VILNIUS GEDIMINAS TECHNICAL UNIVERSITY

FACULTY OF ENVIRONMENTAL ENGINEERING

DEPARTMENT OF ENVIRONMENTAL PROTECTION

Viktorija Krastinytė

AIR QUALITY ASSESSMENT IN THE VICINITY OF OIL REFINERY USING SNOW-CAP AS A TOOL

ORO KOKYBĖS VERTINIMAS NAUDOJANT SNIEGO DANGĄ NAFTOS PERDIRBIMO ĮMONĖS ĮTAKOS ZONOJE

Master’s degree Thesis

Environmental Management and Cleaner Production study programme, state code 621H17003
General Engineering study field

Vilnius, 2012

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Final master thesis

Environmental Management and Cleaner Production, 621H17003

Environmental Engineering

Head ____________________ __________ ________
(Scientific degree/ name, surname) (Signature) (Date)

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(Scientific degree / name, surname) (Signature) (Date)

Vilnius, 2012

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Master Degree Studies **Environmental Management and Clean Production study programme Final work**
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Annotation

In final master thesis air quality was analyzed and assessed in the vicinity of oil refinery using snow-cap as an indicator. Analysis of snowmelt water and snow-dust was used to determine concentrations of anthropogenic pollutants such as: sulphates, chlorides, nitrites, nitrates, ammonium nitrogen, total carbon, total nitrogen and heavy metals: lead (Pb), copper (Cu), chromium (Cr), cadmium (Cd). In this study analysis was conducted considering different distances and the wind direction within the impact zone of the oil refinery. The load of snow-dust was evaluated to determine the pollution level in the study area. For modeling were used ADMS 4 and AERO 2 models to simulate PM dispersion in the atmosphere from 6 point pollution sources (stacks). The results obtained during the simulation were compared with the results of experimental analysis. Structure: introduction, review of the literature, methodology, modeling of PM dispersion in the atmosphere using ADMS 4 and AERO 2 models, results and analysis, conclusions and suggestions, references. Thesis consists of: 80 p. texts without appendixes, 36 pictures, 9 tables, 77 bibliographical entries. Appendixes included.

Keywords: snow-cap, heavy metals, load of snow-dust, oil refinery, air pollution.

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Pavadinimas **Oro kokybės vertinimas naudojant sniego dangą naftos perdirbimo įmonės įtakos zonoje**

Kalba: anglų

Anotacija

Magistro baigiamajame darbe išanalizuota ir įvertinta naftos perdirbimo įmonės įtaka aplinkos oro kokybei, naudojant sniego dangą, kaip indikatorių. Atlikti sniego tirpsmo vandens ir sniego dulkių eksperimentiniai tyrimai, nustatant sulfatų, chloridų, nitritų, nitratų, amonio azoto, bendrosios anglies, bendrojo azoto ir sunkiųjų metalų (švino (Pb), vario (Cu), chromo (Cr) ir kadmio(Cd)) koncentracijas. Tyriamų elementų koncentracijos buvo analizuojamos atsižvelgiant į skirtingus atstumus nuo naftos perdirbimo įmonės įtakos zonos ir vyraujančių vėjų kryptį teritorijoje. Taip pat apskaičiuota sniego dulkių apkrova, pagal kurią nustatytas tirtos teritorijos užterštumo lygis. Atliktas kietųjų dalelių sklaidos atmosferoje modeliavimas iš 6 taršos šaltinių (kaminų), naudojant ADMS 4 ir AERO 2 modelius. Sniego dulkių apkrovos eksperimentinių tyrimų rezultatai buvo palyginti su matematinio modeliavimo gautais rezultatais.

Darbą sudaro: įvadas, literatūros apžvalga, eksperimentinių tyrimų metodikos aprašymas, eksperimentinių tyrimų rezultatai, kietųjų dalelių sklaidos atmosferoje modeliavimas naudojant ADMS 4 ir AERO 2 modelius, išvados ir siūlymai, informacijos šaltinių sąrašas. Darbo apimtis – 80 p. teksto be priedų, 36 iliustr., 9 lent., 77 bibliografiniai šaltiniai.

Atskirai pridedami darbo priedai.

Prasminiai žodžiai: sniego danga, sunkieji metalai, sniego dulkių apkrova, naftos perdirbimo įmonė, oro tarša.

(the document of Declaration of Authorship in the Final Degree Project)

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DECLARATION OF AUTHORSHIP IN THE FINAL DEGREE PROJECT

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I declare that my Final Degree Project entitled ____ ____ ____ is entirely my own work. The title was confirmed on _____________________ (Date) by Faculty Dean’s order No. _____________. I have clearly signalled the presence of quoted or paraphrased material and referenced all sources.

I have acknowledged appropriately any assistance I have received by the following professionals/advisers: ____ ____ ____

The academic supervisor of my Final Degree Project is ____ .

No contribution of any other person was obtained, nor did I buy my Final Degree Project.

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(Signature) (Given name, family name)

CONTENT

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

A – factor which depends from atmosphere temperature;

A_t – the absorption of nitrites;

A_s – the absorption of the sample;

A_b – the absorption of the blank sample;

A_n – daily load of snow-dust, mg/m^2;

ADMS – Atmospheric Dispersion Modeling System;

c – concentration by calibration graphic, mg/l;

C(x,y,z) – the concentration of the emission (in mg/m^3) at any point x meters downwind of the source, y meters laterally from the centerline of the plume, and z meters above ground level;

C_M – maximum ground-level concentration of pollutants under adverse meteorological conditions and dangerous wind speed, mg/m^3;

CMAQ – community multiscale air quality;

d – non-dimensional factor depending from the conditions and parameters of the emissions;

D – mass of the dust, g;

f – conversion factor, f = 35 453 mg/mol;

F – non-dimensional factor assessing speed of settlement of pollutants and depends from the efficiency of cleaning devices (for gaseous pollutants F – 1, for insoluble pollutants factor depends from the efficiency of the cleaning devices – F – 2 (>90%), F – 2,5 (75-90%); F – 3 (<75 %),

FAAS – flame atomic absorption spectrophotometer;

FCC – fluidized catalytic cracker;

GIS – Geographical Information System;

GFAAS – graphite furnace;

H – the height of the source above ground level, m;

HF – hydrogen fluoride;

HOCs – hydrophobic organic chemicals;

LMO – Monin-Obukhov length;

LPG – liquefied petroleum gas;

M – mass of the pollutants per time, g/s;

m_N – mass of nitrites, mg;

m and n – factors assessing the conditions of the emissions of pollutants;

NOHRSC – The National Operational Hydrologic Remote Sensing Center

PM – particular matter;

Q – the quantity or mass of the emissions, g/s;

r – non dimensional factor depending from the speed of the wind;

S – area of the territory of taken snow sample, m^2;

SA – surface area;

SD – standard deviation;

T – snowy period of time before sampling, number of days;

TN – total nitrogen;

TC – total carbon;

TOC – total organic carbon;

ΔT – temperature gradient between the temperature of the pollutants and ambient air, ^0C;

u – the wind speed (in meters per second);

V – capacity of taken sample, ml;

V_1 – air flow, m^3/s,

V_a – amount of sample, ml;

V_b – amount of silver nitrate, ml;

V_M – dangerous wind speed, m/s;

V_s – amount of silver nitrate which was used for titration of sample, ml;

X – concentration, mg/l;

X_M – distance from the pollution source, m;

X_n – concentration of element „n“ in the dust, mg/kg;

η – non-dimensional factor assessing influence of topography;

ρCl – concentration of chlorides, mg/l;

σy and σz – the standard deviations of a statistically normal plume in the lateral and vertical dimensions, respectively.

INTRODUCTION

Problem

Urban ambient air pollution is the result of emissions from multiple sources, mainly stationary, industrial, and domestic fossil fuel combustion, and petrol and diesel vehicle emissions (Spiric *et al*. 2012). Oil refining is one of the major sources of air pollution. Many detailed studies have been carried out in order to quantify oil refinery emissions.

Analysis of the local and global practice showed the growing interest in the theoretical and applied investigations of snow-cap (Kalyuzhnyi *et al*. 1998). Snow can be contaminated with various pollutants which are considerably more acid, have higher concentrations of trace elements and heavy metals. It is known that heavy metal pollution such as Pb, Ni and Cd is common in urban and industrial areas rather than rural areas due to the presence of industrial resources.

Snow is the natural cover during the winter season in southern Canada, northern and eastern JAV, central and northern part of Europe, Siberia and Far East which collects airborne pollutants: dust, soot and soluble particles (aerosols and gases). Snow–cap is an inert medium where pollutants do not migrate actively (Saet *et al.* 1990). Pollutants effectively accumulate in the snow, which acts as an aerodynamic mechanical barrier for particles that are suspended in the air. In comparison to soil, snow-cap functions only as mechanical barrier for airborne pollutants, while soil is not only a mechanical barrier but also the biogeochemical. Pollutants in the soil migrate horizontally and vertically (Planchon *et al.* 2002).

Concentrations of chemical element soluble forms in snow–cap in urban and industrial areas are many times lower in comparison with insoluble ones (snow-dust), therefore, a snowmelt water analysis is not always performed. However, there is a relationship between concentrations of soluble and insoluble particles. This relationship is characterized by inverse proportionality, for example, closer to pollution sources in urban and industrial areas the proportion of soluble forms of metals relatively decreases, while the load of dust increases when approaching the contaminated area (Planchon *et al.* 2002). Generally, a ratio in the snow–cap between soluble and insoluble forms depends on the type of pollution source, the distance from the pollution source and the load of snow-dust.

In general, deposit rate of gaseous air pollutants (sulphur and nitrogen oxides, volatile organic compounds and others) in the snow–cap is limited. In Western Siberia specific studies have shown that the deposit rate of these pollutants is only 0.015 to 0.020. It means that near pollution sources snow–cap collects just 1.5 to 2% of emissions (Planchon *et al.* 2002).

In this study both snowmelt water and snow-dust were analyzed to assess the impact from the oil refinery and its industrial support structures. The load of snow-dust and trace elements of snow–cap were carried out in the influence zone of emissions from the oil refinery. Analysis was conducted considering distances and the wind direction in respect of the oil refinery and its industrial support structures.

Actuality of the work

Studies of the snow–cap quality allow the calculation of pollutant load. Maps of the snow–cap dust load allow detecting the composition of the oil refinery area, also to collect information about air quality of the ground–level determining the pollution level. In this work was monitored the load of snow-dust and estimated concentrations of trace elements to assess ambient air quality in the vicinity of oil refinery using snow-cap as an indicator.

Aim of the work

The aim of the work was to assess the impact of the oil refinery for the ambient air quality using snow–cap as an indicator.

Objectives

1. To evaluate the load of snow-dust from the oil refinery and to estimate concentration of heavy metals (Cu, Cd, Pb, Cr).
2. To estimate concentrations of SO_4^{2-}, Cl^-, NH_4^+, NO_3^-, NO_2, total carbon (TC) and total nitrogen (TN) in snowmelt water.
3. To simulate dispersion of particular matter (PM) and to find dependence between PM in the air and snow–cap.

Object

The snow–cap pollution in the vicinity of JSC *Orlen Lietuva*.

Novelty of the work

In this study determination of heavy metals was done in two ways. Snowmelt water was filtered and analysis of heavy metals were done after digestion of snow-dust. While determination of heavy metals in snowmelt water without filtration were done by using acid (HCl). After results were compared.

Practical meaning of the work

Data from snow–cap analysis is used for assessment of air quality near oil refinery and possible consequences for human health and ecosystems using classification of pollution level according to the load of snow-dust.

Hypothesis

Impact of the oil refinery on the ambient air quality can be assessed using the snow-cap as an indicator.

1. AIR QUALITY NEAR OIL REFINERIES

1.1. IMPACT FOR ENVIRONMENT FROM OIL REFINERY

Oil refinery is an industrial process where crude oil, coal, or natural gases are converted into fuel (including petrol, diesel, paraffin, kerosene). There are various processes which include heating and chemical reactions. Oil refinery pollutes our air, water, and land (Oil refineries…2010).

- Air is polluted by up to 100 pollutants emitted from the stacks and leaking equipment at refinery;
- Land is polluted by the large amount of harmful waste from refinery which needs to be dumped;
- Water is polluted by the fallout from air pollution and by refinery discharging chemical pollutants into waterways. Accidental oil spills also pollute the groundwater and open waterways.

Oil refinery causes smog and air pollution. Oil refinery includes metals like lead. It also includes very small dust particles – PM_{10}, $PM_{2.5}$ and even smaller that gets deep into our lungs and harms our ability to breath. Finally, refinery emits many gases like sulphur dioxide (SO_2), nitrogen dioxide (NO_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), dioxins, hydrogen fluoride (HF), chlorine, benzene (C_6H_6) and others (Oil refineries…2010).

Table 1.1 summarizes the different kinds of wastes generated by oil refineries. All this figures depend on the process configuration so in the table is a general guide.

Table 1.1. Wastes generated by oil refinery (Petrochemical company…2009)

Pollution	**Approximate quantities**
Cooling systems	3.5 – 5 m^3 of wastewater generated per ton of crude
Polluted wastewater	BOD: 150 – 250 mg/l COD: 300 – 600 mg/l Oil: 100 – 300 mg/l (desalted water) Oil: 5000 mg/l in tank bottom Benzene: 1 – 100 mg/l Heavy metals: 0.1 – 100 mg/l

Table 1.1 continuation. Wastes generated by oil refinery (Petrochemical company…2009)

Solid waste and sludge	3 to 5 kg per ton of crude (80% should be considered as hazardous waste because of heavy metals and toxic organic presence)
VOC emissions	0.5 to 6 kg per ton of crude
Others emissions	BTX (benzene, toluene and xylene) 0.75 to 6 g Sulphur oxides 0.2 – 0.6 kg Nitrogen oxides 0.006 – 0.5 kg

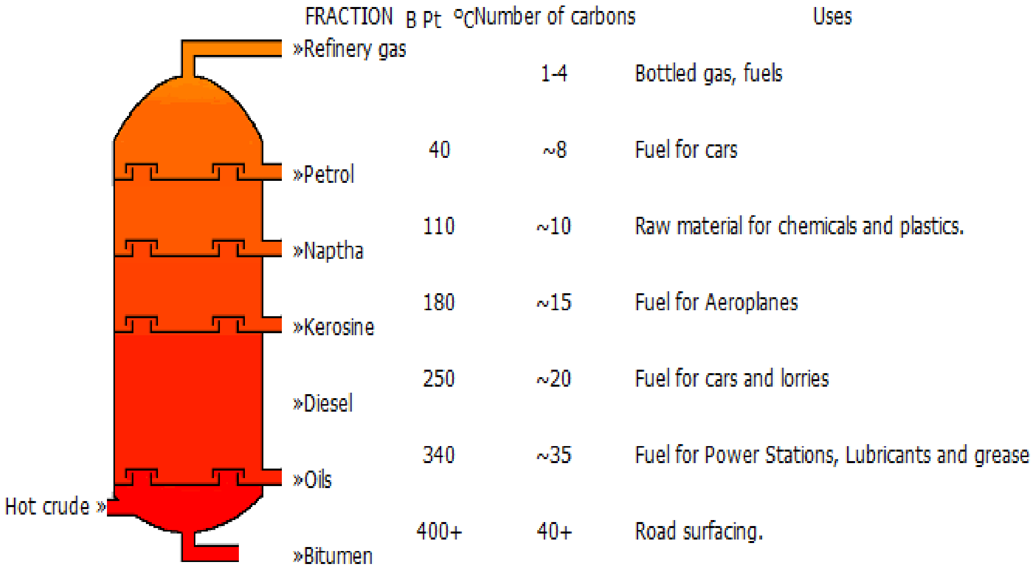
Crude oil and coal both contain relatively high quantities of sulphur. Natural gases contain much less sulphur and therefore are safer. When crude oil or coal is heated at the refinery to produce fuel, the sulphur is converted into a gas called sulphur dioxide. This is a colorless gas with a very strong smell, like rotten eggs. Some of the health effects from daily exposure to outdoor levels of SO_2 are tight chests, worsening of asthma and lung disease, and narrowing of air passages in the throat and chest. Exposure to SO_2 can provoke asthma attacks. SO_2 mixes easily in water, including moisture in the air to form an acid. Acid rain and early morning dew causes much damage to metals, stones, and the environment. Burning of coal in domestic coal stoves also causes SO_2 (Oil refineries…2010).

Many of the gases emitted by refinery are harmful to humans, and can cause permanent damage and even death. They can cause respiratory problems (such as asthma, coughing, chest pain, choking and bronchitis), skin irritations, nausea, eye problems, headaches, birth defects, leukemia, and cancers. There are many ways for a refinery to reduce the amount of pollution it causes. However, this usually requires the refinery to install equipment (Oil refineries…2010).

Oil refinery discharges a lot of different types of oil effluents with high concentration of organic and non–organic compounds with high toxic and persistent such as (sulphides, NO_x, SO_x, CO_x, NH_3, phenols, soot and dust, volatile-hydrocarbons and heavy metals like chromium, iron etc.), which make up a violent attack directly to an equilibrium system of quality, quantity and special properties of environment main components (air, water, soil) by different ways like evaporation, spreading, drifting, oxidation, sedimentation, natural dispersion – etc. affecting directly to O_2 concentration (Environmental impact…2010).

Refinery operations

An oil refinery breaks crude oil down into its various components, which then are selectively changed into new products. This process takes place inside a maze of pipes and vessels. The refinery is operated from a highly automated control room. All refineries perform four basic steps (Oil refineries…2010). The first operation is distillation. This method of physically separating a mixture of compounds was the earliest process used in petroleum refining, and today is still one of the most important. However, since it is not generally possible to separate the complex petroleum mixtures into individual compounds, such mixtures are segregated into fractions or "cuts", each of which is characterized by a carefully controlled boiling range. These cuts are then further processed or utilized in the refinery operations. The petroleum products obtained are light distillates, middle distillates, heavy distillates and residuum. The crude oil is distilled and separated into fractions as shown in the Figure 1.1.



FRACTION	B Pt °C	Number of carbons	Uses
»Refinery gas		1-4	Bottled gas, fuels
»Petrol	40	~8	Fuel for cars
»Naptha	110	~10	Raw material for chemicals and plastics.
»Kerosine	180	~15	Fuel for Aeroplanes
»Diesel	250	~20	Fuel for cars and lorries
»Oils	340	~35	Fuel for Power Stations, Lubricants and grease
»Bitumen	400+	40+	Road surfacing.

Fig. 1.1. Crude oil distillation and separation fractions (Oil refineries…2010)

The second basic type of process, essentially chemical in nature, consists of converting or chemically transforming certain of "cuts" into products of higher commercial value. There are many ways of doing this but all consists fundamentally of altering the molecular structure of components. In the case of the heavy oil, the molecules may be cracked to form lighter, more valuable products, as for instance in catalytic cracking and coking. On the other hand, gaseous products may be polymerized or otherwise combined to form liquid products which may be blended into gasoline. With certain processes, e.g. with the more desirable de-hydrogenation, hydrogenation and isomerization reactions (Figure 1.2). The next results of all these transformations is the productions of mixtures containing new arrays of hydrocarbons of higher value then the starting materials (Introduction to…2010).

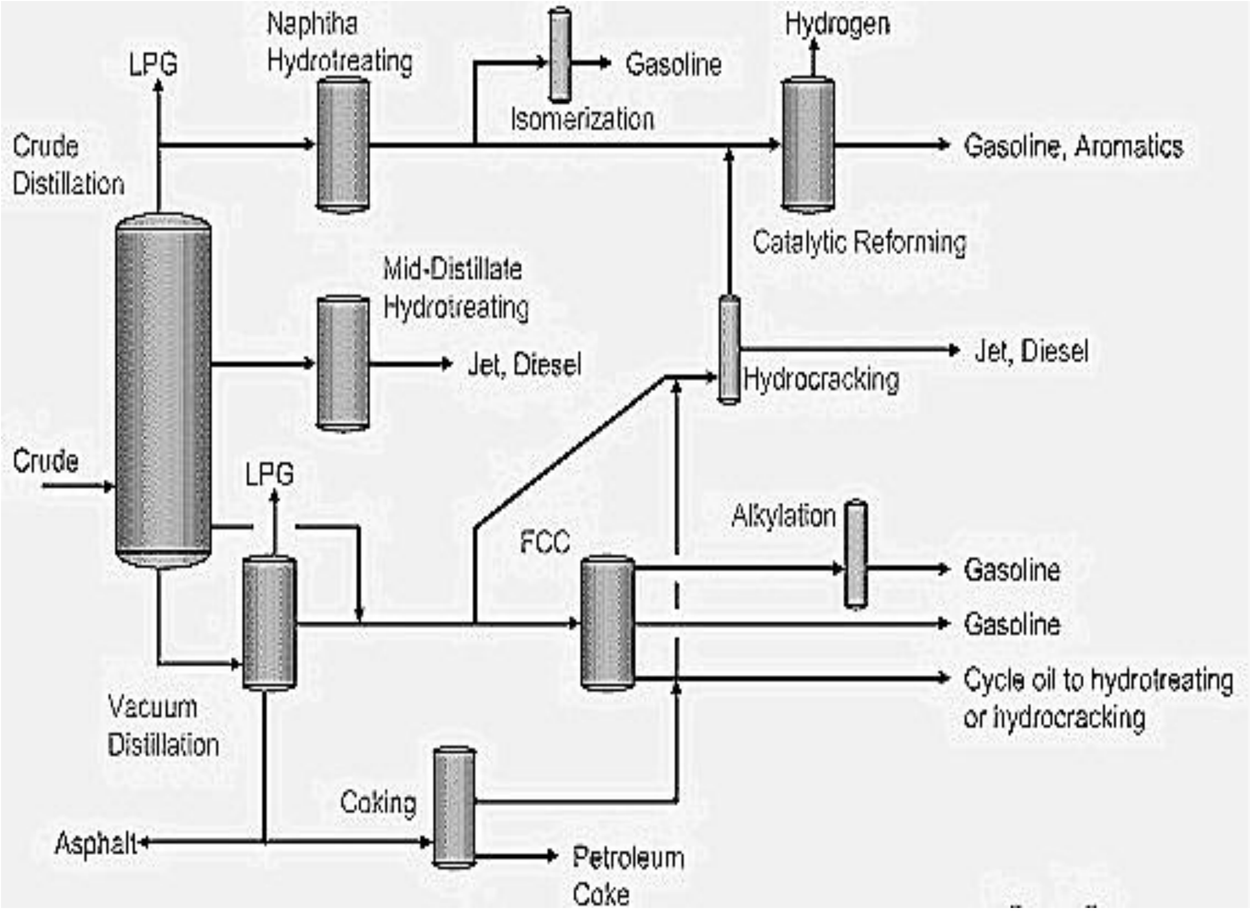


Fig. 1.2. Schematic oil refinery process (Oil refinery…2009)

FCC means fluidized catalytic cracker. LPG – liquefied petroleum gas.

Nearly all the fractions produced by the processes mentioned above contain certain objectionable constituents or impurities. The third basic category is therefore, treating. This group of processes includes the removal of the unwanted components, or their conversion to innocuous or less undesirable compounds. Removal of the impurities is sometimes accomplished by physical treating, as exemplified by the process for manufacturing kerosene, wherein sulphur and certain undesirable hydrocarbons are removed by extraction with liquid sulphur dioxide. Alternatively, the removal may be carried out by converting the unwanted compounds to a form more readily removed as is done in the hydrodesulphurization of diesel fuel. Here sulphur compounds are cracked and hydrogenated. The sulphur is converted to hydrogen sulfide which can be readily separated from the heavier diesel oil by fractionation. An example of the conversion of undesirable components to innocuous compounds which remain in the product is found in the gasoline sweetening processes. There the mercaptans present give the product a foul, objectionable odor. The sweetening process merely transforms the mercaptans to organic disulfides which are less objectionable (Introduction to…2010).

Although sulphur is perhaps the commonest and most troublesome of the impurities found in the petroleum, it is certainly not the only one. Substances such as nickel, vanadium and nitrogen may also be present in the crude oil. These impurities are undesirable because of the difficulty they cause during processing in the refinery or because of some detrimental effect during consumer use of the product. Furthermore, presence of certain hydrocarbons or certain types of hydrocarbons may lower the quality of a specific product. It was mentioned that aromatics are removed from kerosene by SO_2 extraction (Introduction to…2010).

The fourth basic category is blending of the finished cuts into commercially saleable products such as motor gasoline, kerosene, lubricating oils, and bunker fuel oil, according to their specifications. These four basic processes encompass the fundamental operation of a refinery. All other activities are carried out to implement them. The specifications for a given products are established to insure a satisfactory level of product performance. Specifications can be altered from time to time, but a product normally must meet then the existing product specifications (Figure 1.3). Various crudes in the other hand yield fractions with significantly different properties. At first glance, it might appear reasonable to select crudes to best match the product needs of each refinery. A refinery is a sophisticated multi-components process operated in overall balance (Introduction to…2010).

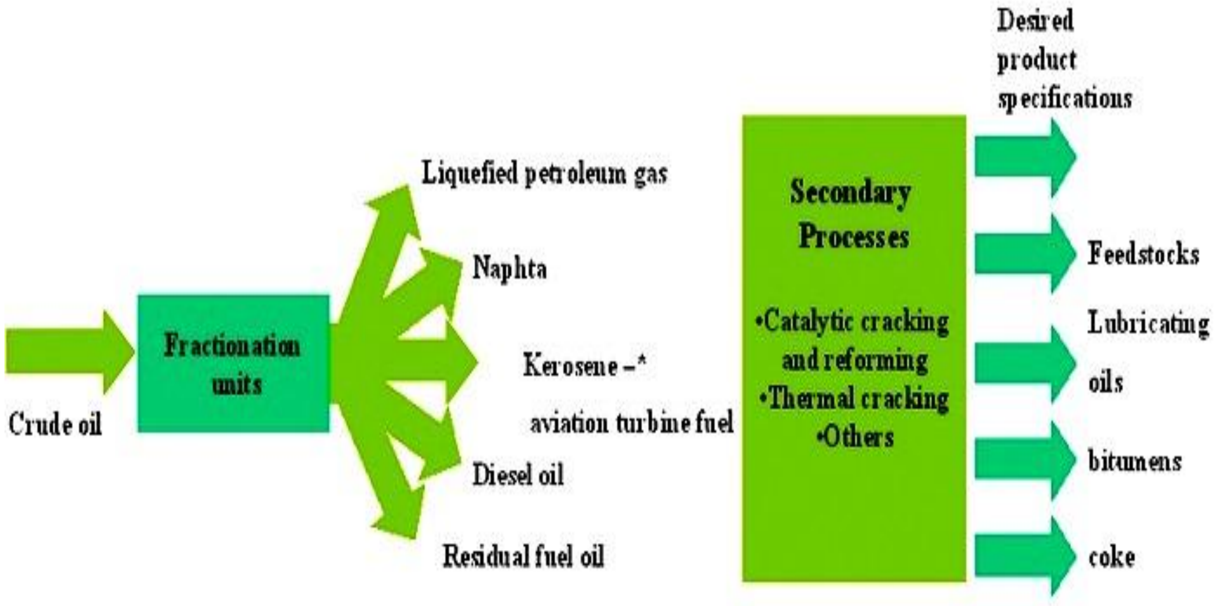


Fig. 1.3. Specification of oil products (Petrochemical company…2009)

Refineries can be categorized into four different types depending on their processes and complexity (Table 1.2)

Table 1.2. Classification of oil refinery (Concawe 2004)

Type I	Simple (non-conversion) refinery: composed of crude oil distillation; reforming; treatment of distillate products, including desulphurization and/or other quality improvement processes.
Type II	Type I plus catalytic cracking and/or thermal cracking and/or hydro cracking.
Type III	Type II plus steam cracking and/or lubricant production within the refinery fence.
Type IV	Refineries not in above categories, e. g those producing only bitumen, lubes, etc. which import their feed stocks from other sources.

Oil refinery uses relatively large volumes of water, especially for cooling systems. In fact, wastewater from the petrochemical industry usually contains hazardous chemicals, as hydrocarbons, phenol or ammoniac nitrogen among others (Petrochemical company…2009).

Public Company JSC *ORLEN Lietuva*

Public Company JSC *ORLEN Lietuva* is a II category group petroleum refining company operating as the only one petroleum refinery in the Baltic States as well as crude oil and petroleum product network and marine terminal. JSC *ORLEN Lietuva* is the most polluted company in Lithuania.

Fig 1.4. JSC *ORLEN Lietuva*

The company manages network of filling-stations of *VENTUS* and *ORLEN Lietuva* trademarks through its subsidiary AB Ventus – Nafta. Production and sales of petroleum products are the key areas of activity of the Company. Oil refinery processes approximately 10 million tons of crude oil a year. Public Company JSC *ORLEN Lietuva* is one of the most well-known companies whose impact on Lithuanian economy is considerable. It is the largest tax-payer in the state, the company having the biggest revenue in Lithuania and one of the largest exporters of the country. The Company is the most important supplier of petrol and diesel fuel in Lithuania, Latvia and Estonia. Company' products are also exported to Western Europe, USA, Ukraine, and other countries. Currently the Company caries out Modernization Program, objectives of which are performance efficiency increase and product quality improvement as well as occupational safety and preservation of the environment to the future generations (Company…2010).

Public Company JSC *ORLEN Lietuva* has negative impact for the environment (Figure 1.5), so company has to give exclusive attention to environmental issues.

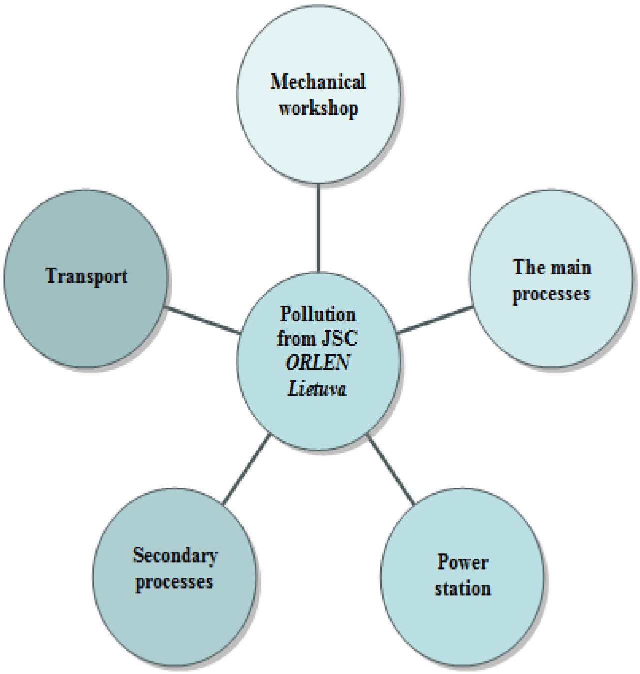


Fig. 1.5. Pollution sources from JSC *ORLEN Lietuva*

The company allocates lots of funds for implementation of environmental protection measures and closely cooperates with Lithuanian and international companies developing environmental programs. JSC *ORLEN Lietuva* has set the task to adhere to all environmental requirements. The company environmental situation is positively assessed by environmental audits carried out by worldwide recognized companies. With a view to ensure sound prevention and elimination of industrial accidents potentially hazard to environment JSC *ORLEN Lietuva* takes charge of technical measures developing, arranges regular drills for emergency response departments, uses civil liability insurance policy (Environmental…2010).

The company has been granted the international certificate ISO 14001:2004 for the environmental management system. The above certificate is testimonial of growing social responsibility of JSC *ORLEN Lietuva* involving environmental concern and preservation of the environment for future generations. JSC *ORLEN Lietuva* endeavors the technologies to meet the best industrial practice recommendations thereby reducing emissions to the environment.

Pollution prevention measures are applied in the company (Environmental…2010). Pollution prevention measures:

- Widespread air-cooled equipment (air coolers);
- Closed-type petroleum product drainage systems;

- High automation level and safe emergency shutdown system;
- Process units equipped with a closed-type system that serves for product routing from vessels and pipelines to the flare system via pressure safety valves in case of excess of the allowable pressure;
- Flare gas is accumulated to the gasholder and by means of compressors returned back to the refinery fuel network;
- End seals applied in crude and petroleum product pumps;
- Each light product storage tank is equipped with a fixed roof and internal floating pontoons with double seals. Storage tanks are coated to ensure light reflection coefficient above 70 %. These measures decrease air pollution more than 90 %. The requirements of Directive 94/63/EC are met;
- Railway tank car and tank truck loading with light products is arranged by means of closed hermetic method capturing volatile organic compound vapor and afterwards recovering and returning back to the process;
- Regular monitoring at industrial storm sewers. Control is to prevent petroleum product and other chemical material entering from the process units into sewage system. Some highly contaminated effluents (process condensate) are treated directly at the place of their formation in order not to contaminate all flow of effluents.

An advanced monitoring system is implemented in the refinery and by the municipality of Mažeikiai district also. The main monitored parameters are trace elements (Ag, Cd, Co, Cr, Cu, La, Mo, Ni, Pb, Sn, V ir Zn) (Table 1.3).

Environmental specialists control pollutant emissions both inside and outside the refinery by means of modern devices. In the recent year’s water and air pollution considerably decreased due to the technical and organization measures implemented (Environmental protection…2010).

Table 1.3. Frequency of observations in the monitoring (UAB „Ingeo“...2010)

Medium	Profile	Number of posts	Frequency of observations
Soil	Ag, Cd, Co, Cr, Cu, La, Mo, Ni, Pb, Sn, V Zn, mg/kg and pH;	30	1 time per year

Table 1.3 continuation. Frequency of observations in the monitoring (UAB „Ingeo“...2010)

Snow-cap (dust)	Ag, Cd, Co, Cr, Cu, La, Mo, Ni, Pb, Sn, V ir Zn, mg/kg, load – kg/km^2 onetime per year.	30	1 time per year
Surface water bottom sediment deposits	Ag, Cd, Co, Cr, Cu, La, Mo, Ni, Pb, Sn, V, Zn, mg/kg and pH;	20	1 time per year

Snow monitoring is done in 30 sites. 5 sites is made in the city of Mažeikiai, 7 sites – in small towns, 9 – in JSC *ORLEN Lietuva* influence zone and 9 – in the rest of the region's territory. Sites are selected in the same places like the soil monitoring (Table 1.4 and 1.5).

Table 1.4. Concentration (mg/kg) of heavy metals found in snow-dust

Location	**Ag**	**Cr**	**Cu**	**La**	**Ni**	**Pb**	**Sn**	**V**	**Zn**	**References**
The whole region of Mažeikiai (mean values)	1.3	98	34.8	104	264.6	76.6	8.4	714	365	(UAB „Ingeo“...2010)
Control areas in Mažeikiai region	0.066	39	7.7	20	13.1	14	2.1	39.2	28	(UAB „Ingeo“...2010)
The region of Mažeikiai	0.8	66	35	67	84	80	9.5	140	400	(Kadūnas *et al.* 2004)
Industrial area near the oil refinery	1.8	140	50	129	365	108	11.2	945	482	(Kadūnas *et al.* 2004)
Maximum permissive concentration according to HN 60:2004	2	100	100	-	75	100	10	150	300	(UAB „Ingeo“...2010)

Table 1.5. Concentration (mg/l) of heavy metals in snowmelt water

Location	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**V**	**References**
The whole region of Mažeikiai (median value)	0.08	3.72	5.38	2.52	2.73	2.29	(Kadūnas *et al.* 2004)
The whole region of Mažeikiai (maximum value)	0.42	19.2	26.6	7.42	9.47	35.7	(Kadūnas *et al.* 2004)

The minimum amounts of ammonium ion were determinated in the south and south-eastern parts of the Mažeikiai region. Nitrates (NO_3^-), as the ammonium ions were distributed unevenly (variation rate 46.6 %). Sulphate`s (SO_4^{2-}) amount (7.3 mg/l) in snowmelt water was 1.8 times higher than was established in 1999 (Kadūnas *et al.* 1999). Higher sulfates content of the spread range included north district of Mažeikiai. The biggest ammount of sulphates in this area was 22.9 mg/l. Chlorine (Cl^-) ions were distributed very evenly (variation rate 24.3 %). The average amount (3.64 mg/l) is 3.5 times lower then was established in 1999 (Kadūnas *et al.* 1999). Chlorine levels increased to 2 medians closer to human settlements in the area of snowmelt water (Kadūnas *et al.* 2004).

1.2. CHEMICAL ELEMENTS IN SNOW-CAP

Analysis of the domestic and world practice shows the growing interest in the theoretical and applied investigations of snow–cap (Kalyuzhnyi *et al.* 1998). The pollution of snow–cap reflects the degree of human impact on the environment, because snow–cap is able to retain and accumulate the substances depositing on its surface from the atmosphere. Information on the chemical composition of snow–cap allows deriving integral pollution estimates of various ecosystems over long periods, to differentiate the areas around towns and industrial regions according to the degree of technogenic impact. This is especially important under the conditions of northern landscapes, where snow–cap persists over 6–8 months. Thus, snow–cap may be considered the most suitable research object for assessing the environmental pollution by industrial aerosols (Meyer and Wania 2008). The data on the amounts of individual pollutants and their total amount accumulated in snow–cap in both the areas adjacent to industrial enterprises and the background areas allow one to assess the environmental impact of various enterprises (Vasilenko *et al*. 1985).

Pollutants effectively accumulate in the snow, which acts as an aerodynamic mechanical barrier for small particles that are suspended in the air. Soluble forms of snow–cap chemical elements in urban areas, in compare with insoluble ones (snow-dust), are many times lower, therefore, a snowmelt water analysis is not always necessary; however, there is a relation between soluble and insoluble forms. This relation is characterized by inverse proportionality, for example, closer to contamination sources in urban areas, the part of soluble forms of metals relatively decreases, while the load of dust increases when approaching the city or contaminated area (Lietuvninkas 2002).

Trace elements in snow

Snow and ice records have provided historical indications of changes in the occurrence of toxic trace elements in the atmosphere in response to anthropogenic emissions of such elements. The atmospheric pollution from the mid-1700s to present times has also been documented for various heavy metals, including Pb, Cd, Cu, and Zn (Murozumi *et al.* 1969; Boutron *et al.* 1991; Candelone *et al.* 1995), Hg, Pt, Pd and Rh (Lee *et al.* 2005). Snow and ice records have provided evidence that the natural cycles of trace elements such as Cr, Cu, Zn, Ag, Pb, Bi, and U have been greatly perturbed in the recent decades even in the remote Antarctic atmosphere. This is primarily due to the long-range transport of manmade pollutants from the surrounding source areas (Rosman *et al*. 1994; Wolff and Suttie, 1994; Wolff *et al.* 1999; Planchon *et al.* 2002, 2003; Vallelonga *et al.* 2002, Lee *et al.* 2005).

Data obtained from Greenland and Antarctic snow and ice have shown that environmental pollution by trace elements has become global, the spatial data on the occurrence of trace elements in temperate to low-latitude snow and ice are required to better characterize the extent of human impact on natural geochemical cycles of these elements. Recently, several studies have reported changes the occurrences of trace elements related to human activities in dated snow and ice from the Alps and high-altitude Bolivian ice cap (Van de Velde *et al.* 1999,).

The trace elements concentrations were measured in snow and ice samples at high-altitude sites in the eastern Tien Shan (Li *et al*. 2007) and on Mt. Muztagh Ata in the eastern Pamirs in northwest China (Li *et al.* 2006), and on Mt. Everest in the Himalayas (Kang *et al.*

2007; Duan *et al.* 2007). Such data provided aspects of changing occurrence of various trace elements in snow and ice from one area to another.

Trace metals captured in permanent snow can be used as tracers of air mass transport, revealing the history of local and global pollution. The trace elements show a distinct seasonality, i.e., higher concentrations during the non-monsoon season than those during the monsoon season (Liu *et al.* 2010). Snow samples indicate the seasonal differences in the concentrations for the measured elements. Glacio chemical studies of snow and ice in the central Himalayas have also revealed seasonal differences in major ions (e.g. Ca^{2+} and SO_4^{2-}) related to the influx of mineral dust between monsoon and non-monsoon seasons (Shrestha *et al.* 2000; Kang *et al.* 2004).

However, there is little documentation or understanding of the changes in snow (or ice) composition laterally over regional scales, or of the dominant controls on its chemical composition. Now that analytical instrumentation enabling analysis at ultra trace levels of chemical elements has become available, regional surveys of snow chemistry can be carried out to answer such questions. Chemistry studies of surface snow in Svalbard seem to confirm an environment charged with relatively high concentrations of pollutants. Ionic measurements in pits by Gorham (1958) found $[SO_4^{2-}]^{*1}$ concentrations of up 14.6 μEq l^{-1}, well above baseline excess sulphate values estimated at ~2 μEq l^{-1} (Simoes, 1990). Gjessing (1977) found that the anthropogenic pollutants in the snow–cap display marked seasonality and concluded that the three main man-made pollutants measured (i.e. NO_3^- , NH_3^+, and $[SO_4^{2-}]^*$) are all highly correlated, suggesting that each is derived from the same source region (Simoes and Zagorodnov 2000). Three main factors could cause changes in concentration at the deposition site (i.e. the original precipitation at the core sites): 1) Modifications in the path followed by air masses transporting impurities from source to receptor 2) The scavenging process 3) Changes in the strength of the source (Neftel *et al.* 1985).

Analysis of heavy metals present in the snow

The amount of concentrations of heavy metals from snowmelt water and snow-dust shows the contamination with heavy metals.

In general, toxic heavy metals such as Pb, Cd, Ni, Zn, Mn, Cu are not found in snow. Even trace amounts of these heavy metals indicate possible pollution. The essential characteristics of atmosphere pollution in an area of heavy snowfall were investigated in detail in Sivas city, Turkey. It was aimed at monitoring heavy metals in snow as an indicator of urban atmosphere pollution. Results showed that snow–cap can be used as a simple and effective indicator of urban and industrial atmosphere pollution (Elik *et al.* 2001).

Investigation of the occurrence of heavy metals in the successive dated snow and ice layers which have accumulated in central Greenland over time has allowed us to obtain valuable information on past and recent changes in the hemisphere scale cycles of these metals. Attention has been paid to short-time scales, i.e. intra-annual variations, although a good understanding of heavy metal variations on such short time scales has the potential to provide very valuable information. It should allows us to better resolve the changing patterns of troposphere transport of heavy metals from the various source over different periods of the year and this will assist in the interpretation of long time series data (Barbante *et al*. 2003).

Compared to storm water runoff, urban roadway snow exposed to traffic and winter maintenance practices has a much greater capacity to accumulate and retain heavy metals and other anthropogenic constituents. Heavy metals once released in the environment are not degraded and partition between the dissolved and particulate-bound fractions. Residence time, solid loadings, alkalinity, hardness, and pH influence partitioning. For residuals analyses, the specific surface area generally increased with decreasing particle size while the predominance of total surface area (SA) was associated with the medium to coarser size fractions. Heavy metal mass trends followed similar general trends to that of the surface areas. Characterization of accretion and partitioning of these metals is a necessary first step toward development of management and treatment strategies designed to address urban snow pollution (Glenn and Sansalone 2002). Amounts of metals in snow-cap can be determined in two ways (Figure 1.6).

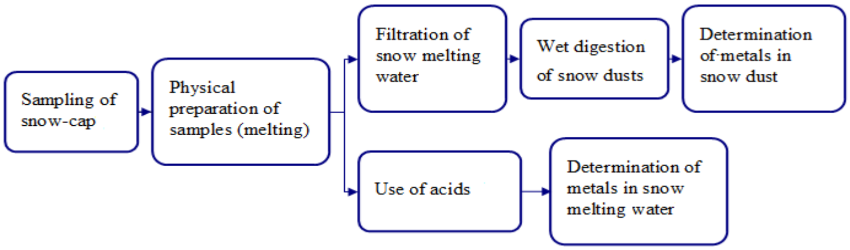


Fig. 1.6. Heavy metals determination in snow-cap

Snowmelt water can be filtered and analysis of heavy metals can be done after digestion. While determination of heavy metals in snowmelt water without filtration can strightly be done by using acids. The snow pollution with heavy metals decreases in snow-dust with increasing distance from the sources of emission (Zajac 1981).

Snow analysis, if it is possible to sample snow-cap of the winter period, enables us to distinguish the deposition of pollutants during a cold period. If the experimental data can provide a distinctive spatial concentration pattern close to the point pollution source then calculations can be performed to describe the washout of heavy metals from the atmosphere (Čeburnis *et al.* 2001).

Organic pollutants in snow trace elements

The release of organic pollutants from snowmelt water poses risks to aquatic and terrestrial organisms and to humans who rely on drinking water and food production from regions that are seasonally snow-covered. Measured and model-predicted spring peak concentrations in waters receiving snowmelt motivate a thorough investigation of organic pollution behavior during melting. On the basis of the current understanding of snow metamorphosis, snowmelt hydrology and chemical partitioning in snow provide a qualitative picture of the processes involved in the release of organic pollutants from a melting snow–cap. The elution sequence of organic substances during snowmelt is strongly dependent on their environmental partitioning properties and the physical properties of the snow–cap. Water-soluble organic pollutants can be discharged in greatly elevated concentrations at an early stage of melting, while the bulk of the hydrophobic chemicals attached to particles are often released at the end of the melt period. Melting of a highly metamorphosed and deep snow–cap promotes such shock load releases, whereas a shallow snow–cap over a relatively warm ground experiencing irregular melting over the winter season is unlikely to generate notable peak releases of organic substances. A more quantitative understanding of the behavior of organic pollutants in varying snowmelt scenarios will depend on controlled laboratory studies combined with field investigations. Reliable numerical process descriptions will need to be developed to integrate water quality and pollution fate models (Meyer and Wania 2008).

In contrast to inorganic snow chemistry, which has generated a wealth of information in the past several decades, the study of the fate of organic chemicals in association with snow and ice has been largely neglected. The limited understanding of the physics and chemistry of these systems, and difficulties in conducting field studies under reproducible and controllable conditions has retarded the development of quantitative models describing snow pollution interactions. In order to assess and evaluate the environmental fate and behavior of hydrophobic organic chemicals (HOCs) in cold ecosystems it is of particular importance to gain an extensive and, if possible, quantitative understanding of:

1. The efficiency and nature of snow scavenging of HOCs from the atmosphere;
2. The behavior of organic chemicals in snow–cap, especially as they age;
3. The release of organic chemicals from the snow–cap into the ecosystem during melting;
4. The potential preservation of a depositional record of organic chemicals in glacier ice (Wania *et al.* 1998).

Acidification

Snow acts as a reservoir for acids in wintertime by absorbing and storing atmospheric pollutants. Falling snow collects pollutants in the atmosphere and snow also accumulates pollutants on the ground from the dry deposition of gases, aerosols, and atmospheric particles. Normally, snow protects vegetation from the harmful effects of dry deposition for several months. The solubility of sulphur dioxide in snow is highest just before the snow melts because the amount of water in the snow is at its highest. "Black snow" is colored by carbon rich particles and it has higher concentrations of acids than the other snow. The pH of black snow can be nearly as low as vinegar – about pH 3.0. Black snowfalls have been observed on Cairngorm Mountain in the Scottish Highlands where pollutants from Eastern Europe accumulate. When black snow forms just above the base of the snow drift, it can deliver especially high solute concentrations to the soil below (Spring acid…2011).

A deep blanket of snow contains many layers from different snow falls with different levels of pollutants. Concentrated bands of impurities are formed as the snow melts and refreezes. Since wind and other forces redistribute and mix the layers in a snow drift, measuring the total amount of chemical in the snow drift is difficult. Undisturbed polar snow is an accurate record of the past atmospheric conditions. Sampling of snow cores in the Greenland ice sheet have revealed an increase in the amount of acids deposited, especially in the last forty years.

When snow begins to melt in the spring there is a concentrated surge of ions. Sulphate ions and nitrate ions liquefy first; hydrogen ions and chloride ions follow just after. Most precipitation stays in the snow pack until the snow reaches the melting point. This concentrated surge of ions is known as acid shock. Acid shock can cause the sudden death of many fish simultaneously. After a spring thaw the pH of lake and stream water plummets and the concentration of aluminum in the water rises. Fish are very sensitive to aluminium, as it blocks their gills and hinders their breathing. Although such fish kills are rare in North America and in Britain, animals are still weakened by the sudden high acidity of the water (Spring acid…2011).

At the end of the northern winter 1996-1997 21 snow samples were collected from 17 arctic localities in Norway, Sweden, Finland, Svalbard, Russia, Alaska, Canada, Greenland and Iceland. The snow was moderately acidic with pH values between 4.6 and 6.1. The most acid samples ($pH < 5.11$, the 25th percentile) were from the sector of northern Europe between Sweden and Nova Zemblya. Samples from more remote areas or higher latitudes tend to have a higher pH. Snow composition varies regionally by up to four orders of magnitude in terms of major element concentrations. Therefore, while attempting to reconstruct past changes in snow (or ice) composition, it is important to consider that at least part of the reported variability can depend on geographic location and weather pattern changes (influence of sea spray, etc.) from winter to winter or within any season's accumulated snow–cap. Mineral dust inputs were detected by 'excess' Ca contents relative to seawater dilution trends, as observed in Alaska, Svalbard, Greenland and Sweden. There was no overall correlation between melt water pH and total SO_4^{2-} concentration, although some samples defined a trend of decreasing pH with increasing non-sea salt SO_4^{2-}. A weak local relationship existed between pH and NO_3^- in Sweden, Finland and Russia. No arctic-wide contamination or acidification process was detected, suggesting that long-range atmospheric transport is not operating at this scale (Caritat *et al.* 2004).

Analysis in the vicinity of JSC *Orlen Lietuva* on 2004 years showed that ammonium ions (NH_4^+) was distributed unevenly in the district acidic – neutral snowmelt water. The snowmelt water most enriched with ammonium ions in the northern part of the Mažeikiai district. Here with ammonium ions the most enriched weakly acidic ($pH=6.74$) snowmelt water which was accumulated closer *JSC Orlen Lietuva.* Ammonium ions were distributed like mosaic in the snowmelt water.

1.3. AIR QUALITY MODELS

Air quality model provides descriptions and documentation for three types of air quality models: dispersion – these models are typically used in the permitting process to estimate the concentration of pollutants at specified ground-level receptors surrounding an emissions source, photochemical modeling – these models are typically used in regulatory or policy assessments to simulate the impacts from all sources by estimating pollutant concentrations and deposition of both inert and chemically reactive pollutants over large spatial scales and receptor models – these models are observational techniques which use the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations. Also provided with the dispersion modeling section are source code and associated user's guides and documentation for preferred/recommended models, screening models, and alternative models (Technology transfer…2010).

Air quality models use mathematical and numerical techniques to simulate the physical and chemical processes that affect air pollutants as they disperse and react in the atmosphere. Air pollution is represented by an idealized plume coming from the top of a stack of some height and diameter. One of the primary calculations is the effective stack height. Once the plume has reached its effective stack height, dispersion will begin in three dimensions. Dispersion in the downwind direction is a function of the mean wind speed blowing across the plume. Dispersion in the cross-wind direction and in the vertical direction will be governed by the Gaussian plume equations of lateral dispersion. Lateral dispersion depends on a value known as the atmospheric condition, which is a measure of the relative stability of the surrounding air. The model assumes that dispersion in these two dimensions will take the form of a normal Gaussian curve, with the maximum concentration in the center of the plume. The "standard" algorithm used in plume studies is the Gaussian plume model, developed in 1932 by O.G. Sutton. The algorithm is calculated using equation (1.1):

$$C(x,y,z)=\frac{Q}{2*\pi*u*\sigma y*\sigma z}*\exp\frac{-y^2}{2*\sigma y^2})*(\exp(\frac{-(z-h)^2}{2*\sigma z^2})+\exp(\frac{-(z+h)^2}{2*\sigma z^2})) \qquad (1.1)$$

where *C*(x,y,z) – the concentration of the emission (in mg/m^3) at any point x meters downwind of the source, y meters laterally from the centerline of the plume, and z meters above ground level; *Q* – the quantity or mass of the emission (in grams) per unit of time (seconds); *u* – the wind speed (in meters per second); *H* – the height of the source above ground level (in meters); *σy* and *σz* – the standard deviations of a statistically normal plume in the lateral and vertical dimensions, respectively.

This algorithm has been shown in a number of studies to be fairly predictive of emission dispersion in a variety of conditions (Gaussian plume…1996). Based on inputs of meteorological data and source information like emission rates and stack height, these models are designed to characterize primary pollutants that are emitted directly into the atmosphere and, in some cases, secondary pollutants that are formed as a result of complex chemical reactions within the atmosphere. These models are important to our air quality management system because they are widely used by agencies tasked with controlling air pollution to both identify source contributions to air quality problems and assist in the design of effective strategies to reduce harmful air pollutants. For example, air quality models can be used during the permitting process to verify that a new source will not exceed ambient air quality standards or, if necessary, determine appropriate additional control requirements. In addition, air quality models can also be used to predict future pollutant concentrations from multiple sources after the implementation of a new regulatory program, in order to estimate the effectiveness of the program in reducing harmful exposures to humans and the environment (Air quality…2010).

Snow models

There is only small part of snow models. The first and most widely used is that of Dunkle and Bevans (1956). Snowmelt modeling has traditionally been governed by the operational need for runoff forecasts. Parsimony in terms of model complexity and data requirements was a major concern (Kirnbauer *et al.* 1993). In 1976, Eric Anderson compiled a detailed history of numerical modeling of snow–cap. In the 1940s, the U. S. Army Corps of Engineers and the U. S. Weather Bureau initiated the Cooperative Snow Investigations U. S. Army Corps of Engineers 1955. The purposes of these investigations were to promote a fundamental understanding of snow hydrology. Kuzmin`s summary of these studies (Kuzmin 1961) presented a thorough and complete discussion of snow–cap energy exchange over a melting snow–cap, from both a theoretical and practical viewpoint (Armstrong and Brun 2008). In the 1960s with the development of digital computers, researchers were able to construct conceptual simulation models of the snow accumulation and ablation. Conductivity of the snow varied with snow density. The snow surface temperature was determined by various iterative that sought to reduce to an acceptable level the difference between the value of the charge in the heat storage term in the energy balance equation and the value of the same term as determined from changes in snow–cap temperature. None of models included the densification of the snow–cap. Humphrey and Skau used periodic measurements of the density profile to account for changes in snow density. Obled made comparison between computed and observed values of snow–cap outflow and water equivalent (Armstrong and Brun 2008).

Measurements methods had changed over time due to advances in instrumentation and additional types of data were collected to provide more and better information for testing snow–cap energy exchange model. In addition to providing better data for model testing, research enhanced the understanding of the energy transfer process and the numerical techniques needed to solve the basic snow–cap energy exchange equations. Clearly, a new, more theoretically sound, all more complete snow–cap energy balance model needed to be developed. The result was Andreson`s point energy and mass balance model (Anderson 1976). This model was based on surface energy balance equations and equations for energy transfer within the snow–cap. The snow–cap was divided into finite layers and the model included the mathematical representations of densification of the snow layers and the retention and transmission of liquid water (Armstrong and Brun 2008).

During the late 1980s, with the increased knowledge of snow process and meteorology, the availability of snow and weather data sets, and the general use of faster computers, more sophisticated snow models were developed and used in a research or operational context in the fields of hydrology, avalanche forecasting, and climate analysis. A major conceptual breakthrough came from snow metamorphism studies, in which researchers simulated layering, a fundamental characteristic of the snow–cap (Brun *et al.* 1992). The challenge remains to determine how sophisticated snow models need to be for their intended scope of use. For that purpose, International Commission on Snow and Ice initiated a project called SNOWMIP, which compared the results from recent snow models when used on different climate conditions (Essery and Yang 2001).

The presence of snow on the earth`s surface affects physical, chemical, and biological processes over a wide range of spatial scale and has important societal effects. In addition, the timing of snowmelt and the subsequent fate of melt water play an important role in the hydrological cycle and water resources (Gray and Prowse 1993). To accommodate various applications, large numbers of snow models have been designed over the past few decades.

Consequently, an active line of research is being established that links physically based snowmelt models, geographical information system analysis, remote sensing technology, and assimilated data sets from mesoscale meteorological models in studies of small catchments and watersheds (Liston and Sturm 1998). However, relatively speaking, what is the most lacking are the research and the application of snow water and energy budget analyses at continental and global scales. A question that remains unresolved is the level of complexity required for snow models at those scales. A closely related question is how to relate a one-dimensional, vertical snow–cap model to heterogeneous surfaces in each of the land grids. The preliminary analysis from a recent survey of snow models indicates that there are many sophisticates snow models currently available which are appropriate at the point or local scale, and that a wide range of model have been developed for application in small catchments and watersheds (Armstrong and Brun 2008).

The NOHRSC Snow Model (NSM)

The National Operational Hydrologic Remote Sensing Center (NOHRSC) Snow Model (NSM) is an energy and mass balance model used by the National Oceanic and Atmospheric Administration’s National Weather Service for moderate-resolution spatially distributed snow analysis and data assimilation over the United States. To help capitalize on these potential benefits the NOHRSC site in Minneapolis, Minnesota uses advanced snow data collection and modeling technology to generate daily and hourly gridded NSAs at high spatial resolution (1 km^2) for the country. The NSA products and data sets use ground based, airborne, and satellite snow observations coupled with numerical weather prediction model forcing to drive an energy and mass balance snow model. In this way, all available snow information is used to generate the “best estimate” of snow–cap characteristics across the country. The NOHRSC NSA products and data sets are used by the NWS, other government agencies, the private sector, and the public to support operational and research hydrology programs across the nation. The NSA products and data sets include estimates of: snow water equivalent, snow depth, snow–cap temperatures, snow sublimation, snow evaporation, estimates of blowing snow, modeled and observed snow information, airborne snow data, satellite snow cover, historic snow data, and time-series for selected modeled snow products (Snow modeling...2010).

Because snow water equivalent observations are not sufficient in time or space across the coterminous United States to infer reasonably the distribution of snow water equivalent, it is helpful to model the snow–cap using available numerical weather prediction (NWP) model output data sets as input to a fully distributed, energy-and-mass-balance snow model (Cline, 1997). Consequently, the NOHRSC developed the NOHRSC snow model (NSM) to simulate, in near real-time, snow water equivalent and other snow–cap properties, for the coterminous United States. The NSM consists, essentially, of three components: 1) data ingest, quality control, and downscaling procedures, 2) a snow accumulation and ablation model, and 3) snow model data assimilation and updating procedures. Hydro meteorological observations and NWP output are used to force the NSM, run at 1 km^2 resolution, for the country. Furthermore, after the model is initialized, periodic (or sometimes daily) observations of snow water equivalent, snow depth, and areal extent of snow cover are assimilated into the modeled snow states at the appropriate time step (Snow modeling...2010). The NOHRSC snow model uses hourly (NWP) model output products and static data sets as input. The model includes an energy-and-mass-balance snow model, a blowing snow model, and a radioactive transfer model. Unadulterated model output (i.e, snow water equivalent and snow depth) are compared to available snow observations, differences are calculated, the model is reinitialized to include information from snow observations, and final products are generated (Figure 1.9).

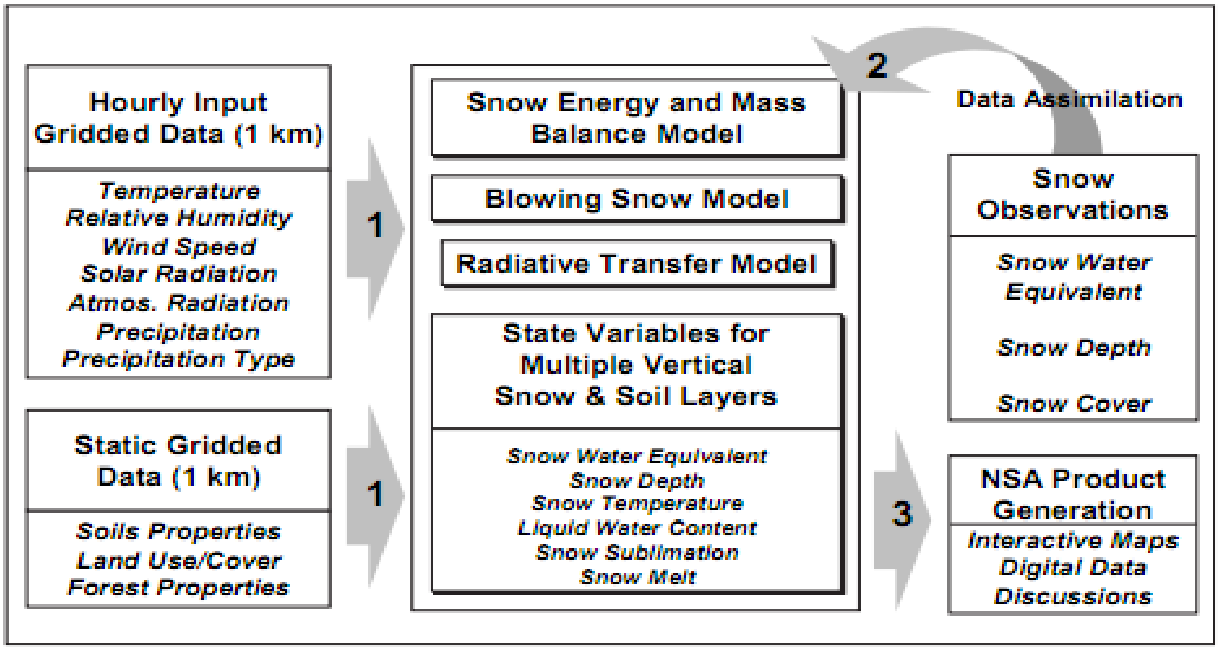


Fig 1.7. The NOHRSC snow model (Snow modeling...2010).

The NSM is an energy-and-mass-balance, spatially-uncoupled, vertically-distributed, multi-layer snow model. The NSM incorporates the mathematical approach of Tarboton and Luce (1996) to address the snow surface temperature solution and Jordan (1990) to address the snow thermal dynamics for energy and mass fluxes as represented in SNTHERM.89 (a one dimensional mass and energy balance model of snow and frozen soil). It accounts for the net mass transport from the snow surface to the atmosphere by sublimation of the saltation transported and suspension-transported snow as developed by Pomeroy et al. (1993). The NSM is forced by hourly, 1 km^2, gridded, meteorological input data downscaled from mesoscale NWP

Rapid Update Cycle (RUC2) model analyses with the three major-layer state variables of water content, internal energy, and thickness. It generates total snow water equivalent, snow–cap thickness, and energy content of the pack along with a number of energy and mass fluxes at the snow surface and between the snow and soil layers. Development of the NSM was motivated by the need for moderate spatial resolution (~1 km) commensurate with operational, optical, remote sensing data sets used to update the model. Additionally, high temporal resolution (hourly) is required to provide adequate representation of the physical processes in shallow snow–cap. The current multi-layer snow model is moderately comprehensive with a strong physical basis. It requires only a few input state variables, is parsimonious and efficient in computation, and is appropriate for representing most prevailing snow–cap conditions (Snow modeling...2010).

REVIEW OF CHAPTER 1

1. The analysis of literature related with oil refineries and their influence for pollution of air, water and land. The main processes, amount of pollutants and information about JSC *ORLEN Lietuva* environmental situation and environmental protection programs are also reviewed.

2. There were given information about theoretical and applied investigations of snow cover in recent years and was determined that snow–cap may be considered as the most suitable research object for assessing the environmental pollution by industrial aerosols. The pollution of snow–cap reflects the degree of human impact on the environment, because snow–cap is able to retain and accumulate the substances depositing on its surface from the atmosphere. Information on the chemical composition of snow–cap allows one to derive integral pollution estimates of various ecosystems over long periods, to differentiate the areas around towns and industrial regions according to the degree of technogenic impact.

3. Snow and ice records have provided historical indications of changes in the occurrence of toxic trace elements in the atmosphere in response to anthropogenic emissions of such elements. Trace metals captured in permanent snow can be used as tracers of air mass transport, revealing the history of local and global pollution. The trace elements show a distinct seasonality (Liu *et al.* 2010). The atmospheric pollution from the mid-1700s to present times has also been documented for various heavy metals, including Pb, Cd, Cu, and Zn (Murozumi *et al.* 1969; Boutron *et al.* 1991; Candelone *et al.* 1995), Hg, Pt, Pd and Rh (Lee *et al.* 2005). Now that analytical instrumentation enabling analysis at ultra trace levels of chemical elements has become available, regional surveys of snow chemistry can be carried out to answer such questions.

4. It is also discussed about organic pollutants which pose risks to aquatic and terrestrial organisms and to humans who rely on drinking water and food production from regions that are snow-covered. Organic pollutants from industrial enterprises form technologically polluted areas of different size (Fismes *et al*. 2002). The diffusion of atmospheric pollutants facilitates the distribution of polycyclic aromatic hydrocarbons over considerable distances (up to 10 km) from the plants.

5. The air quality models are also reviewed. It is discussed about the history and origin of snow models too.

2. METHODS OF SNOWMELT WATER AND SNOW-DUST ANALYSIS

2.1 SITE DESCRIPTION

Snow–cap samples were taken around the vicinity of the oil refinery near the town of Mažeikiai, in a North-Western region of Lithuania (56°23′15″N 22°10′34″E). There are 13 enterprises located in the Mažeikiai region which is characterized by higher PM pollution in the Mažeikiai area. Oil refining constitutes about 92 % of the total PM emissions in the region. In the vicinity of the oil refinery there are no other pollution sources. Effects from other sources are presumed to statistically insignificant. Snow–cap samples were taken at the distance of 100 m from any roads. To identify the impact of oil refinery for ambient air quality, sampling sites were grouped into four zones according the prevailing wind direction (Fig. 2.1). These zones were organized at a distance of 0.2 to 3 km from the JSC *ORLEN Lietuva* sanitary protection zone. The snow–cap was sampled at 11 sites. 4 sites to the north-west direction (Zone 1), 2 sites – to the north-east direction (Zone 2), 2 sites – to the south-west (Zone 3) and 3 sites were chosen to the south-east (Zone 4). Analysis of soluble and insoluble forms of heavy metals was done according on distances: 0.5 km, 1.5 km and 2 km around the oil refinery.

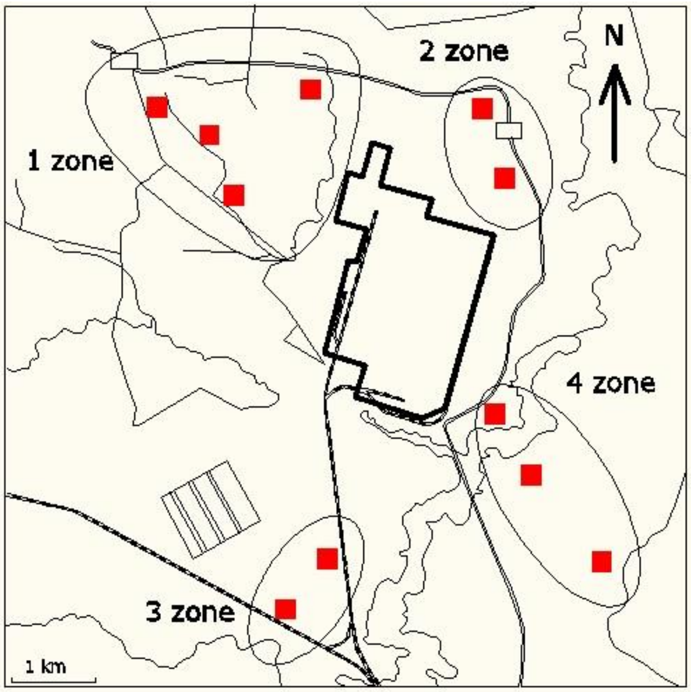


Fig. 2.1. Sites of samples in the vicinity of JSC *ORLEN Lietuva*

The background areas were chosen with account for the experimental data on the qualitative and quantitative composition of snow–cap, and parameters were stable and independent of emissions from JSC *Orlen Lietuva.*

The prevailing wind direction during the winter season was observed as being south-easterly and north-westerly during 2006-2010 periods (Figure 2.2).

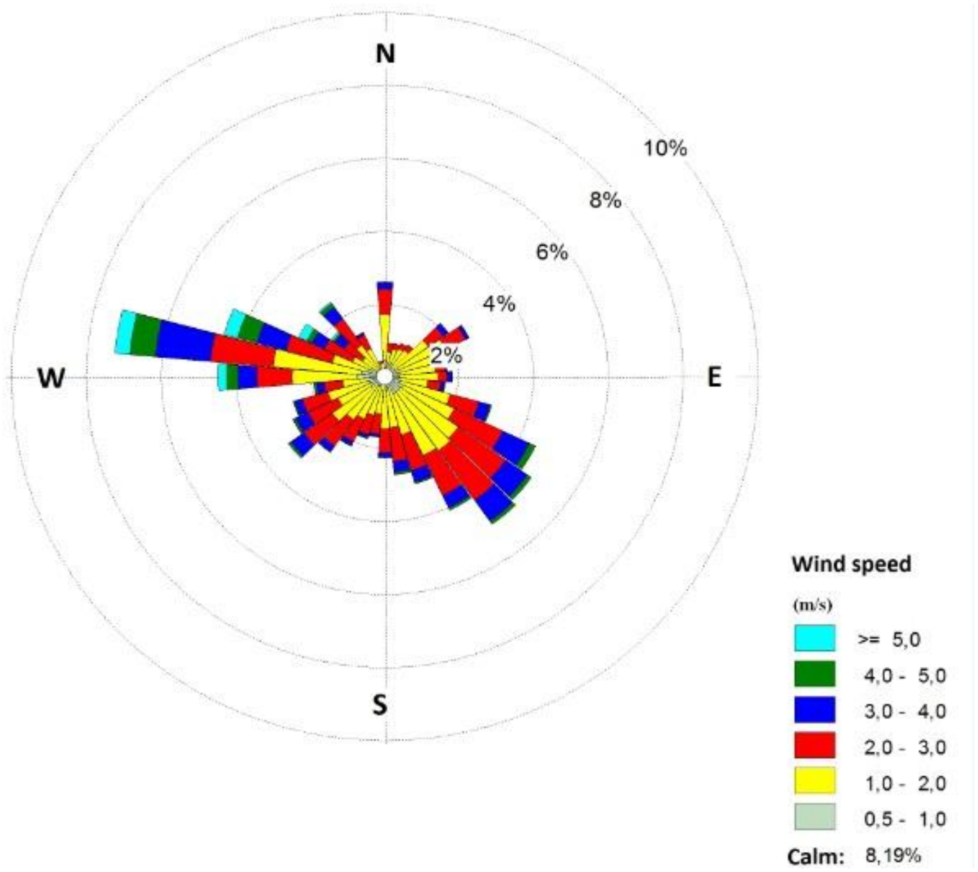


Fig. 2.2. Wind direction during 2006-2010 winter periods

More samples were taken in the prevailing wind direction trying to assess influence of wind direction for the concentration of pollutants.

2.2 SNOW – CAP SAMPLING

Snow–cap samples were taken of undisturbed snow–cap in the middle of February, 2011. The temperature was – -3 ^{0}C, without snow. Snow cover was 19 days continuously. Each composite sample consists of 14 to 28 sub samples taken by snow sampling tool (Figure 2.3).

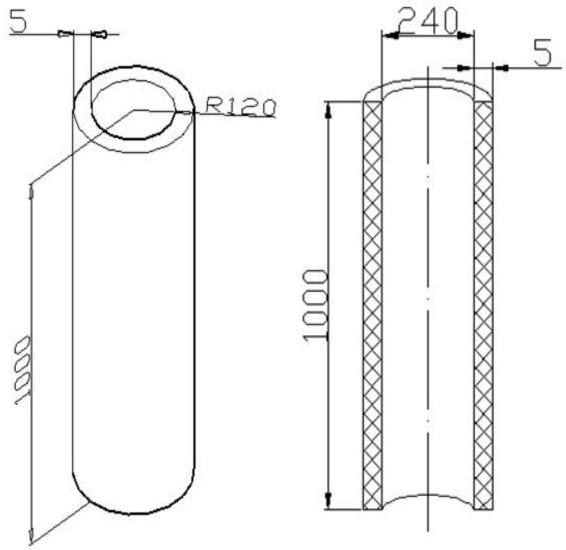


Fig. 2.3. Snow sampling tool

The sampling tool was developed at the Department of Environmental Protection of Vilnius Gediminas Technical University. The dimensions of tool were 1 m of length, with an internal diameter of 12 cm and external diameter of 5 mm.

The samples were taken through the entire layer of the snow–cap and a mass of the samples was about 10–20 kg of each.

2.3 PHYSICAL PREPARATION OF SAMPLES

Later all residues, leaves, debris, soil particles were removed and then the samples were immediately transferred into plastic bags. Before transference it is necessary to determine whether the plastic bag is not leaky, clean and suitable for snow transportation. It is necessary to ensure sufficiently low temperature and possibly resulting melt water conservation during snow samples transportation and keeping in a warehouse.

Extreme care was taken at all the time during sample collection, handling, transport, and analysis to assure sample integrity. All equipment used for the sampling was clean. The samples were melted at room temperature, in clean plastic buckets. Then was determined the pH values of snowmelt water.

The total volume of melting water was calculated by weighing each sample as received and correcting for the weight of the empty sample bag. The samples were filtered. Buckets, which took place during the snowmelt thoroughly, was washed with the filtrate of the sample and water was returned to the filter back. Filters with the aerosol particles were dried in a clean room, on the fresh sheets of paper. Dried filters were folded and placed inside the special packages. The samples volume of filtrate were poured into plastic bottles and quickly transferred to the laboratory.

2.4 CHEMICAL ANALYSIS OF SNOWMELT WATER

Snowmelt water was filtered through a glass fibre borosilicate non-ash filter for analysis. To determine the sulphate concentration in snow–cap, a 5 ml complex reagent and Hydrochloric acid (HCl) was added to the sample water. The light absorption intensity at λ=400 nm in 2 cm cells was measured after 40 minutes. To determine the light absorption intensity photocolorimetric KFK-2MP with violet light filter was used.

Concentration of sulpfate`s was recalculated using equation (2.1):

$$X = \frac{c \cdot 5}{V} \tag{2.1}$$

where X – sulphate concentration, mg/l, c – sulfate concentration by calibration graphic, mg/l; V – capacity of taken sample, ml.

For light absorption intensity determination was used photo colorimetric with violet light filter (Figure 2.4).

Fig. 2.4. Photocolorimetric *KFK-2MP* (google.lt)

Ammonium nitrogen (NH_4^{-2}-N) concentration was determined by pouring into the glass 1 ml of Segnet`s salt and 1 ml of Nesler`s reagent. After 10 minutes absorption intensity was measured with photocolorimetric in 1 cm length cells. The resultant absorption intensity was subtracted from the absorption intensity of the sample which was analyzed. Result was calculated using equation (2.2):

$$X = \frac{C \cdot 50}{V} \tag{2.2}$$

where X – ammonium concentration, mg/l, C – ammonium ion concentration mg NH_4^+ N/l by calibration graphic; V – capacity of the sample, ml.

For determination of chlorides (Cl^-) Mor`s method was used. 100 ml of sampled water was mixed with 1 ml of potassium chromate. The sample was than titrated with silver nitrate solution, till the solution became reddish brown in color. Concentration of chloride was calculated using equation (2.3):

$$\rho_{Cl} = \frac{(V_s - V_b) \cdot c \cdot f}{V_a} \tag{2.3}$$

where ρ_{Cl} – concentration of chlorides, mg/l; V_a – amount of sample, ml; V_b – amount of silver nitrate, ml; V_s – amount of silver nitrate which was used for titration of sample, ml; c – concentration of silver nitrate, $AgNO_3$; f – conversion factor, f = 35 453 mg/mol.

Nitrite analysis was done using a molecular spectrometric absorption method. The necessary volume of the sample and 1 ml of coloured reagent was poured into the flask and diluted with deionised water. The maximum absorption wavelength was measured using photocolorimetric at λ=540 nm in 1 cm cells after 20 minutes. Distilled water was used for comparison. Absorption was calculated using equation (2.4).

$$A_t = A_s - A_b \tag{2.4}$$

where A_t – the absorption of nitrites, A_s – the absorption of the sample; A_b – the absorption of the blank sample;

The mass of nitrites was estimated from the calibration graph. Concentration of nitrites was calculated using equation (2.5):

$$C = \frac{m_N}{V} \tag{2.5}$$

where: m_N – mass of nitrites, mg; V – volume of sample, ml.

Determination of the nitrates concentration was done by the spectrometric method using the acid of sulfosalicylic. The sample water was mixed with 1 ml±0.01 ml of salicylate solution and evaporated. Later 1 ml±0.01 ml of sulphur acid was poured and mixed with the dry residual and then mixed with 10 ml±0.01 ml. of an alkaline solution and 10 ml±0.01 ml. of water which was then analyzed. Absorption was measured with photocolorimetric (λ=415 nm) in 5 cm length cells. Absorption of nitrates were calculated the same as nitrites using equation (2.5) (AAM 1994).

Total carbon (TC) and total nitrogen (TN) was determined using apparatus TOC-V by SHIMADZU at 900^{o}C temperature (Figure 2.5).

Fig 2.5. Total organic carbon analyzer – TOC – V CSN by Shimadzu (google.lt)

50 ml of snowmelt water was mixed with 5 ml of HCl to determine concentration of heavy metals. Concentrations of elements of samples were determined by flame atomic absorption spectrophotometer (FAAS).

2.5 CHEMICAL ANALYSIS OF SNOW-DUST

Snowmelt water was filtered through glass fibre borosilicate non–ashen filter and dried to determine the daily load of dust and to measure concentration of heavy metals (Cd, Cr, Cu, Pb). Total concentration of heavy metals was determined after digestion process. Each sample was mixed with 3 ml of HNO_3 (65 %) and 9 ml of HCl (37%), poured into special vessels and then placed into Milestone ETHOS digestor and heated for 42 min. (Figure 2.6).

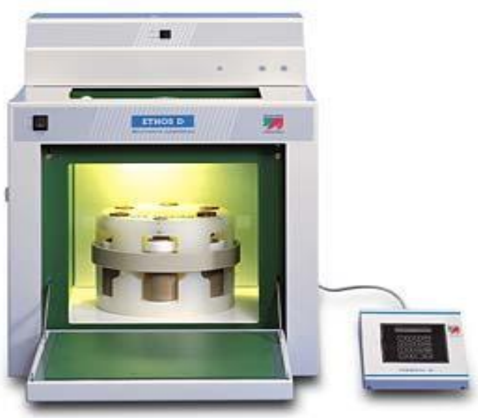


Fig 2.6. *Milestone* ETHOS digester (google.lt)

The solution was then poured into 50 ml flask and diluted with deionised water to reach the mark of 50 ml (Butkus and Baltrėnatė 2007; Baltrėnas *et al.* 2009; Pundytė *et al.* 2010). The total concentration of elements of samples were determined by flame atomic absorption spectrophotometer (FAAS). A graphite furnace (GFAAS) was employed to determine metal concentrations (Cu, Cd and Pb) when they were too low to detect accurately by FAAS (Figure 2.7) (Baltrėnaitė *et al.* 2010, Butkus and Baltrėnatė 2007, Pundytė *et al.* 2010).

Fig 2.7. *210 VGP* atomic absorption spectrophotometer of the company *Buck Scientific* (google.lt)

To determine the pollution level in the oil refinery was calculated the daily load of snow-dust. The calculation of load of snow-dust was made after drying of filters. Filters with dust particles were dried in a clean drying chamber on the fresh sheets of paper. Daily load of snow-dust was calculated using equation (2.6):

$$A_n = \frac{D \cdot X_n}{S \cdot T} \cdot 10^{-3}; \tag{2.6}$$

where A_n – daily load of snow-dust, mg/m^2, X_n – concentration of element „n“ in the dust, mg/kg; D – mass of the dust, g; S – area of the territory of taken snow sample, m^2; T – snowy period of time before sampling, number of days.

Snowy period of time was determined using information of the nearest weather station data.

Table 2.1. Classification of contamination level according to load of snow-dust (Saet *et al.* 1990)

Risk level	**Daily snow-dust load, mg/m^3**
Medium risk	The average daily load of snow-dust 250–450 mg/m^2
High risk	The average daily load of snow-dust 450–800 mg/m^2
Particularly high risk	The average daily load of snow-dust in excess of 800 mg/m^2

Table 2.1 is based on many long term and reliable geochemical research studies by Russian scientists (Rare-element Geochemical and Mineralogical Institute, Moscow, Russia). Research was carried out by doctors, hygienists, environmentalists and experts in soil and plant sciences. The main mediums accumulating pollutants were studied: snow–cap, soil, ponds and river bottom sediments, children and adults bio substrates (mostly hair). Consistently the researched mediums, which transported pollutants, were the air and river water. Large varieties of industries as well as various pollution sources were studied. Classification of pollution level, associated health risk and the nature of the diseases were studied continually for children and adults.

In order to assess the load of snow–cap dust in different areas load factors were calculated (Table 3). The calculation was made by using equation (2.7).

$$K = \frac{A_{nn}}{A_{ns}}; \tag{2.7}$$

where K – the load factor, A_{nn} – the daily load of snow-dust in the northern areas of oil refinery impact zone, mg/m^2, A_{ns} – the daily load of snow-dust in the southern areas of oil refinery impact zone, mg/m^2.

2.6. STATISTICAL ANALYSIS

All samples were prepared in triplicate. 5 blank samples were prepared for each analysis. Statistical analysis was made by SigmaPlot 11 program, where Duncan`s method for pair–wise multiple comparison procedures was used. One way ANOVA analysis was performed to determine if the means of concentrations were affected by a distance from the pollution source. The differences were considered significant at $p = <0.001$. Results depending from each prevailing wind direction according to the factory were averaged and the standard deviation (SD) was calculated. Correlation coefficients were calculated to determine the relation between the daily load of snow-dust and the concentration of heavy metals and were carried out with the programme Excel.

REVIEW OF CHAPTER 2

1. Snow–cap samples were taken around the vicinity of the oil refinery near the town of Mažeikiai, in a North-Western region of Lithuania (56°23′15″N 22°10′34″E). Snow–cap samples were taken of undisturbed snow–cap in the middle of February, 2011. The temperature was – -3 ^{0}C, without snow. To identify the impact of oil refinery for ambient air quality, sampling sites were grouped into four zones according the prevailing wind direction.

2. Both snowmelt water and snow-dust were typically analyzed. All residues, leaves, debris, soil particles were removed. Before transference it was necessary to determine whether the plastic bag is not leaky, clean and suitable for snow transportation.

3. Analyses were done after filtration. Samples were filtered through glass fiber borosilicate non ashen filters. The daily load of snow-dust was calculated to determine pollution level in the oil refinery impact zone.

4. For snowmelt water analysis was used methodology which is based on ISO standards for water quality evaluation. The basic snowmelt water properties were measured as pH, chlorides, sulphates, nitrates, nitrites, ammonium nitrogen, total organic carbon and nitrogen content.

5. Total concentration of heavy metals (Cu, Cd, Cr and Pb) was determined after digestion process. Each sample was mixed with 3 ml of HNO_3 (65 %) and 9 ml of HCl (37%), poured into special vessels and then placed into Milestone ETHOS digester and heated for 42 min. 50 ml of snowmelt water was mixed with 5 ml of HCl to determine concentration of heavy metals.

6. The total concentration of heavy metals in snow-dust and snowmelt water was determined by flame atomic absorption spectrophotometer (FAAS). A graphite furnace (GFAAS) was employed to determine metal concentrations (Cu, Cd and Pb) when they were too low to detect accurately by FAAS.

3. RESULTS AND ANALYSIS

3.1 LOAD OF SNOW-DUST

According to the classification of the daily load of snow dust a lower than medium-risk level of pollution was determined in the vicinity of the oil refinery. After the correlation analysis of the daily load of snow-dust and metals concentration, negative coefficients were obtained, showing, that high concentration of pollutants are regularly related to low rate of load. In contrary, separate metal concentration correlate positively – an increased concentration of one metal is regularly related with a high concentration of other metal.

The data analysis showed that the highest daily rate of a snow-dust load (45.81±12.35 mg/m2) was in the Zone 1 (Figure 3.1).

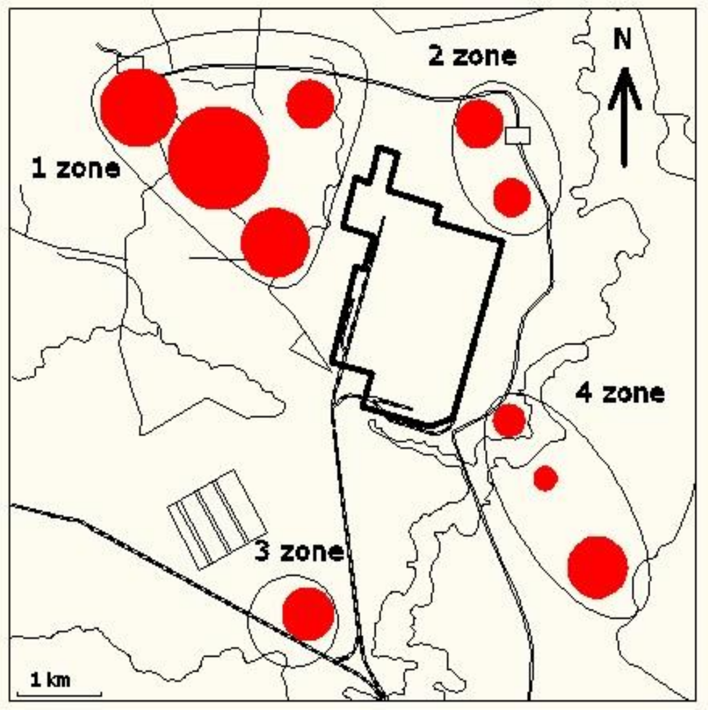


Fig. 3.1. Principal scheme of a snow-dust load in the JSC *ORLEN Lietuva* impact zone

Prevailing winds in the region probably had an influence because northwest and southeast winds blow in to the oil refinery impact zone. Comparing Zone 1 and 4 with Zone 2 and 3 the daily load of snow was 1.2 times higher.

The results obtained from calculating snow-dust load coefficients in different zones are presented in Table 3.1.

Table 3.1 Snow-dust load coefficients, comparing the loads in zones

Ratio of snow-dust daily load in different zones	Daily load coefficient, K
Zone 1/Zone4	1.88
Zone 2/Zone 3	0.82
Zone 3/Zone 4	1.34
Zone 1/Zone 2	1.72
Zone 2/Zone 4	1.09
Zone 1/Zone 3	1.40

Values of the coefficients confirm the existing impact of the oil refinery on the air quality, otherwise the coefficients should be equal to 1.

3.2 CONCENTRATION OF CONTAMINANTS

Sulphates, chlorides and three forms of nitrogen – ammonium, nitrite and nitrate – were analyzed in the snowmelt water. Their accumulation in snow–cap is mostly related to the emission of gaseous pollutants, resulting from combustion of organic materials. Nitrite (<0.25 mg/l) and ammonium (0.1 mg/l) concentrations were below the analytical method detection limit in all samples.

The concentration of sulphates and chlorides in the snowmelt water in all samples was lower than concentration limits defined in the European Council directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption (Council directive 1998). Limit value of sulphates and chlorides in a drinking water is 250.0 mg/l. Almost all concentrations of chlorides in samples were below the analytical method detection limit (<5 mg/l). The highest concentration of sulphates was detected in the Zone 2 at 0.9 km distance from the refinery, in the weakly alkaline snowmelt water (pH 7.6) – 4.18±1.35 mg/l. Higher concentration of chlorides (13.5±0.7 mg/l) was detected only in the Zone 1 at 0.9 km distance from the oil refinery. Sulphate concentrations in the southern part of the territory are two times lower than in the northern part. In six samples, the concentration of sulphates was below the method detection limit (<2 mg/l). The average concentration of sulphates was 7.3 mg/l, determined in assessment study in 2004 (Kadūnas *et al.* 2004).

Results showed that the highest nitrate concentration (1.1±0.1 mg/l) was detected in the Zone 2 and the lowest one – in the Zone 4 (0.14±0.06 mg/l) (Figure 3.2). In the southern direction from the oil refinery, the concentration of nitrates was three times lower. These were similar to the highest concentration of nitrates (1.1 mg/l), determined in assessment study in 2004 (Kadūnas *et al.* 2004). In respect to snow-dust, higher concentrations of these elements were detected in snow–cap of northern territory part, i.e. in the direction of pollutants in air masses, generated by oil refinery, transition.

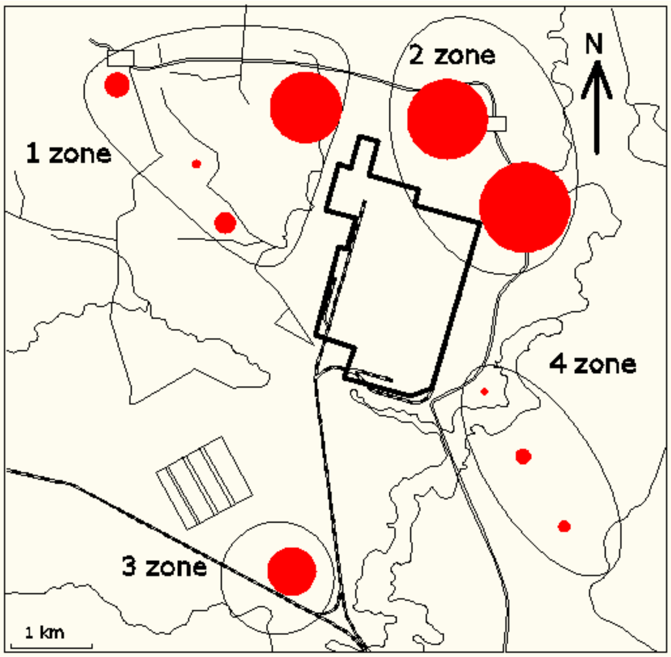


Fig. 3.2. Principal scheme of nitrates in the JSC *ORLEN Lietuva* impact zone

One of the dangerous atmosphere pollution sources in oil refinery industry is boiler-house and combustion processes, which increase concentration of carbon dioxides in the atmosphere. Two types of fuel are used in the oil refinery processes: fuel oil and gases. Organic carbon source can be various organic compounds from the oil refinery processes. During the research, amounts of organic and inorganic carbon were determined in JSC *ORLEN Lietuva* impact zone (Table 3.2).

Table 3.2. Concentration of organic and inorganic carbon in the impact zone of oil refinery

No. of zone	Inorganic carbon, %	Organic carbon, %
1	70	30
2	60	40
3	72	28
4	22	78

The highest concentration of the total carbon was detected in the Zone 3 (5.30±0.51 mg/l). Here the major part of it consists of inorganic carbon (72%). The concentration of organic carbon detected in the Zone 4 (4.21±4.10 mg/l) was 4-8 times higher, in compare with the concentration of organic carbon detected in other zones. In the south-east zone, the highest concentration of organic carbon (10.04 mg/l) was found at the point located at 2 km distance from the oil refinery. Comparison of the northern and southern zones showed, that higher concentrations of organic and inorganic carbon were detected in the southern part of the territory.

The highest amount of total nitrogen (TN) was determined in Zone 4 – 1.42±0.39 mg/l (Figure 3.3).

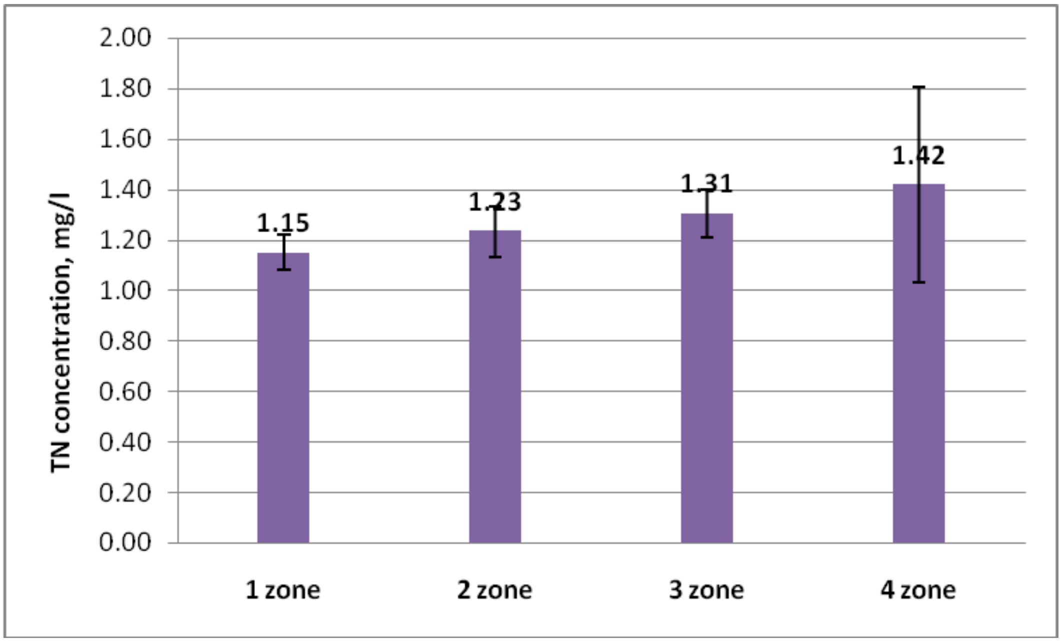


Fig. 3.3. Distribution of total nitrogen (TN) in the snowmelt water in the JSC *ORLEN Lietuva* impact zone

However, amount of TN is not distinctive according the pollution source.

Concentration of heavy metals

The main pollution source of heavy metals in the vicinity of oil refinery is combustion of fuel oil. Heavy metals are common constituents of the fuel. Values of concentrations were influenced by the local pollution in the industrial area and by effect of the seasonal wind from the northwest and southeast. The heavy metal concentrations in the snow–cap clearly increased towards prevailing wind direction. Concentrations of heavy metals in snow–cap were identified after the heavy metals analysis of both: snowmelt water and mineral dust accumulated in the snow. Concentrations of heavy metals were different at different distance from the oil refinery.

Cr concentration

Sources of Cr can be oil refining process and oil product combustion (Kadūnas *et al.* 2004). The concentration of Cr in oil refinery impact zones was detected only in snow-dust, Cr concentration in the snowmelt water in all samples was below the analytical method detection limit. The highest concentration of Cr was found 1.6 km away from the oil refinery (170.13±02.03 mg/kg) (Figure 3.4).

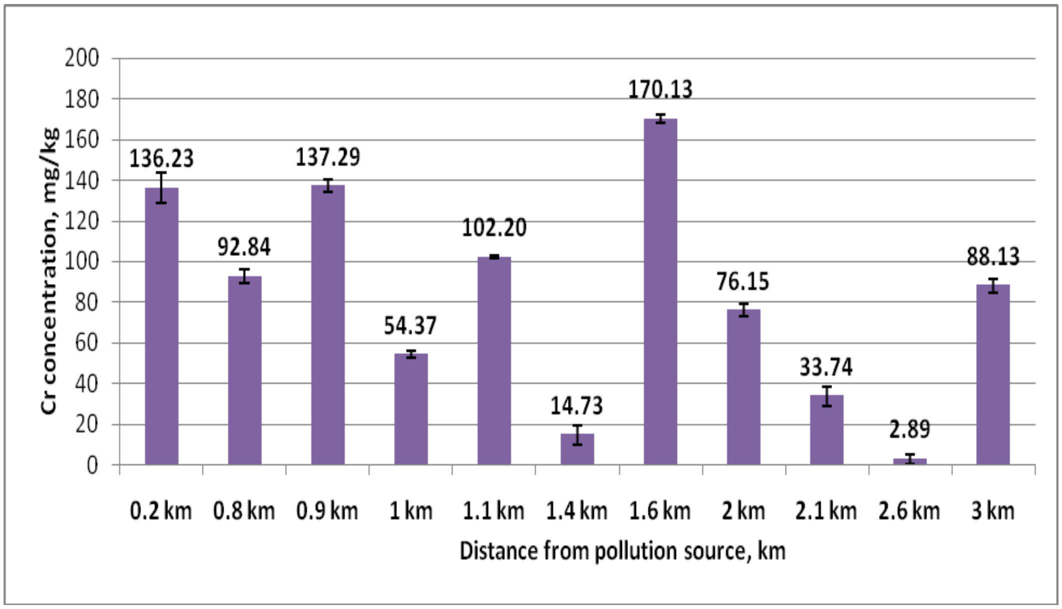


Fig. 3.4. Cr distribution of snow mineral dust, depending on the distance from JSC *ORLEN Lietuva*

Different sampling points in Cr content vary. Similar concentrations of the Cr were found at 0.9 km (137.29±4.95 mg/kg) and 0.2 km (136.23±2.85 mg/kg) from the oil refinery, as well as 0.8 km (102.20±2.90 mg/kg) and 3 km (88.13±4.70 mg/kg). The lowest concentration of Cr (2.89±0.60 mg/kg) in the area affected by the oil refinery was found 2.6 km away from the oil refinery. It can be argued that the overall effect of Cr concentration was not dependent on how far the samples were taken. Statistical analysis showed that the distance from the oil refinery of all investigated heavy metal concentration is not affected. The most significant difference between Cr concentrations was detected in Zones 2 and 3, where Cr concentrations differ about 13 times (Figure 3.5). The highest concentration of Cr in snow-dust was found in the Zone 2 (112.25±57.88 mg/kg).

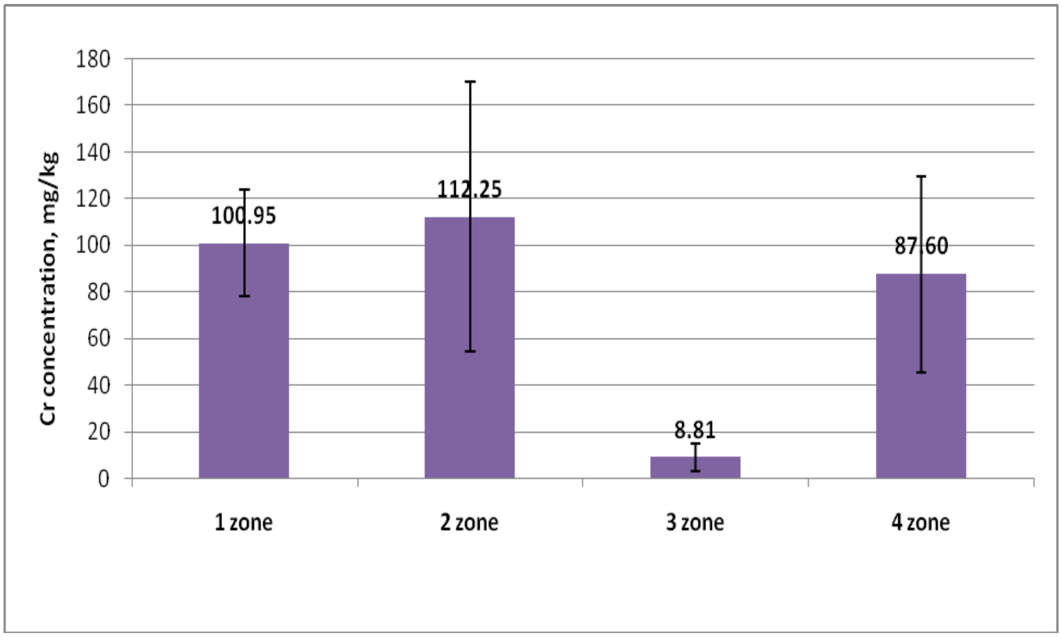


Fig. 3.5. Distribution of Cr in the snow-dust depending on the prevailing wind direction in the JSC *ORLEN Lietuva* impact zone

The lowest concentration of Cr was detected in the Zone 3, where also the lowest concentration of Cr at 2.6 km distance from the oil refinery was detected. Background concentration of Cr was determined 8.06±1.26 mg/kg. It was 1.1 times lower than the lowest Cr concentration in the impact zone of the oil refinery. Comparing northern and southern zones showed detection of higher concentration of Cr in the northern part of the territory.

Pb concentration

The highest concentration of Pb according to the wind direction in respect of the oil refinery was fixed in the Zone 4 (244.36±0.21 mg/kg), the lowest in the Zone 3 (2.64±0.21 mg/kg) (Figure 3.6). Background concentration of Pb was determined 2.17±0.24 mg/kg. It was 1.2 times lower than the lowest Pb concentration in the impact zone of the oil refinery. Comparing northern and southern zones showed that higher Pb concentration was determined in the northern part of the area. Meanwhile, distribution of Pb concentration in the snowmelt water was slightly differently than in snow-dust (Figure 3.7). Most of Pb in snowmelt water was detected in the Zone 2 (0.22±0.03 mg/l). On the contrary to the Pb content in snow-dust, the least of Pb in the snowmelt water was detected in the Zone 4 (0.004±0.01 mg/l).

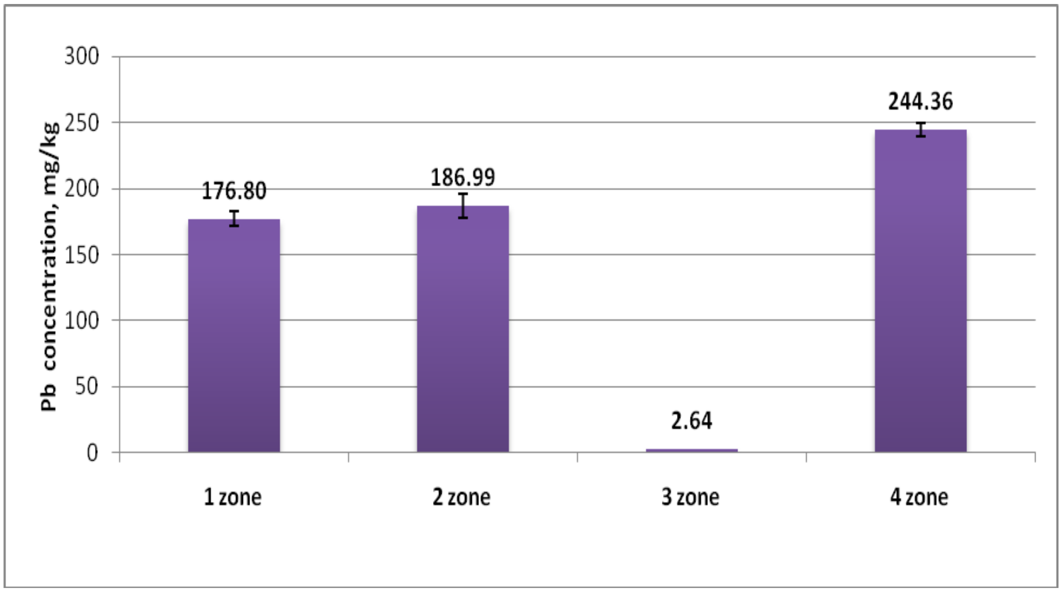


Fig. 3.6. Distribution of Pb in the snow-dust depending on the prevailing wind direction in the JSC *ORLEN Lietuva* impact zone

According to the analysis conducted in oil refinery territory in 2004, the highest concentration of Pb was 160 mg/kg (Kadūnas *et al.* 2004). In the study area, the general Pb concentration in snow–cap was inversely proportional to the snow-dust load: the lowest in the Zone 4 and the highest in the Zone 3. Concentration of Pb in snowmelt water was mostly associated with the same finely dispersed aerosol particles, of which they are easier to extract.

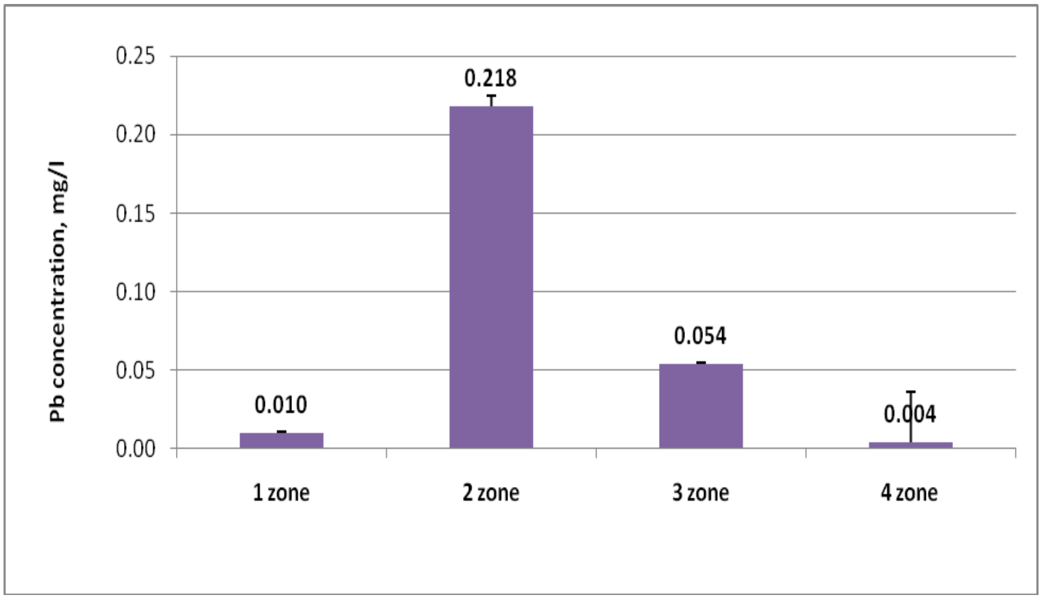


Fig. 3.7. Distribution of Pb in the snowmelt water depending on the prevailing wind direction in the JSC *ORLEN Lietuva* impact zone

Since they were more characteristic to the lower snow-dust load areas, soluble Pb concentrations were significantly higher in the Zone 2, in compare to the Zone 3 or the Zone 1.

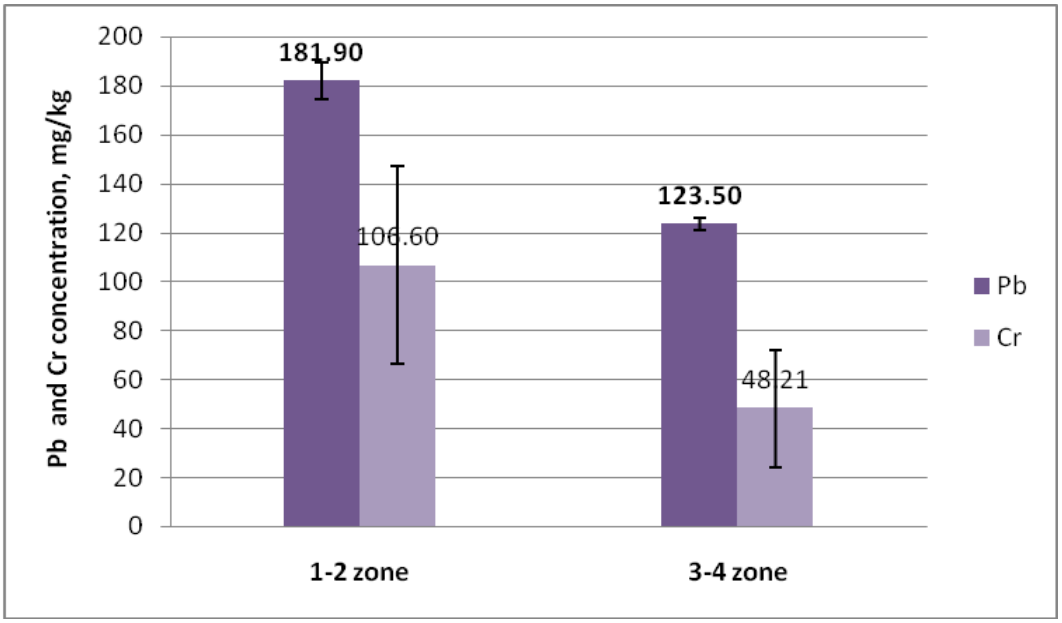


Fig. 3.8. Comparison of Pb and Cr content in northern and southern zones

Comparing northern and southern zones (1-2 and 3-4 Zones) showed that higher Pb and Cr contents in snow-dust were detected in the northern part of the area (Figure 3.8). Concentration of Pb in northern part is 1.5 times and Cr concentration was determined 2.2 times higher than in southern part.

Cu concentration

Cu is a typical element-pollutant in regional and transregional transference, related to fossil fuel combustion (Kadūnas *et al.* 2004).

The statistical data analysis of Cu concentration distribution in the snow–cap according to the wind direction showed the increased concentration of Cu in the northern area from the oil refinery. The highest concentration Cu was detected in the Zone 2 (71.31±3.47 mg/kg). The lowest one was in the Zone 3 (4.51±0.68 mg/kg) (Figure 3.9). Background concentration of Cu was determined 3.92±1.39 mg/kg. It was 1.2 times lower than the lowest Cu concentration in the impact zone of the oil refinery. The analysis conducted in 2004 showed that the highest detected concentration of Cu in snow-dust was 70 mg/kg, the median concentration – 35 mg/kg.

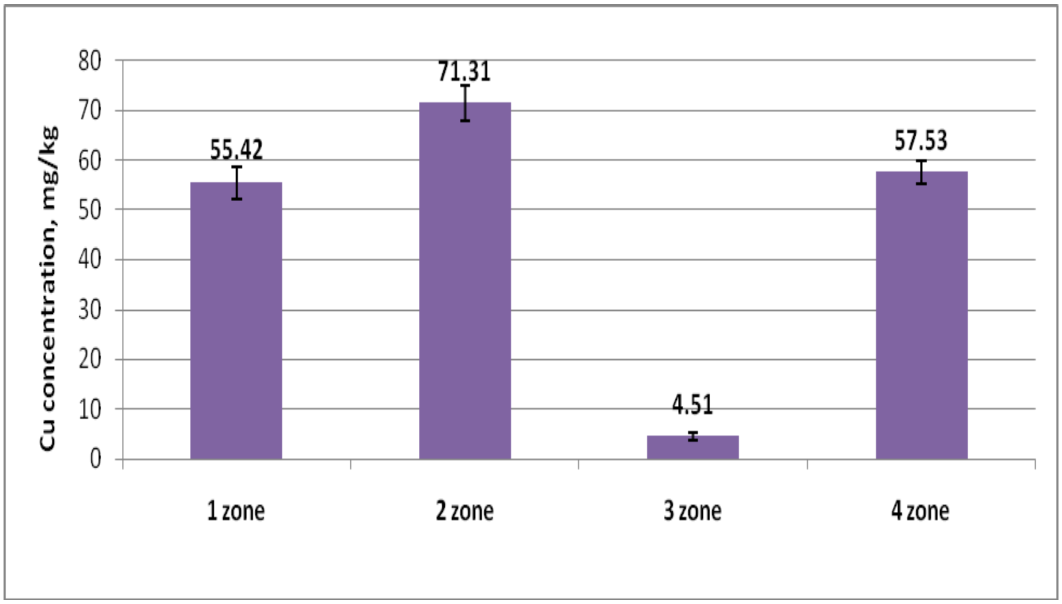


Fig. 3.9. Distribution of Cu in the snow-dust depending on the prevailing wind direction in the JSC *ORLEN Lietuva* impact zone

According to our data, the median concentration of Cu was 50.5 mg/kg, this suggests that during the past seven years the concentration of Cu in snow–cap has increased significantly. Comparing of northern and southern zones showed a higher concentration of Cu detected in the northern part of the area. Distribution of Cu concentration in the snowmelt water was nearly the same as in snow-dust. Most of Cu in snowmelt water was detected in the Zone 2 (0.36±0.012 mg/kg) (Figure 3.10).

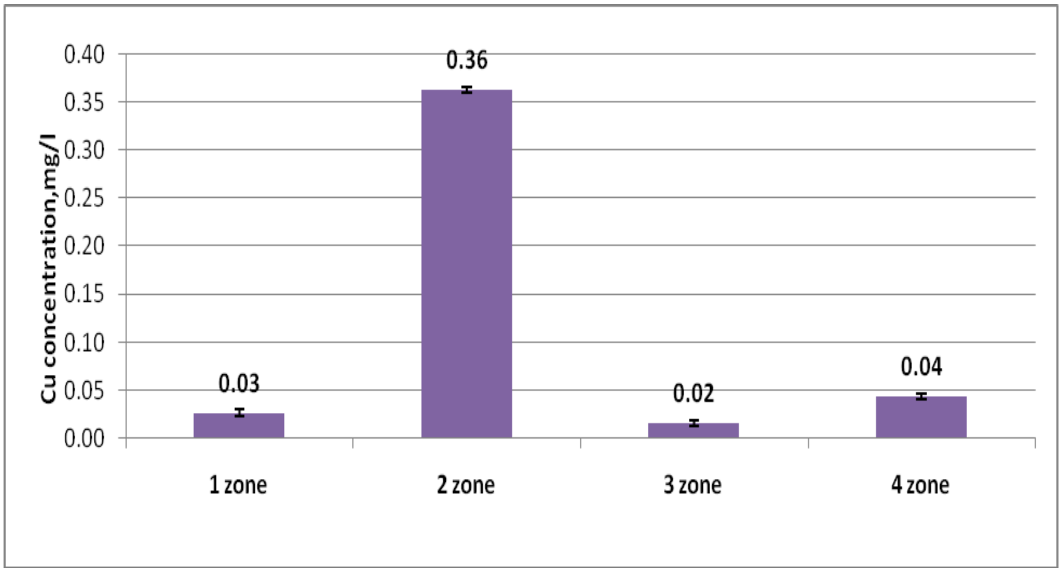


Fig. 3.10. Distribution of Cu in the snowmelt water depending on the prevailing wind direction in the JSC *ORLEN Lietuva* impact zone

The least of Cu in the snowmelt water was detected in the Zone 3 (0.02±0.001mg/kg).

Cd concentration

In oil refinery impact zone, Cd concentration was detected only in snow-dust, since Cd concentration in all samples of the snowmelt water was below the analytical method detection limit. Concentrations of Cd in snow–cap were relatively low in compare to the concentrations of other heavy metals detected in analyzed snow–cap. Cd concentrations differ at different distances from the oil refinery (Figure 3.11).

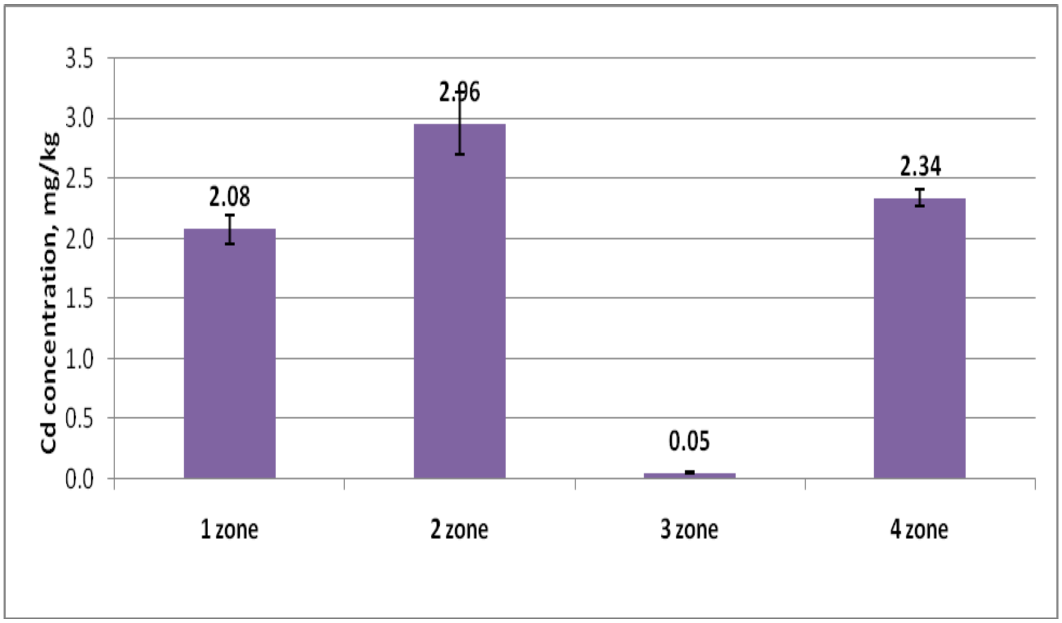


Fig. 3.11. Distribution of Cd in the snow-dust depending on the prevailing wind direction in the JSC *ORLEN Lietuva* impact zone

The highest concentration of Cd was found in the 2 Zone – 2.96±0.26 mg/kg, where also the highest Cd concentration at 1.6 km distance was detected. Minimal Cd concentration was found in the Zone 3.

Comparing of northern and southern zones (1-2 and 3-4 Zones) showed that a higher concentration of Cd and Cu was found in the northern part of the area (Figure 3.12). Concentration of Cu and Cd in northern part was determined 2 times higher than in southern part.

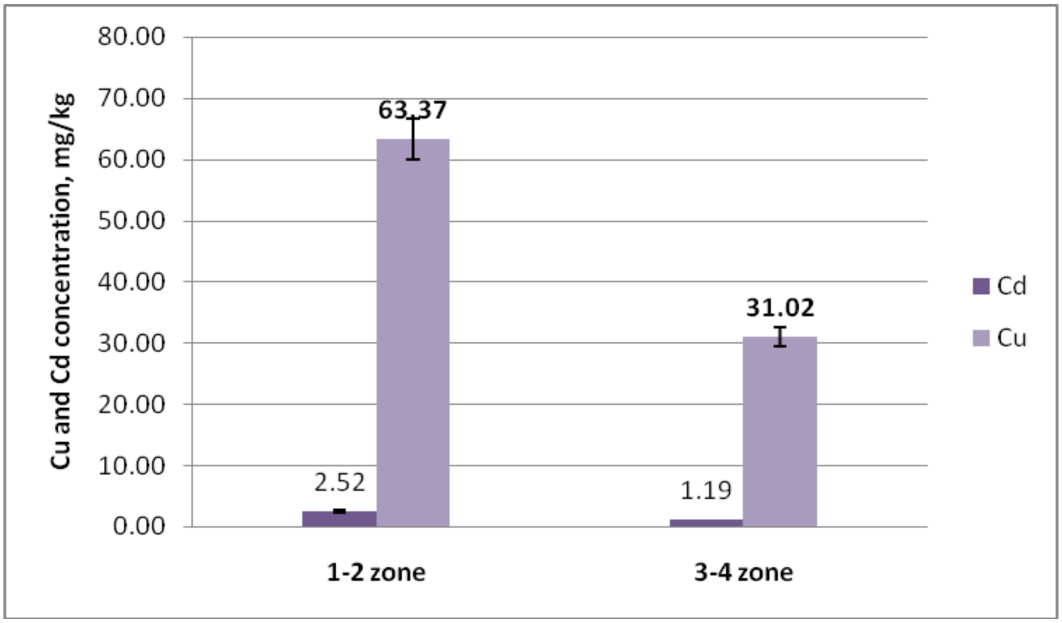


Fig. 3.12. Comparison of Cu and Cd content in northern and southern zones

As can be seen from Figure 3.5-3.12 according to the mean concentration the sequence of heavy metals was the following: Pb>Cr>Cu> Cd.

Soluble and insoluble forms

Generally, a ratio in the snow–cap between soluble metal forms and insoluble ones depends on the type of pollution source, on the distance between the latter and the snow-dust load, and their nature (Lietuvninkas 2002). Distances for analysis were grouped in 0.5 km, 1.5 km and 2 km around the oil refinery. Concentrations of heavy metals in snow-dust were determined thousands times higher than those in the snowmelt water.

The concentration of lead (Pb), chromium (Cr) and copper (Cu), cadmium (Cd) varied. The highest concentration of Cd (3.22±0.09 mg/kg), Cu (72.49±14.96 mg/kg) and Pb (325.91±3.20 mg/kg) was determined in the closest sampling sites from the oil refinery – 0.5 km. Concentration of these pollutants decreases while increases the distance from the pollution source. The biggest amount of Cr (114.53±21.7 mg/kg) was determined in the 1.5 km distance from the pollution source. The minimum amount of Cr was found 2 km around from oil refinery – 50.23±33.99 mg/kg, 2.3 times higher concentration comparing with the highest concentration of Cr (Figure 3.13). In oil refinery impact zone, Cd and Cr concentrations were detected only in snow-dust, since Cd and Cr concentrations in all samples of the snowmelt water were below the analytical method detection limit.

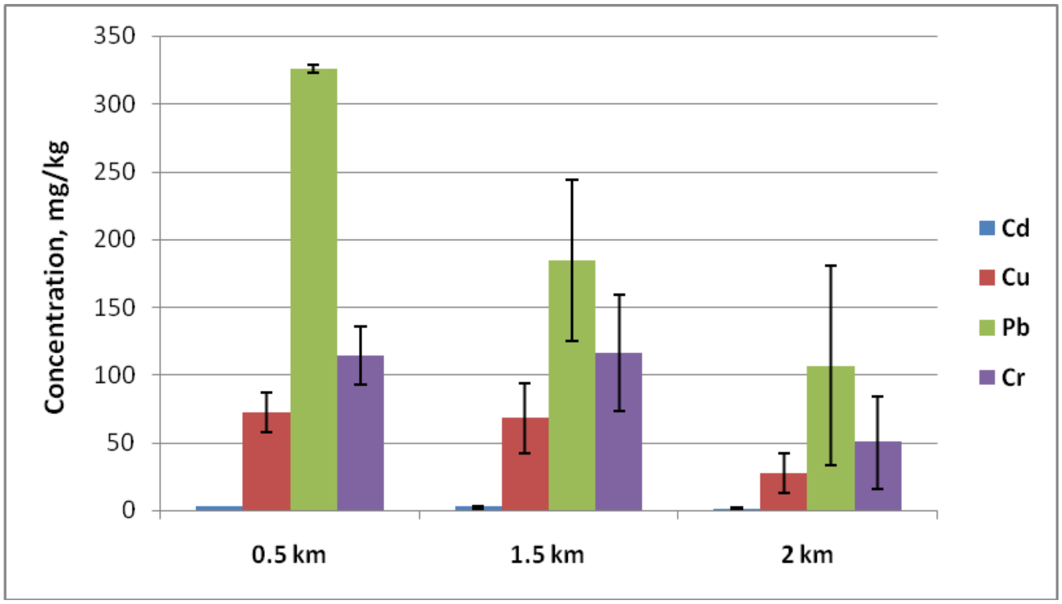


Fig. 3.13. Distribution of heavy metals in the snow-dust, depending on the distance from the oil refinery

The biggest concentration of Pb (0.012±0.025 mg/l) and Cu (0.200±0.03 mg/l) was determined at 1.5 km distance from oil refinery. The lowest concentration of Pb was determined near the oil refinery (0.5 km) – 0.004±0.003 mg/l (Figure 3.14).

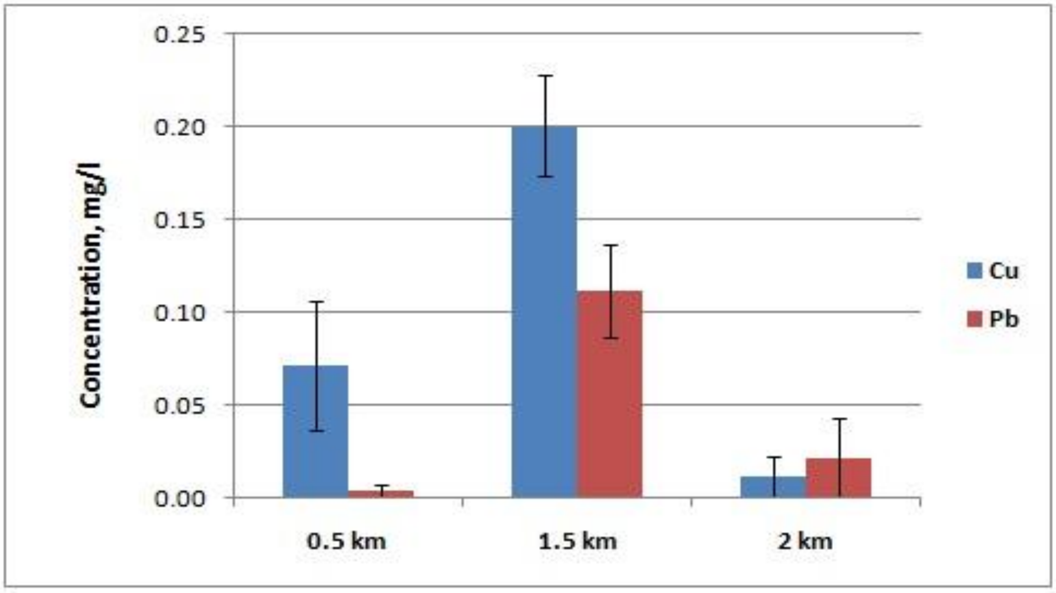


Fig. 3.14. Distribution of heavy metals in the snowmelt water, depending on the distance from the oil refinery

Results confirms the trend that closer to contamination source the part of soluble forms of metals relatively decreases, while the concentration of insoluble forms of metals increases when approaching the contaminated area.

REVIEW OF CHAPTER 3

1. According to the classification of the daily load of snow dust a lower than medium-risk level (<250–450 mg/m^2) of pollution was determined in the vicinity of the oil refinery.

2. After the correlation analysis of the load of snow-dust and metals concentration, negative coefficients were obtained, showing, that high concentration of pollutants is regularly related with the low rate of load.

3. Values of the coefficients calculated of snow-dust load in different zones confirm snow-dust transition in the north-west direction, i.e. the real impact of the oil refinery and an approximate intensity of it – otherwise, the coefficients should be equal to 1.

4. Three forms of nitrogen – ammonium, nitrite and nitrate – were analyzed in the snowmelt water. Their accumulation in precipitation is mostly related with the emission of gaseous pollutants, resulting from combustion of organic materials. There was also detected the concentration of sulphates and chlorides, depending on their position in respect of the oil refinery.

5. Concentrations of heavy metals in snow–cap were identified after the heavy metals analysis of the snowmelt water and mineral dust accumulated in the snow. Different samples distance from JSC *ORLEN Lietuva* determined variable amounts of heavy metals. During the analysis, concentrations of copper (Cu), cadmium (Cd), lead (Pb) and chromium (Cr) were detected.

6. Distribution of Pb and Cu concentration in the snowmelt water was slightly differently than in snow mineral dust. Amount of Pb and Cu in snowmelt water were determined hundred times lower than Pb and Cu concentration in snow-dust.

7. Comparing northern and southern zones (1-2 and 3-4 Zones) showed that higher contents of heavy metals in snow-dust were detected in the northern part of the area. Concentration of Pb in northern part is 1.5 times, Cr – 2.2 times, Cu and Cd – 2 times higher than in southern part.

8. The technogenic in a snow–cap oil refinery impact zone is characterized by complex internal structure, which depends on the migration features of different physical state (solids, gases) pollutants in air masses, prevailing direction of air masses transference, and infrastructure of the impact zone (location of roads and industrial objects, intensity of traffic, etc.) – in the 3 Zone, where the is railway the load of snow-dust was determined 1.3 times higher than in Zone 4.

9. Mažeikiai district municipality performs the soil and other coatings monitoring program, where the snow–cap is object also. During study were determined background concentrations of Cu (7.7 mg/kg), Cr (39 mg/kg) and Pb (14 mg/kg). In this study concentration values were significantly higher (Pb 12 times, Cr 2 times and Cu 6 times more) so it can be said that environment was effected by oil refinery.

10. Analysis of soluble and insoluble forms of heavy metals confirms the trend that closer to contamination source the part of soluble forms of metals relatively decreases, while the amount of insoluble forms of metals increases when approaching the contaminated area.

4. SNOW-CAP MODELING

The main task for modeling was to simulate PM in the air and breaks up the dependence between the pollutants in the air and snow–cap. For modeling was used ADMS 4 (Atmospheric Dispersion Modeling System) and AERO 2 programs. Results were assessed according allowed values of PM emissions.

4.1 DESCRIPTION OF THE ADMS PROGRAM

ADMS 4 is a practical, short-range dispersion model that simulates a wide range of buoyant and passive releases to the atmosphere either individually or in combination. It is a "new generation" dispersion model using two parameters, namely the boundary layer height *h* and the Monin-Obukhov length *LMO* to describe the atmospheric boundary layer and using a skewed Gaussian concentration distribution to calculate dispersion under convective conditions. The model is applicable up to 60 km downwind of the source and provides useful information for distances up to 100 km. ADMS 4 is supplied with a Mapper that can be used to visualize, add and edit sources, buildings and output points.

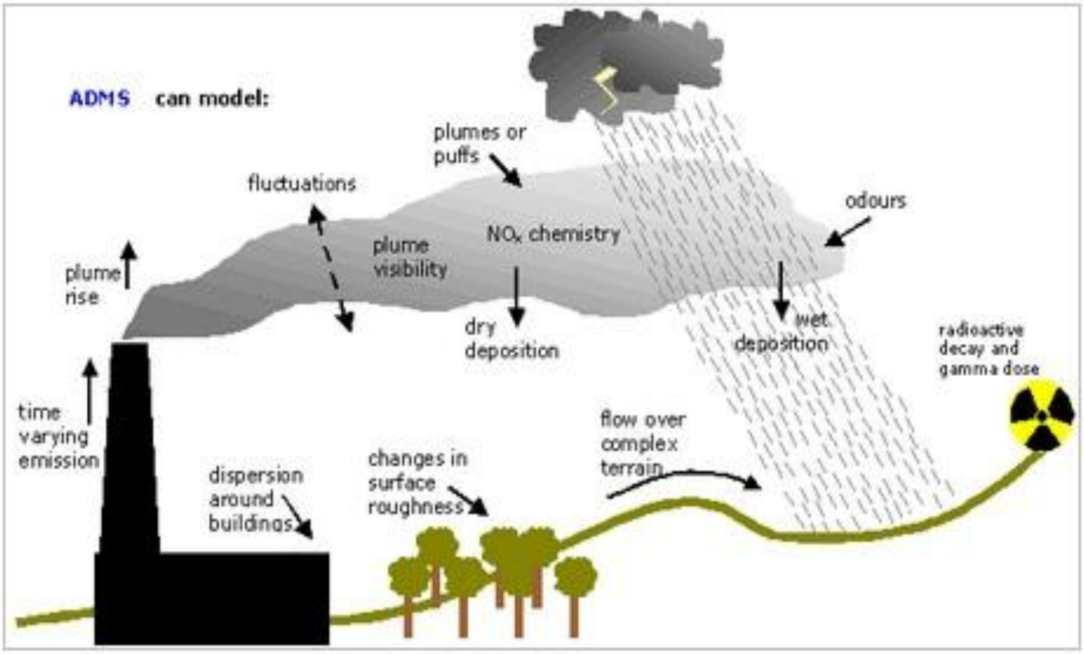


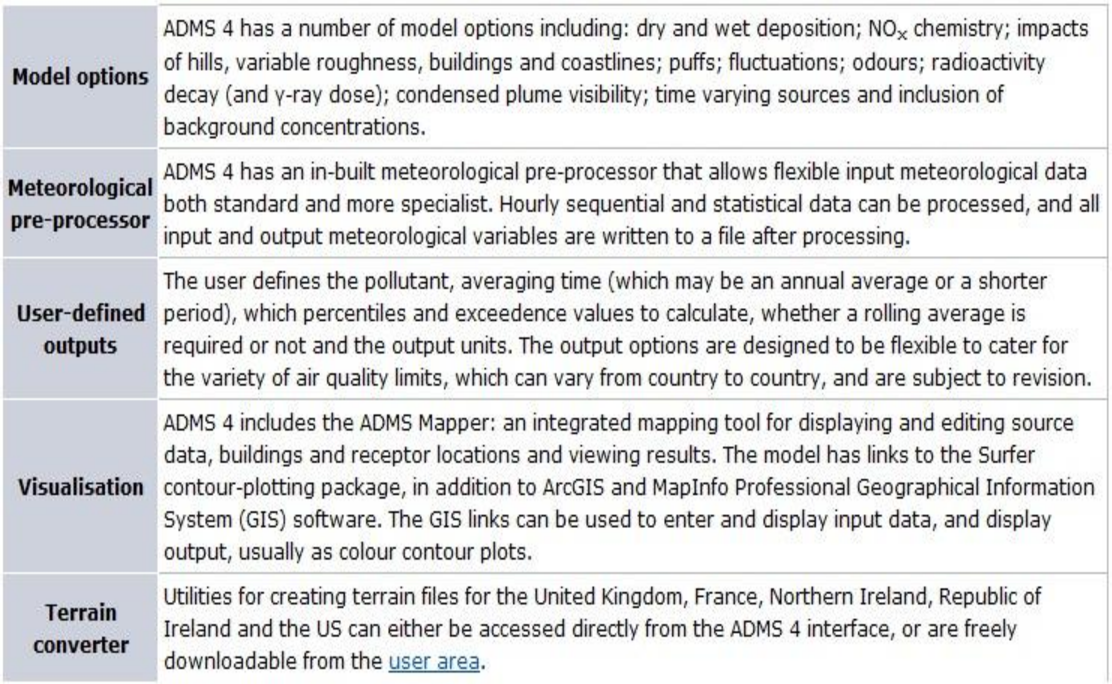
Fig. 4.1. ADMS model options

ADMS 4 can be used to assess the effect of emissions from a number of industrial source types:

- Point source e.g. emissions from a stack or vent.
- Area source e.g. evaporative emissions from a tank.
- Line source e.g. emissions from a conveyor belt at a quarry.
- Volume source e.g. fugitive emissions.
- Jet source (directional releases) e.g. emissions from a ruptured pipe (Figure 4.1).

It also links to other software packages, such as Surfer, ArcGIS, MapInfo and ArcView GIS (Geographical Information System) software, for display of results and easy data entry. Separate User Guides are provided for using the ADMS Mapper and links to ArcGIS, MapInfo and ArcView (ADMS manual …2007). The ADMS 4 model includes:

Table 4.1. Content of ADMS 4 model



Model options	ADMS 4 has a number of model options including: dry and wet deposition; NO_x chemistry; impacts of hills, variable roughness, buildings and coastlines; puffs; fluctuations; odours; radioactivity decay (and γ-ray dose); condensed plume visibility; time varying sources and inclusion of background concentrations.
Meteorological pre-processor	ADMS 4 has an in-built meteorological pre-processor that allows flexible input meteorological data both standard and more specialist. Hourly sequential and statistical data can be processed, and all input and output meteorological variables are written to a file after processing.
User-defined outputs	The user defines the pollutant, averaging time (which may be an annual average or a shorter period), which percentiles and exceedence values to calculate, whether a rolling average is required or not and the output units. The output options are designed to be flexible to cater for the variety of air quality limits, which can vary from country to country, and are subject to revision.
Visualisation	ADMS 4 includes the ADMS Mapper: an integrated mapping tool for displaying and editing source data, buildings and receptor locations and viewing results. The model has links to the Surfer contour-plotting package, in addition to ArcGIS and MapInfo Professional Geographical Information System (GIS) software. The GIS links can be used to enter and display input data, and display output, usually as colour contour plots.
Terrain converter	Utilities for creating terrain files for the United Kingdom, France, Northern Ireland, Republic of Ireland and the US can either be accessed directly from the ADMS 4 interface, or are freely downloadable from the user area.

Typical applications include:

- Permitting/IPPC authorizations;
- Stack height determination;
- Odor modeling;
- Environmental impact assessments;
- Safety and emergency planning (ADMS 4…2000).

Process and a statement of the equations

ADMS 4 is a new generation Gaussian plume air dispersion model, which means that the atmospheric boundary layer properties are characterized by two parameters. Rather than in terms of the single parameter Pasqual-Gifford class. The Gaussian plume model for single and multiple sources are the most common air pollutant models. Equation (4.1) is the equation that describes the three-dimensional concentration field generated by point source(s) under stationary meteorological and emission conditions (Vaitiekūnas and Špakauskas 2003):

$$C(x,y,z)=\frac{Q}{2\pi\cdot u\cdot\sigma_y\sigma_z}\exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2}\right)\right]\left\{\exp\left[-\frac{1}{2}\left(\frac{(z-H)^2}{\sigma_z^2}\right)\right]+\exp\left[-\frac{1}{2}\left(\frac{(z+H)^2}{\sigma_z^2}\right)\right]\right\}. \tag{4.1}$$

where C – pollutant concentration, kg/m^3 or m^3/m^3 or pph, etc; Q – stack emission rate, g/s; σ_y, σ_z – standard deviation of the plume concentration distribution along y and or z.

It is straightforward to model this equation and to link it to a graphical package to output contours of concentrations at distances from the source(s). In many cases, most interest is in concentrations at ground level and so equation (4.1) reduces to:

$$C(x,y,z)=\frac{Q}{2\pi\cdot u\cdot\sigma_y\sigma_z}\exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2}\right)\right]\exp\left[-\frac{1}{2}\left(\frac{H^2}{\sigma_z^2}\right)\right]. \tag{4.2}$$

where H – height of the emission, m.

The modeling of these equations, with facilities for multiple sources and complex topography, is a feature of many proprietary computer models.

Dispersion under convective meteorological conditions uses a skewed Gaussian concentration distribution (shown by validation studies to be a better representation than a symmetrical Gaussian expression). The Gaussian plume model is a (relatively) simple mathematical model that is typically applied to point source emitters, such as coal-burning electricity-producing plants. One of the key assumptions of this model is that over short periods of time (such as a few hours) steady state conditions exist with regard to air pollutant emissions and meteorological changes. Air pollution is represented by an idealized plume coming from the top of a stack of some height and diameter.

Description of model setup

The system has a number of distinct features which can be summarized as follows:

(i) Concentration distributions are Gaussian in stable and neutral conditions, but the vertical distributions is non-Gaussian in convective conditions to take account of the skewed structure of the vertical component of the turbulence.

(ii) A meteorological pre-processor which calculates the required boundary layer parameters from a variety of input data: wind speed, day time cloud cover or wind speed, surface heat flux and boundary layer height. Meteorological data may be raw, hourly averaged or statistically analyzed data.

(iii) Calculation of averages of means concentration and deposition and mean concentration percentiles for averaging time from 10 minutes to a year.

(iv) A range of modules allow for the effects of plume rise, complex terrain, street canyons, noise barriers and buildings

(v) Explicit NO_x chemistry modeling (NO, NO_2, O_3, VOC) and sulphate chemistry including a grid-based trajectory model to account for the chemical reactions between the background data site and the domain of interest. Changes in primary NO_2 and changes in background ozone can be modeled.

(vi) Full integration with a Geographical Information System (ArcGIS and MapInfo) allowing easy emission set-up, output presentation and analysis.

(vii) Links to pollution concentration monitoring data for display of results against monitored data and meteorological forecasts for air quality forecasting (ADMS urban…2010).

The model interface is designed so that the user can enter the data required for the modeling in as straightforward a way as possible. The interface consists of several main screens.

4.2 DESCRIPTION OF THE AERO 2 PROGRAM

AERO 2 program is baised on Gauss model. The calculation of the concentration of airborn pollutants in the air can be calculated from one point pollution source assessing adverse weather conditions and dangerous wind speed. Model uses the following equations.

1) Maximum ground-level concentration of pollutants under adverse meteorological conditions and dangerous wind speed was calculated using equation (4.3).

$$C_M = \frac{AMFmn\eta}{H^2 \cdot \sqrt[3]{V_1 \Delta T}} \tag{4.3}$$

where C_M – maximum ground-level concentration of pollutants under adverse meteorological conditions and dangerous wind speed, mg/m^3; A – factor which depends from atmosphere temperature; F – non-dimensional factor assessing speed of settlement of pollutants and depends from the efficiency of cleaning devices (for gaseous pollutants F – 1, for insoluble pollutants factor depends from the efficiency of the cleaning devices – F – 2 (>90%), F – 2,5 (75-90%); F – 3 (<75 %)), M – mass of the pollutants per time (g/s); m and n – factors assessing the conditions of the emissions of pollutants; η – non-dimensional factor assessing influence of topography; H – height of the pollution source (stack), m; V_1 – air flow, m^3/s, ΔT – temperature gradient between the temperature of the pollutants and ambient air, ^{0}C.

2) Dangerous speed of the wind was calculated using equation (4.4).

$$V_M = 0.65\sqrt[3]{V_1 \Delta T / H} \tag{4.4}$$

where V_M – dangerous wind speed, m/s.

3) Distance from the pollution source under adverse meteorological conditions and emissions levels to the maximum value was calculated using equation (4.5).

$$X_M = \frac{(5-F) \cdot d \cdot H}{4} \tag{4.5}$$

where X_M – distance from the pollution source, m; d – non-dimensional factor depending from the conditions and parameters of the emissions.

4) Maximum ground-level concentration of pollutants according the wind speed under adverse meteorological conditions is calculated using equation (4.6).

$$C_{MM} = r \cdot C_M \tag{4.6}$$

where C_M – maximum ground-level concentration of pollutants under adverse meteorological conditions and dangerous wind speed, mg/m^3; r – non dimensional factor depending from the wind speed.

4.3 MODELING METHODOLOGY

In this case the main sources of pollution were 6 smoke stacks – 45 m, 76 m, 120 m, two 180 m height stacks with different parameters and 250 m. Input of emissions (PM) was used in units per second e.g. g/s for a point source. To set up ADMS 4 model run, were worked through the screens entering the relevant data: height (m), diameter (m), velocity (m/s), temperature (^{0}C), coordinates of pollution source (X,Y). In this case was used point sources type, because of emissions from the stacks. Meteorological data was obtained from national meteorological service (Figure 4.2). Meteorological data was used hourly sequential. Oil refinery is near the open grassland, so for surface roughness was used 0.02.

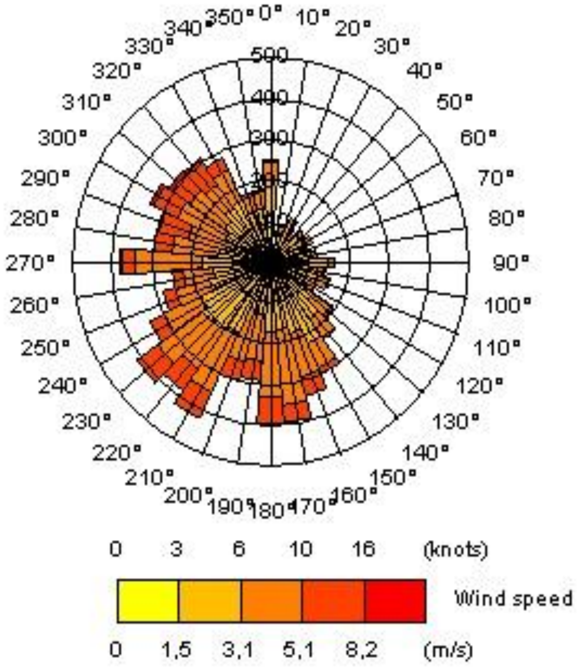


Fig. 4.2. Wind rose

To set up a AERO 2 model run were worked through the screens entering the relevant data: height (m), diameter (m), velocity (m/s), temperature of disposable pollutants (^{0}C), temperature of ambient air (^{0}C), factor assessing speed of settlement of pollutants. For modeling *F* – non-dimensional factor assessing speed of settlement of pollutants which depends from the efficiency of cleaning devices was chosen 2, because efficiency of the cleaning devices >90%. Maximum ground-level concentration of PM was determined under adverse meteorological conditions and dangerous wind speed. Dangerous wind speed is the wind speed where concentration of pollutants reach the highest concentration. Results of calculation of dangerous wind speed depends from the temperature and the high of the point pollution source. Distances from the pollution source were invented by accident.

Software package was used Surfer – a contour plotting package for easy and effective display of results. Surfer is a Golden Software package that can be used to create color contour plots of output such as concentration and deposition, 3D surface plots of terrain and vectors plots of wind velocity. Contours can be overlaid on digital base maps. Pollutants in ambient air were restricted in accordance with national criteria and a list of environmental pollution limit values, so results were analyzed according pollution limit values.

4.3 MODELING RESULTS

120 m stack emits the biggest amount of PM comparing with other pollution sources, so AERO 2 program calculated that the highest concentration of PM – 12 μg/m^3 was determined from 120 stack, there the most dangerous wind speed was determined also (Figure 4.3).

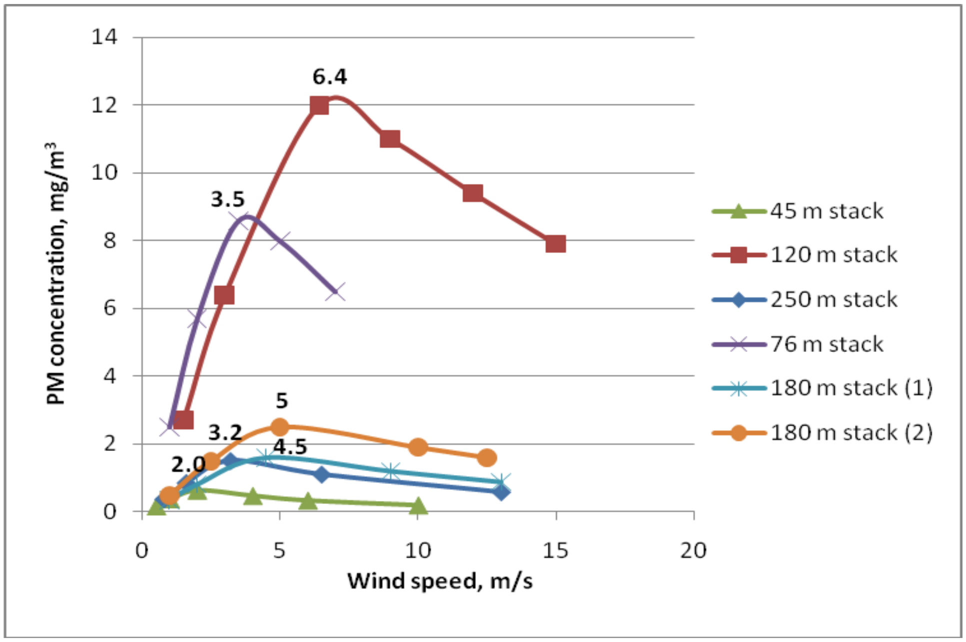


Fig. 4.3. PM distribution dependence from the dangerous wind speed in the impact zone of oil refinery

Figure 4.3 shows PM concentration dependence from the wind speed. Highest PM concentrations was determined where wind speed was the most dangerous.

The highest PM concentration was determined at 2 km. distance from the pollution source Obtained results showed that from the lowest stack (45 m) PM accumulated on the ground closest to the pollution source comparing with others – 0.5 km distance (Figure 4.4, 4.4a).

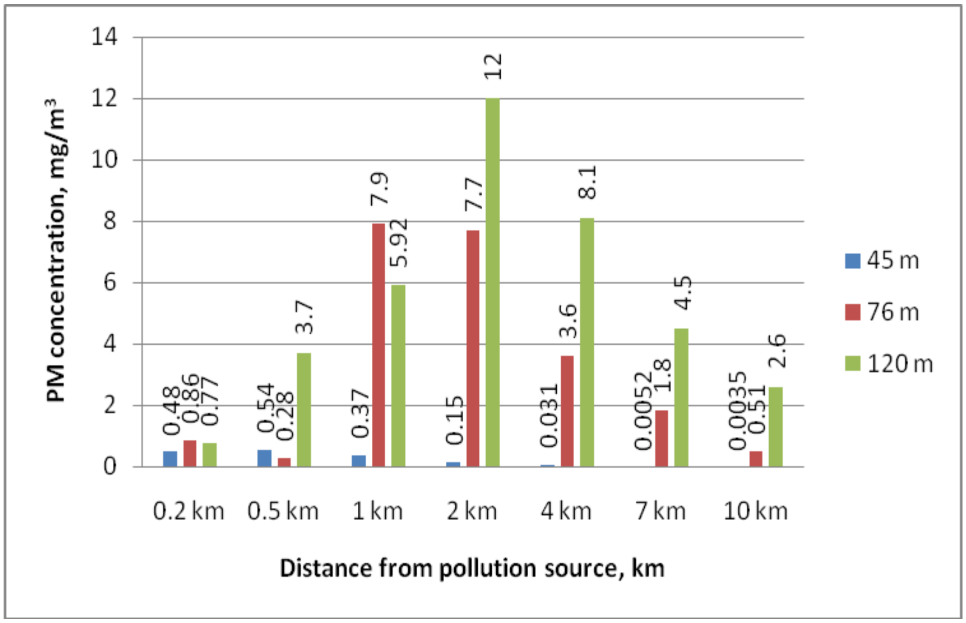


Fig. 4.4. Distribution of PM according distances from the impact zone of oil refinery

While the maximum concentration of PM 1.5 µg/m^3 from the highest stack (250 m) was determined at 2 km distance from pollution source. Highest PM concentrations from other stacks were determined at 1 – 2 km distance from pollution source.

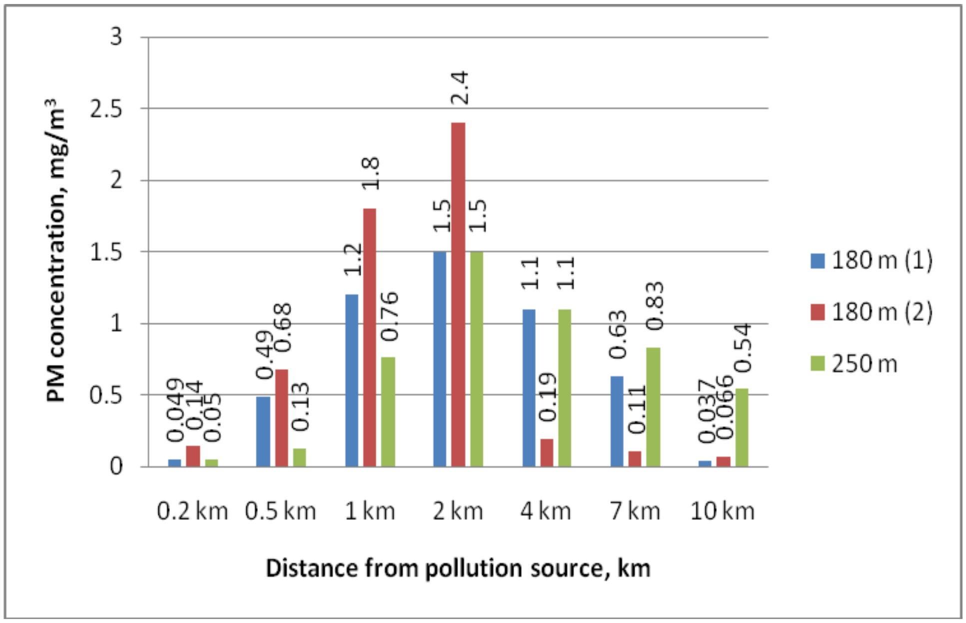


Fig. 4.4a. Distribution of PM according distances from the impact zone of oil refinery

To find out how the high of stack depends for the distribution of PM was made comparison between 250 m and 100 m stacks with the same input parameters. Results confirmed the trend that more stack is low more near the pollution source PM accumulates (Figure 4.5).

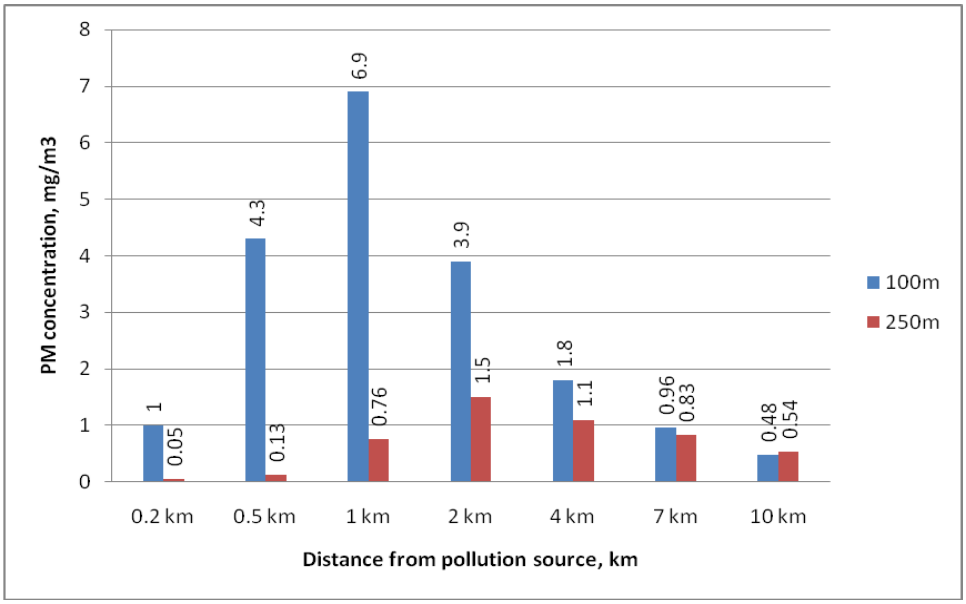


Fig. 4.5. Dependence between high of the pollution source (stack) and distribution of PM

ADMS 4 program calculated the dispersion of PM from multiple PM emission sources. For PM evaluation daily dispersion was calculated using 90.4 percentile. The highest PM daily concentration – 4.5 µg/m^3. Emissions did not exceed the allowed PM values – 50 µg/m^3.

Hourly emissions also did not exceed the allowed PM values – 40 µg/m^3. The highest determined hourly PM concentration – 1.2 µg/m^3. The general view of PM hourly and daily dispersion is presented in Figure 4.6 and Figure 4.7.

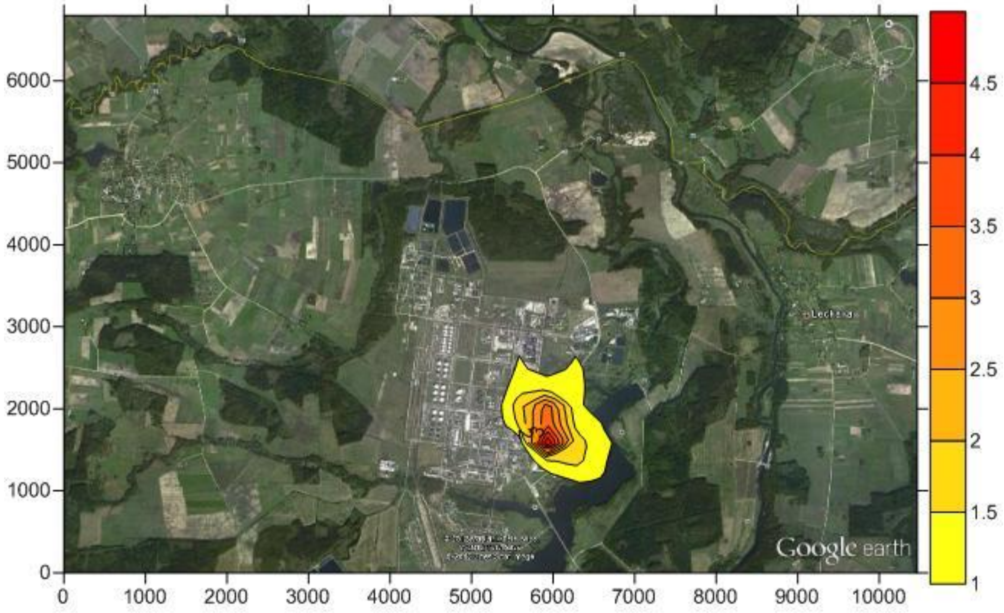


Fig. 4.6. Daily distribution of PM in the snow–cap in the vicinity of oil refinery

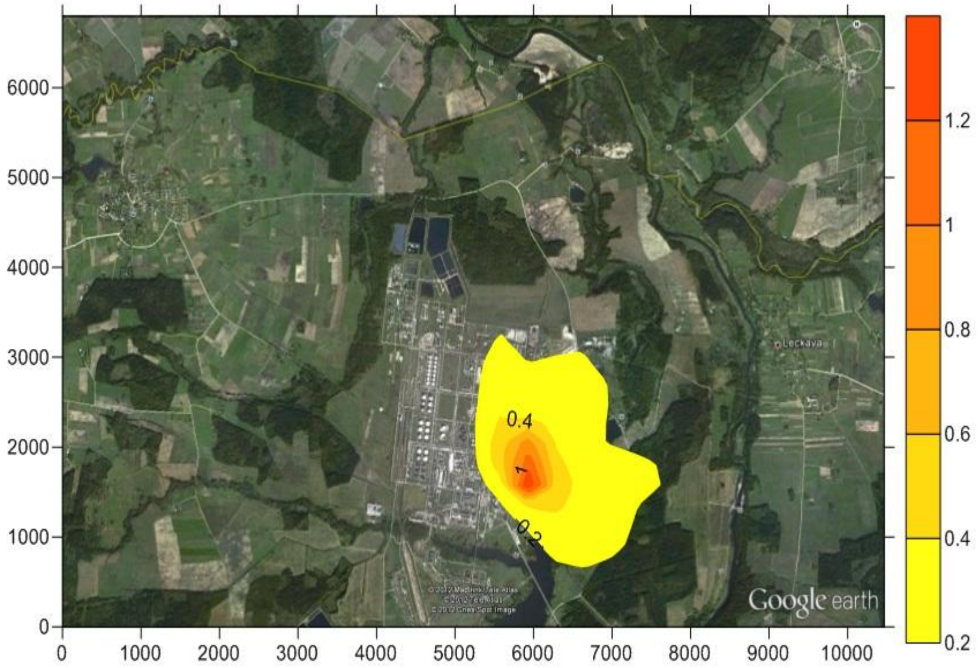


Fig. 4.7. Hourly distribution of PM in the snow–cap in the vicinity of oil refinery

Dispersion of PM was determined approximately at 1.5 – 2.2 km distance. PM concentration both hourly and daily were determined many times lower than was allowed, so oil refinery did not do significant impact for the environment.

Trying to find the tendency how the pollutants deposited on the ground-level (snow–cap) the results obtained during the simulation were compared with the results of experimental analysis (the daily load of snow-dust and insoluble form of heavy metals in the snow-dust). The highest concentrations of analyzed heavy metals in snow-dust and the daily load of snow-dust were determined approximately at 1.5 – 2 km distance from pollution source as well as highest concentration of PM determined with ADMS 4 and AERO 2 models. So we can state that snow–cap accumulated insoluble forms of pollutants.

REVIEW OF CHAPTER 4

1. The main task for modeling was to simulate PM in the air and breaks up the dependence between the pollutants in the air and snow–cap and to show concentration dependence from the wind speed. For modeling was used ADMS 4 (Atmospheric Dispersion Modeling System) and AERO 2 models. Results were assessed according allowed values of PM emissions. Hourly emissions is limited to 40 μg/m^3, daily – 50 μg/m^3.

2. Meteorological data was obtained from national meteorological service. Data usually comprises: hourly surface data comprising day, time and wind speed, wind direction, near surface temperature, precipitation, cloud cover or solar radiation as a minimum. The height at which the wind speed was measured has to be entered also.

3. ADMS 4 program calculated the dispersion of PM from multiple PM emission sources. For PM evaluation daily dispersion was calculated using 90.4 percentile. The highest PM concentration – 4.5 μg/m^3. Emissions did not exceed the allowed PM values. The highest determined hourly PM concentration – 1.2 μg/m^3.

4. Trying to find the tendency how the pollutants deposited on the ground-level (snow–cap) the results obtained during the simulation were compared with the results of experimental analysis (the daily load of snow-dust and insoluble form of heavy metals in the snow-dust). The highest concentrations of analyzed heavy metals and the daily load of snow dust were determined approximately at 1.5 – 2 km distance from pollution source as well as highest concentration of PM determined with ADMS 4 and AERO 2 models. So we can state that snow–cap accumulated insoluble forms of pollutants.

CONCLUSIONS

1. There is a clear technogenic transformation of the snow–cap chemical composition in the oil refinery impact zone: in prevailing wind directions (Zones 1 and 4) a 1.2 times higher daily load of snow dust was detected, in which concentrations of dangerous heavy metals Cr – 1.6, Cd – 17, Cu – 1.5 and Pb – 2.2 times were determined higher.

2. Closer to contamination area the part of soluble forms of metals relatively decreases, while the concentration of insoluble forms of metals increases 2.7 times when approaching the contaminated area. Analysis of heavy metals in snowmelt water and snow-dust confirms the trend that soluble forms of snow–cap in compare with insoluble ones (snow-dust) are many times lower. In this study soluble forms were determined thousands of times lower.

3. Concentrations of gaseous air pollutants (sulphur, chlorides and nitrates) were detected mostly in northern part of the oil refinery, while in other parts was not detected at all, it confirms the trend that accumulation of gaseous pollutants in the snow–cap is low in the vicinity of oil refinery.

4. Assessing the oil refinery impact for the environment was determined that hourly and daily emissions of PM concentration did not exceed the allowed values and according to the classification of the daily load of snow-dust, was determined a lower than medium-risk level of contamination in the oil refinery impact zone. The daily load was lower than <250 mg/m^2.

5. The highest concentrations of analyzed heavy metals (Cr, Pb, Cu, Cd) and the highest daily load of snow dust were determined approximately at 1.5 – 2 km distance from pollution source as well as highest concentration of PM determined with ADMS 4 and AERO 2 models. So we can state that snow–cap accumulated insoluble forms of pollutants.

6. Snow–cap as a natural short-term pollutant-depositing medium could be successfully used in Lithuanian conditions for indication of atmospheric air condition and identification of pollution sources, accordance with the rules of sampling methodology, meteorological conditions and estimating according to the severity scale.

RECOMMENDATIONS

1. According to our investigation data we recommend to analyze only the snow-dust to determine concentration of heavy metals, while analysis of snowmelt water in snow–cap is thousands of times lower. Low concentration shows higher error of determination.
2. An assessment of oil refinery total impact for ambient air quality can be improved using other methods at parallel, for example passive samplers, for the components which are non-deposited or poorly deposited in the snow–cap (SO_2, NO_x, VOC).
3. The models AMDS 4 and AERO 2 can be recommended for PM dispersion modeling in the impact zone of oil refinery.

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1. Krastinytė, V.; Baltrėnaitė, E.; Lietuvninkas, A. 2012. Analysis of snow-cap pollution for the air quality assessment in the vicinity of oil refinery. *Environmental Technology* (under review).

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1. Krastinytė, V.; Baltrėnaitė, E.; Lietuvninkas, A. 2012. Soluble and insoluble forms of pollutants in the snow-cap around vicinity of oil refinery. In:15th Conference of Junior Researches, Science – Future of Lithuania" 12 th April conference proceedings. Vilnius. (Under review).
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1. Krastinytė, V.; Baltrėnaitė, E.; Lietuvninkas, A. 2011. Analysis of the snow-cap as a tool to assess ambient air quality. 14th Lithuanian Conference of Junior Researches – "Science – Future of Lithuania" in Vilnius, April 14 th. (Poster presentation).

2. Krastinytė, V.; Baltrėnaitė, E.; Lietuvninkas, A. 2012. Soluble and insoluble forms of pollutants in the snow-cap around vicinity of oil refinery. 15th Lithuanian Conference of Junior Researches – "Science – Future of Lithuania" in Vilnius, April 12 th. (Poster presentation).

3. Krastinytė, V.; Baltrėnaitė, E.; Lietuvninkas, A. 2012. Air quality assessment in the vicinity of oil refinery using snow-cap as a tool. 12 th. Latvian Conference of Junior Researches in Riga, April 21st. (Oral presentation).

Participation in the internship

1. ERASMUS Internship from June 1th to August 30th at Plant Biology Department, Szeged University, Hungary. Participation in Cross-Border Co-operation project "Hungary-Romania" 2007-2013 Szeged-Timisoara axis for the safe food and feed. Master thesis statistical analysis was consulted by Prof. Erdei Laszlo and Peto Andrea.

2. Laster Master Degree semester studies at Ryga Technical University, under to 2012 year agreement No. 26354: General agreement of educational and scientific education between Vilnius Gediminas Technical University and Riga Technical University. The last part of Master thesis (modeling) was consulted by Dr. Ilze Dzene.

3. BALTECH scholarship award to participate in internship at Riga Technical University.

ANNEXES