOCs concentration at bleeder was up to 514 mg/m^3 on average, while when filling 20000 m^3 capacity storage tank, it was 567 mg/m^3 . Meanwhile when filling 10000 m^3 capacity storage tank with light oil products, VOCs concentration was up to 1500 mg/m^3 .
 - c) VOCs concentration at the bleeder is higher when filling a tanker (100000 m^3 capacity) with fuel oil than when filling tanks – up to 1079 mg/m^3 . This is due to the fact that the tanks are equipped with buoyant pontoon preventing which reduce evaporation of liquid oil products.

4. Having analyzed the data of VOCs concentration research recorded during different seasons and multifactor transfer analysis (reliability – 95 %) was determined, that VOCs concentration depends on wind speed, when the wind speed is higher than 3 m/s ($P < 0.05$). If the wind speed is lower, there is no statistical correlation between VOCs concentration and wind speed ($P > 0.05$). The dependence of VOCs concentration on the ambient air pressure and relative humidity is very insignificant.
5. Created numerical model allows predicting VOCs transfer in lower atmospheric boundary layer depending on meteorological conditions and loading indicator in oil terminals and nearby. Prandtl ($Pr_D = 0.71$) and atmosphere instability ($A = 1.3$) coefficients were determined. When applying those coefficients average arithmetic error decreases up to ± 3.9 %.
6. After VOCs concentration research in oil terminal railway trestle and its result analysis during loading-unloading operations for VOCs emission reduce recommending using loading-unloading cover of railway tank.
7. Numerical model recommend use to predict for the highest permitted VOCs concentration overdose, determining the possibility of increase capacity of loading products in oil terminals and for choosing safe distance from oil terminals to urban area as well as for VOCs recuperation and burning systems installation and rational usage.

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ORO TARŠOS LAKIAISIAIS ORGANINIAIS JUNGINIAIS TYRIMAS IR JOS MAŽINIMAS NAFTOS TERMINALUOSE

Tiriamoji problema

Šiuo metu aplinkos taršos tyrimai ir šiuolaikinių aplinkosauginių technologijų diegimas tampa prioritetine kryptimi ne tik mūsų šalyje, bet ir visame pasaulyje. Intensyvinant ir vystant gamybinius procesus pasireiškia ir žmogaus neigiama įtaka gamtai: neišvengiama taršalų gausėjimo, kaupiasi gamybos atliekos, pažeidžiama gamtinių procesų pusiausvyra, beatodairiškai eikvojami gamtiniai resursai.

Užteršta atmosfera turi didžiausią neigiamą įtaką žmogaus sveikatai. Ši tarša lemia ir „šiltnamio“ efekto susidarymą. Atmosferos tarša yra ypač padidėjusi paskutiniaisiais dešimtmečiais dėl intensyvios energetikos, pramonės ir transporto plėtros. Ypatingai atmosferos žemutinių sluoksnių tarša lakiais organiniais junginiais (LOJ) fiksuojama tuose Vakarų Lietuvos regionuose, kuriuose vystoma naftos perdirbimo pramonė, naftos gavimo verslovės, koncentruojami naftos ir jos produktų paskirstymo terminalai. Šios atmosferos taršos LOJ problemos paastrėja, kai naftos perdirbimo ir paskirstymo terminalai yra netoli gyvenviečių, ar tiesiog ribojasi su jomis.

Darbo aktualumas

LOJ išmetimas iš stacionarių taršos šaltinių Lietuvoje pastaraisiais metais padidėjo beveik 4 kartus – nuo 5,952 tūkst. t (1998 m.) iki 22,208 tūkst. t (2006 m.), tuo tarpu Klaipėdoje oro tarša LOJ padidėjo nuo 0,564 tūkst. t (1998 m.) iki 3,551 tūkst. t (2006 m.), t. y. daugiau nei 6 kartus. Todėl aplinkosauginėms problemoms Klaipėdos mieste ir jūrų uoste turi būti skiriamas ypatingas dėmesys. Kadangi šiame pajūrio regione yra sudėtingos meteorologinės sąlygos, tai atmosferos taršos LOJ įvertinimui būtini ir šiuolaikiniai moksliniai tyrimai.

Svarbu nustatyti LOJ koncentracijas ne tik tiesiogiai jų emisijos vietose, bet ir įvertinti jų sklaidimą pažemės atmosferos sluoksnyje. Šios problemos sprendimui būtina atlikti sistemingą kompleksinį LOJ koncentracijos, meteorologinių elementų ir krovos indikatorius tyrimą naftos terminalų teritorijose ir už jų ribų. Kad tinkamai įvertinti LOJ sklaidą šioje pajūrio vietovėje būtina atlikti skaitinį modeliavimą ir atmosferos taršos mažinimui pasiūlyti optimalius technologinius sprendimo variantus. Taip pat toks kompleksiškas tyrimas leistų nustatyti naujų pramoninės objektų išdėstymą miestuose bei naujų gyvenamųjų rajonų planavimą šalia esamų pramonės objektų.

Darbo tikslas ir uždaviniai

Darbo tikslas – įvertinti atmosferos taršą LOJ naftos terminaluose, nustatyti meteorologinių elementų ir krovos indikatorius įtaką LOJ koncentracijos kitimui pažemės atmosferos sluoksnyje, sudaryti LOJ koncentracijos pasiskirstymo matematinį modelį, parengti mokslškai pagrįstas taršos LOJ mažinimo rekomendacijas.

Darbo uždaviniai

1. Nustatyti naftos terminaluose pagrindines LOJ išmetimo zonas ir atlikti šių taršalų koncentracijų tyrimus.
2. Ištirti LOJ koncentraciją pažemės atmosferos sluoksnyje naftos terminalų teritorijoje ir už jos ribų atsižvelgiant į meteorologinius elementus (oro temperatūrą, atmosferos slėgį, vėjo kryptį ir greitį, santykinę oro drėgmę) ir krovos indikatorių.
3. Sudaryti skaitinį modelį, leidžiantį prognozuoti LOJ, išsiskyrimus iš esamų, ir rekonstruojamų terminalų, sklaidą uosto zonoje.
4. Remiantis tyrimų rezultatais ir jų analize, pasiūlyti technologinius sprendimus, leidžiančius sumažinti ar išvengti LOJ emisijos į atmosferą naftos terminaluose.

Mokslinis naujumas

Rengiant disertaciją buvo gauti šie aplinkos ir kraštovarkos inžinerijos mokslui nauji rezultatai:

1. Įvestas naujas rodiklis – krovos indikatorius, įtakojantis LOJ koncentracijos kitimui pažemės atmosferos sluoksnyje. Nustatyta LOJ koncentracijos kitimo priklausomybė nuo krovos indikatoriaus.
2. Atliktas kompleksinis LOJ koncentracijos priklausomybės nuo meteorologinių elementų ir krovos indikatoriaus tyrimas naftos terminaluose ir už jų ribų skirtingų metų sezonais.
3. Pajūrio regionui nustatyta LOJ koncentracijos kitimo priklausomybė nuo vėjo greičio (0–5 m/s.).
4. Sudarytas LOJ sklaidos pažemės atmosferos sluoksnyje skaitinis modelis, kuris priklausomai nuo meteorologinių elementų ir krovos indikatoriaus, leidžia prognozuoti LOJ sklaidą naftos terminaluose ir už jų teritorijos ribų.
5. Remiantis LOJ koncentracijų tyrimais naftos terminaluose taršai mažinti pasiūlytas naujos konstrukcijos technologinis sprendimas – geležinkelio cisternų pakrovimo-iškrovimo dangtis.

Tyrimų metodika

Darbe panaudoti analitiniai bei matematinės statistikos analizės metodai. Taikyta Naftos produktų lakiųjų organinių junginių (LOJ) koncentracijos tyrimo metodika. LOJ sklaidos pažemės atmosferos sluoksnyje modeliavimui parinktas PHOENICS 3.5 programinės įrangos paketas, kurio pagrindas – diferencialinių lygčių sprendimo skaitiniais metodais.

Praktinė vertė

1. LOJ koncentracijos tyrimas skirtingais metų sezonais leido nustatyti meteorologinių elementų įtaką LOJ emisijai ir sklaidai pažemės atmosferos sluoksnyje.
2. LOJ koncentracijos tyrimų, meteorologinių elementų bei krovos indikatorius kompleksinis vertinimas leido sudaryti skaitinį LOJ sklaidos modelį, kurį panaudojus galima apskaičiuoti LOJ koncentracijas už naftos terminalų teritorijos neatliekant brangiai kainuojančių kontrolinių matavimų.
3. Atlikti konstrukciniai pakeitimai geležinkelio cisternos pakrovimo-iškrovimo sistemoje leis sumažinti LOJ išmetimus naftos terminaluose.

Ginamieji teiginiai

1. LOJ koncentracijos kitimai priklauso nuo oro temperatūros, vėjo greičio ir krovos indikatorius. Santykinė oro drėgmė ir atmosferos slėgis nežymiai įtakoja atmosferos taršą LOJ.
2. Didžiausia momentinė LOJ koncentracija naftos terminaluose yra geležinkelio estakadose.
3. LOJ sklaidos skaitinis modelis naudotinas prognozuojant DLK viršijimus, nustatant naftos terminalo krovos pajėgumo didinimo galimybę, parenkant naftos terminalų saugų atstumą nuo gyvenamųjų rajonų, diegiant ir racionaliai panaudojant LOJ neutralizavimo įrenginius (deginimo bei rekuperacines sistemas ir kt.).

Darbo apimtis

Darbą sudaro bendra darbo charakteristika, 7 skyriai, literatūros sąrašas ir publikacijų sąrašas. Bendra disertacijos apimtis – 130 puslapiai, 79 iliustracijos ir 31 lentelės.

Pirmajame (įvadiniam) skyriuje nagrinėjamas problemos aktualumas, formuluojamas darbo tikslas bei uždaviniai, aprašomas mokslinis darbo naujumas, pristatomi autorės pranešimai ir publikacijos, disertacijos struktūra.

Antrame skyriuje išnagrinėti pagrindiniai naftos terminalų elementai ir LOJ garavimas terminalo zonoje, prevencinės priemonės, leidžiančios sumažinti atmosferos teršimą, LOJ taršos objektuose. Skyriuje aptariama meteorologinių elementų (oro temperatūros, vėjo greičio ir krypties, santykinės oro drėgmės ir atmosferos slėgio) įtaką LOJ koncentracijos kitimui ir sklaidai pažemės atmosferos sluoksnyje. Pateiktos dujinių taršalų sklaidos pažemės atmosferos sluoksnyje modeliavimo programinės įrangos paketai.

Trečiajame skyriuje pateiktos metodikos: LOJ koncentracijos ore tyrimo; oro mėginių ėmimo stebėjimo postuose; krovos indikatorius skaičiavimo.

Ketvirtajame skyriuje pateikta naftos terminalo 2002–2005 metų LOJ koncentracijos ore monitoringo duomenų analizė. Taip pat pateikti atliktų LOJ koncentracijos tyrimų už naftos terminalų teritorijos ribų skirtingų metų sezonais bei naftos terminaluose rezultatai ir jų analizė.

Penktame skyriuje pateikta LOJ sklaidos pažemės atmosferos sluoksnyje skaitinio modeliavimo metodika, modeliavimo rezultatai bei modeliavimo rezultatų testavimas – palyginimas su eksperimentiniais rezultatais.

Šeštame skyriuje pasiūlytas technologinis sprendimo variantas, leidžiantis sumažinti naftos produktų garavimus geležinkelio estakados zonoje.

Septintame skyriuje pateiktas rezultatų apibendrinimas.

Bendrosios išvados ir rekomendacijos

1. Didžiausios LOJ koncentracijos buvo nustatytos žiemą ir vasarą atitinkamai – $3,12 \text{ mg/m}^3$ ir $1,98 \text{ mg/m}^3$:
 - padidinta LOJ koncentracija žiemą susijusi su degalų gamybos ypatumais, t. y. šaltuoju metų periodu degalai gaminami lokesni;
 - pagrindinė LOJ koncentracijos padidėjimo vasarą priežastis yra aukšta oro temperatūra (iki 25°C);
 - pavasarį ir rudenį LOJ koncentracijos skiriasi iki 10 %.
2. Pasiūlytas naujas rodiklis – krovos indikatorius įvertinantis krovos intensyvumą naftos terminaluose ir kraunamų produktų rūšį. Nustatyta LOJ koncentracijos kitimo priklausomybė nuo krovos indikatorius.
3. Nustatyta, kad didžiausios LOJ koncentracijos naftos terminaluose susidaro šiose technologinėse zonoje:
 - a) didžiausia LOJ koncentracija nustatyta naftos terminalų geležinkelio estakadų zonoje benzino A–92 iškrovimo metu – 3778 mg/m^3 . Ši

- koncentracija yra momentinė ir priklausomai nuo tuo metu vyraujančių meteorologinių elementų sumažėja iki 10–15 mg/m³.
- b) 5000 m³ tūrio talpyklų pripildymo mazutu metu LOJ koncentracija ties alsuokliu vidutiniškai siekė 514 mg/m³, o 20 000 m³ tūrio – 567 mg/m³. Tuo tarpu šviesiųjų naftos produktų pildymo į 10 000 m³ tūrio talpyklą metu LOJ koncentracija siekė net 1500 mg/m³.
 - c) 100 000 m³ tūrio tanklaivio pildymo mazutu metu LOJ koncentracija ties alsuokliu yra didesnė nei talpyklų pildymo metu ir siekė 1078,65 mg/m³. Tai paaiškinama tuo, kad talpyklose įrengti plūdrieji pontonai slopinantys naftos produktų garavimą ir produktų krovos į talpyklą operacijos laikas yra mažesnis lyginant su krova į tanklaivį.
4. Atlikus LOJ koncentracijos tyrimo skirtingais sezonais duomenų analizę ir daugiafaktorinę dispersinę analizę su 95 % patikimumu nustatyta, kad LOJ koncentracijos kitimas pažemės atmosferos sluoksnyje priklauso nuo vėjo greičio, kai jo stiprumas yra didesnis, nei 3 m/s ($P < 0,05$). LOJ koncentracija tik nežymiai priklauso nuo atmosferos slėgio bei santykinės oro drėgmės ($P > 0,05$).
 5. Sudarytas LOJ sklaidos skaitinis modelis leidžia prognozuoti LOJ koncentracijos kitimus gretimoje naftos terminalams teritorijoje esant skirtingiems meteorologiniams elementams ir krovos intensyvumui. Vidutinė aritmetinė modeliavimo paklaida lyginant su tyrimo rezultatais parinkus Prandtlio ($Pr_D = 0,71$) ir atmosferos nestabilumo ($A = 1,3$) koeficientus, sudaro $\pm 3,9$ %.
 6. Atlikus LOJ koncentracijos tyrimus naftos terminalo estakados zonoje pakraunant / iškraunant naftos produktus į geležinkelio cisternas ir jų rezultatų analizę, LOJ emisijai mažinti rekomenduojame įdiegti naujos konstrukcijos geležinkelio cisternos pakrovimo-iškrovimo dangtį.
 7. LOJ sklaidos skaitinį modelį siūlome taikyti prognozuojant DLK viršijimus, nustatant naftos terminalo krovos pajėgumo didinimo galimybę, parenkant naftos terminalų saugų atstumą iki gyvenamųjų rajonų, diegiant ir racionaliai naudojant LOJ emisiją mažinančias sistemas.

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**RESEARCH OF POLLUTION BY VOLATILE ORGANIC
COMPOUNDS IN AMBIENT AIR AND ITS REDUCTION IN OIL
TERMINALS**

Summary of Doctoral Dissertation

**Technological Sciences, Environmental Engineering and Landscape
Management (04T)**

Tatjana Paulauskienė

**ORO TARŠOS LAKIAISIAIS ORGANINIAIS JUNGINIAIS TYRIMAS
IR JOS MAŽINIMAS NAFTOS TERMINALUOSE**

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