UNIVERSITY OF NOVA GORICA
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COLLECTION, ANALYSIS AND CHARACTERIZATION OF PARTICULATE MATTER DEPOSITION IN AND AROUND KOPER

MASTER'S THESIS

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ABSTRACT

Air pollution with particulate matter is a serious environmental-health problem. For many years the inhabitants in the vicinity of the Port of Koper (Slovenian coast) have been pointing out the problem of the pollution of their residential area with emissions from the terminal EET in the Port of Koper. The research described in this thesis was undertaken to identify the particulate matter deposition and to estimate the influence of the Port of Koper on the total dust deposition in the surrounding area. Six sampling sites were used during the preliminary study of 2005/06, and during 2007/08 study ten sampling sites were placed around the Port of Koper. During study of 2005/06 (preliminary study) high values of particulate matter deposition were observed, the limiting value was exceeded 11 times, the highest value exceeded the limiting value by 12 times. During the study of 2007/08, monthly particulate matter deposition was considerably lower and did not exceed the recommended values at any of the sampling sites. Samples were analyzed gravimetrically, content of individual metals was determined, gamma-ray emitter's activity of coal and iron ore was measured, particles were examined using electron microscopy, and the ratio of stable carbon isotopes was measured. For a quick screening of the polluted environment, a new device for quick estimation of direction and quantity of airborne particulate matter and therefore determination/estimation of the main emission sources of dust particles in the observed area was developed. Based on the analysis of samples using electron microscopy coal particles were detected and therefore dust deposition can be attributed to activity in the EET in Port of Koper. Also according to the results of alternative sampling device, the Port of Koper is one of the sources of dust particles in the study area. Low values of particulate matter deposition during study 2007/08 could be attributed to the introduction of preventive measures (by the Port of Koper) and mild weather conditions (low wind speed and humidity of the terrain).

Key words: air pollution, particulate matter deposition, port activities, coal and iron ore

POVZETEK

Onesnaženost zraka s prašnimi delci je resen okoljski in zdravstveni problem. Prebivalci v okolici Luke Koper (slovenska obala) že vrsto let opozarjajo na problem emisij prašnih delcev s terminala za razsute tovore (EET) v Luki Koper v njihovo okolje. Predstavljena raziskava se je izvedla z namenom ugotavljanja razsežnosti problema in definiranjem doprinosa Luke Koper k celotni masi prašne usedline na opazovanem območju. V preliminarno študijo je bilo vključenih 6, v študijo 2007/08 pa 10 vzorčevalnih mest. V obdobju preliminarne študije (2005/06) so bile izmerjene vrednosti prašne usedline visoke, mejna vrednost je bila presežena 11 krat, najvišja vrednost je mejno presegala za 12 krat. V obdobju 2007/08 so bile vrednosti zbrane prašne usedline nizke in niso v nobenem primeru presegle priporočenih vrednosti. Vzorci so bili analizirani gravimetrično, določena je bila vsebnost kovin v posameznem vzorcu, izmerjena aktivnost sevalcev gama v premogu in železovi rudi, izvedena je bila analiza z uporabo elektronskega mikroskopa, merjeno je bilo razmerje stabilnih izotopov ogljika. Razvita je bila nova naprava za določanje hitre ocene smeri razširjanja ter ocene količine lebdečih delcev in s tem identifikacijo glavnih emisijskih virov na opazovanem območju. Z uporabo elektronskega mikroskopa smo v vzorcih prašne usedline dokazali med ostalimi delci prisotnost premoga, s čimer smo dokazali povezavo med prašno usedlino in dejavnostjo na terminalu EET v Luki Koper. Tudi rezultati uporabe alternativnih merilnikov kažejo na Luko Koper kot na enega od virov prašnih delcev v okolju. Zmanjšanje vrednosti prašne usedline v obdobju 2007/08 pa pripisujemo uvedbi preventivnih ukrepov (s strani Luke Koper) in ugodnim vremenskim razmeram (nizke jakosti vetra in vlažnost terena) v času opazovanja.

Ključne besede: onesnaženost zraka, prašna usedlina, luška dejavnost, premog in železova ruda

ABBREVIATIONS

ACGIH - American Conference of Governmental Industrial Hygienists
AED - Aerodynamic Equivalent Diameter
ARSO - Environment Agency of the Republic of Slovenia = Agencija Republike Slovenije za okolje
CEN - The European Committee for Standardization = Comité Européen de Normalisation
DIN - Deutsches Institut für Normung (German Institute for Standardization)
DNA - Deoxyribonucleic acid
EET - European Energy Terminal
EIMV - Milan Vidmar Electric Power Research Institute = Elektro inštitut Milan Vidmar
EPA - Environmental Protection Agency (USA)
IARC - International Agency for Research on Cancer (WHO)
IJS - Jožef Stefan Institute = Inštitut Jožef Stefan
ISO - International Organization for Standardization
MOP - Ministry of the Environment and Spatial Planning of the Republic of Slovenia = Ministrstvo za okolje in prostor Republike Slovenije
PAH - Polycyclic Aromatic Hydrocarbons
PINT - Primorska Institute of Natural Sciences and Technology = Primorski inštitut za naravoslovne in tehnične vede
PM - Particulate Matter
PM_{10} - Particulates with an aerodynamic diameter smaller than or equal to 10 µm
$PM_{2,5}$ -Particulates with an aerodynamic diameter smaller than or equal to 2,5 µm
ROS - Reactive Oxygen Species
SEM/EDXS - Scanning Electron Microsopy / Energy Dispersive X-ray Spectroscopy
TSP - Total Suspended Particles
VDI - Association of German Engineers = Verein Deutscher Ingenieure
WHO - World Health Organization
WTC - World Trade Center

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1 INTRODUCTION

Airborne particulate matter has various origins. The sources may be natural or anthropogenic, linear, point or dispersed, the particulate matter could be also primary or secondary by origin. Their presence due to their concentration, chemical composition and size, however, has negative impacts on human health and on the environment. Fine particles have the ability to penetrate deep into the respiratory system, and larger particles are disturbing because of their deposition on the land, plants, etc. Particulate matter from airborne deposition is often a complex mixture of particles having different sizes, chemical composition and origins. Not only size but also chemical structure and physical properties of particles are important due to estimation their influence on public health and environmental quality.

There are many point and linear sources of different air pollutant emitters in the coastal area around the Gulf of Koper. In this area, there is the largest petroleum products warehouse in Slovenia (emissions of benzene, toluene), a chemical company Kemiplas (emission of formaldehyde, acetaldehyde), a waste incinerator and an ironworks in Trieste (dioxins, furans, dust particles). In addition, pollution from traffic (individual transport, heavy trucks, ships, railway transport) increases the ground-level ozone in summer months. A lot of pollution comes also from Italy as long distance transport of pollution (especially transport of polluted air with the western winds from the Po river basin) (Klein et al., 2007; Gauss et al., 2008; Nyiri et al., 2009). Origin of the particles deposited in Ankaran and its near-by residential areas could be a combination of the combustion, traffic, industry, agriculture, land use etc., and, in our case deposition of different materials (coal and iron ore) from the stockpiles at the Port of Koper. Emissions of airborne particles therefore can originate from other sources also from various ore depots, coal pits or even quarries and as such represent nuisance in residential areas. In addition, natural sources such as soil dust, pollen, parts of animals (insects) and parts of plants could contribute to the total deposited material in observed area.

Various epidemiological studies (for details see Section 1.3) confirmed correlations between increased concentrations of particulate matter in air and increased incidences of respiratory and cardiovascular diseases. Additionally, for several years the inhabitants of Ankaran and the near by residential area have been complaining about deposition of dust, which may originate from coal and iron ore handling and warehousing at the European Energy Terminal (EET) in Port of Koper (see Figures 3 and 4).

Till now no study dealing with the contributions of particulate matter emissions from Port of Koper to surrounding area has been conducted. The purpose of this master's work was the collection, analysis and characterization of dust deposition in the area of the Municipality of Koper to determine what, if any, impact the outdoor coal and iron ore storage depots have on the deposition of particulate matter on the residential areas. The simple method of collecting dust deposition was used (Bergerhoff sedimentators). Additionally collected samples were analyzed by various methods with the goal to identify the source of particles and their characterization. Also a simple measurement device, based on deposition and/or adhesion was developed.

1.1 Port of Koper and its activities at EET

The Port of Koper is a multi-purpose port, located in coastal region of Slovenia. The basic port activity is carried out at specialized terminals, which are technically and organizationally suitable for handling and warehousing of specific cargo groups. General transfer of port operations and warehousing performed on twelve specialized terminals (Passenger terminal, Fruit terminal, General cargo terminal, Timber terminal, Container and Ro-Ro terminal, Liquid cargoes terminal, Livestock terminal, Terminal for cereals and fodder, Terminal for minerals, Alumina terminal, Car terminal and European energy terminal) (http://www.luka-kp.si). Port of Koper is fully embedded in the international trade and global commerce. Only 30 percent of transfer is made for Slovenian needs, all the rest of the transit for the wider hinterland - notably Austria, Italy, Hungary, Czech Republic, Slovakia, southern Germany, Italy and the Balkan countries (Port of Koper, 2009).

Economic Zone Area of Port of Koper covers 2,720,000 m^2, of which 247,000 m^2 of closed warehouses, 76,000 m^2 covered warehouses, 900,000 m^2 of open storage areas, 49,000 m^3 shore tanks and 81,000 tones of silos. The port has two piers with a total of 25 berths and total quay length of 3,1 km (Port of Koper, 2009; Topič, 2009).

EET - European Energy Terminal

At the European Energy Terminal (EET) in the Port of Koper, large amounts of coal and iron ore are handled and warehoused. Cargo comes mainly from Indonesia, South America and South Africa. The terminal includes a closed conveyor belt system which links 630 m of quay with a open storage areas and wagon loading station. The terminal offers additional services including screening, blending and crushing. The storage capacity of the ore depot is 500.000 tones for coal ore and 300.000 tones for iron ore. The area covered by the coal and iron ore is 108.500 m^2. The daily capacity for unloading coal is 17.000 t (cape size vessel) or 15.000 t (panamax vessel) and for iron ore (cape size vessel) is 25.000 t (http://www.luka-kp.si; Topič, 2009).

One of the major sources of dust in the area of the Port of Koper represents the activities at the EET. It is important to emphasize that the emission of particles results not only from the manipulation of ore (off- or on- loading) but also from ore storage. The landfill itself represent a significant source of emission, particularly during strong winds (Poljšak et al., 2006). Dust control measures which the Port already introduced include construction of an 11 m high anti-dust emission wall, spraying the body of the landfill with water and wet cleaning of the transportation roads around the landfill at least twice per day. However, when a strong wind blows unexpectedly, the dusting is not suppressed completely. Because the landfill is not completely closed, it is still exposed to the weather conditions (e.g. strong winds).

The quantities of bulk cargoes manipulation on the EET during the period from September 2005 to October 2006 are shown in Table 1 and Figure 1. Those for the time period from December 2007 to May 2008 (time period of the study) are shown in Table 2 and Figure 2. Unloading of iron ore is quite constant during entire year with the exception of March when unloading is minimal. Quantity of unloaded iron was increased in year 2007/08 by 16% compared to 2005/06. The amount of the unloaded coal varies throughout the year. Maximum unloading and up-loading in both time intervals (2005/06 and 2007/08) occur during January, February and March, during this period significantly increased also the total ore unloading / up-loading. Another higher values occur during October and November. In time period 2005/06 total amount of unloading iron ore were 1.633.283 tons and 4.100.269 tons of coal while in time period 2007/08 total amount of unloaded iron ore were 1.899.269 tons and 4.395.897 tons of coal, what means manipulation with bulk cargo in Port of Koper increased in year 2007/08 compare to the year 2005/06 by 10%, mainly on account of transfer of iron ore (16%) and slightly less (7%) for unloading of coal. In 2007/08 amount of the coal manipulated at EET is much higher (41%) compare to year 2005/06 since additionally loading on the ship is included.

Table 1: EET - manipulation with coal and iron ore for the time period from 1st September 2005 to 31th October 2006 (in tons)

	IRON ORE	COAL	IRON ORE AND COAL
September	*	289,435	289,435
October	324,453	271,903	596,356
November	*	343,636	343,636
December	166,496	232,945	399,441
January	191,590	497,371	688,961
February	139,603	471,791	611,394
March	3,639	708,295	711,934
April	142,575	269,685	412,260
May	191,711	320,364	512,075
Jun	145,462	287,287	432,749
July	164,200	270,301	434,501
August	163,554	137,256	300,810
SUM	1,633,283	4,100,269	5,733,552

Source: Department of environment and health at work of Port of Koper

* - data were not available

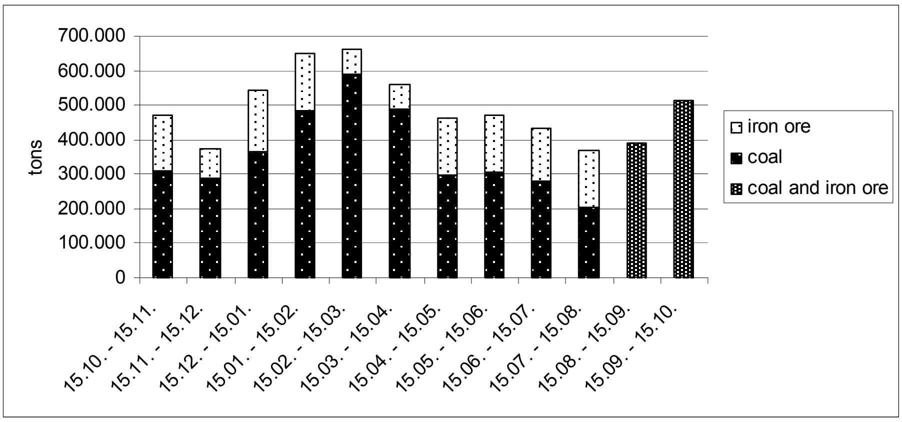


Figure 1: Quantities of coal and iron ore manipulation at EET - 2005/06

Table 2: EET - manipulation with coal and iron ore for the time period from 1st December 2007 to 30th November 2008 (in tons)

	IRON ORE			COAL		
	upload	unload	sum	upload	unload	sum
December 07	0	163,700	163,700	120,161	281,501	401,662
January 08	0	164,225	164,225	121,948	345,892	467,840
February 08	0	159,625	159,625	99,051	586,923	685,974
March 08	0	7,464	7,464	167,423	405,117	572,540
April 08	0	221,804	221,804	126,250	278,393	404,643
May 08	0	116,094	116,084	83,097	405,498	488,595
Jun 08	0	191,944	191,944	92,760	270,422	363,182
July 08	0	165,997	165,997	133,052	222,476	355,528
August 08	0	191,340	191,340	139,237	228,495	367,732
September 08	0	161,916	161,916	55,651	498,859	554,510
October 08	0	191,922	191,922	101,589	431,528	533,117
November 08	0	163,248	163,248	147,626	440,793	588,419
SUM	0	1,899,279	1,899,269	1,387,845	4,395,897	5,783,742

Source: Department of Environmental and Occupational Health of Port of Koper

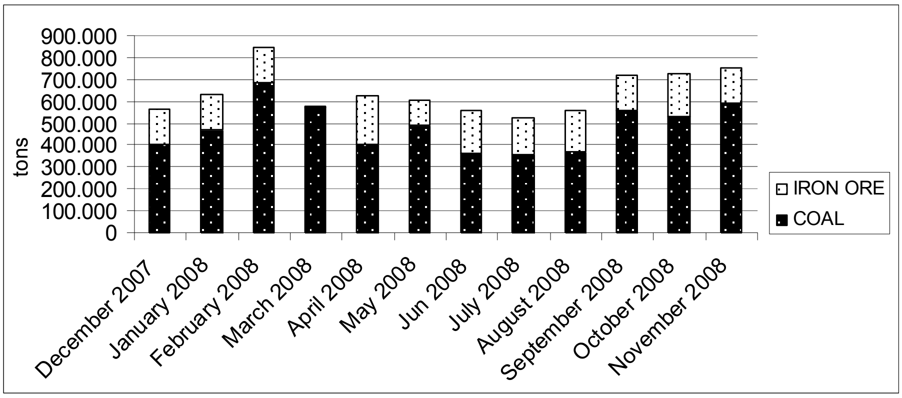


Figure 2: Quantities of coal and iron ore manipulation at EET - 2007/08

1.2 Inhabitants in near by residential area and their perceptions of dust emissions

For many years the inhabitants of Ankaran (distance from the iron ore and coal storage sites is approximately 1800 m) and its surroundings (the closest residential area is 1000 m from the storage sites) have been complaining about the pollution of their residential area with emissions from the terminal EET in the Port of Koper. Particulate matter depositions are visibly perceived on their yards, places of residence, linen and vegetables (Figure 3 and Figure 4). The results of the study of environment pollution in Ankaran (ARSO, 2005) made by the Environment Agency of the Republic of Slovenia (ARSO) show the 24 hour limiting value for particles PM_{10} was exceeded. With respect to wind direction, the distribution showed an increased concentration of particles during the mistral wind. Consequently, it can be assume, considering the location of the sampling site, a direct influence of the Port of Koper, specially the landfill EET on the dust emissions. The same study ascertained a very strong correlation between the particles PM_{10} and the presence of iron. The correlation factor was 0.91.

Figures 3 and 4: Rožnik residential area (approx. 1000 m from landfill) – after strong wind, October 2006. 3. clean gauze and 4. gauze after wiping the floor.

The mentioned perceptions of the inhabitants were one of the reason for starting the study presented in this master thesis work.

The presence of Škocjanski zatok and the nearby Youth Health and Holiday Centre, Debeli rtič, are additional reasons why the area around Port of Koper is sensitive.

1. Škocjanski zatok Nature Reserve is the largest brackish wetland in Slovenia. It is located on the outskirts of the coastal city of Koper and consists of brackish lagoon surrounded by reedbeds and agricultural land which is to be turned into a freshwater marsh. An outstanding quality of the Nature Reserve is its rich flora and fauna which boasts a number of rare or endangered Slovenian species (http://www.skocjanski-zatok.org).
2. Also the Youth Health and Holiday Centre Debeli rtič, is the only sea health centre for children in Slovenia. The health services in the spa are based on the favorable and mild climate and the sea water, a benefit for natural health treatment of children with respiratory diseases. They are specialized for respiratory diseases (bronchial asthma, chronic obstructive

pulmonary diseases, pulmonary emphysema, post-injury conditions as well as postoperative conditions of the thorax and lungs) and have some special programs for children with asthma.

1.3 Particles in air and their influence on health

Air pollution has both acute and chronic effects on human health. Health effects range from minor irritation of eyes and the upper respiratory system to chronic respiratory disease, heart and vascular disease, lung cancer and death. Among other pollutants, particulate matter is severe health and environmental problem. Particles in air can impact the health merely because of their presence, or because of a specific chemical composition or morphological structure, they can have additional harmful influences on health. In most cases, the most susceptible organs are the lungs and the respiratory tract. Some air pollutants, such as fine particles, can also damage other organs. Humans come in contact with different air pollutants primarily via inhalation and ingestion, while dermal contact usually represents a minor route of exposure for air pollutants. Air pollution additionally contributes to the contamination of food and water, which makes ingestion in several cases additional route of pollutant intake.

The presence of particles in the air is associated with asthma, chronic bronchitis and reduction of pulmonary function (Vallero, 2008; Likar and Bauer, 2006). Several epidemiological studies (Hoek et al., 2002; Clancy et al., 2002; Miller et al., 2007) showed a connection between the elevated concentration of particles in the air and the increase of diseases of the respiratory tract and cardiovascular diseases, regardless of the chemical structure of the particulate matter. Hospital admission for cardiovascular and respiratory diseases are related with concentration of fine particles in air (Dominici et al., 2008). Exposure to particles in air can affect health, while elevated concentration of fine particle has a direct influence on morbidity and mortality (Samet et al., 2000; Hoek et al., 2002; Clancy et al., 2002; Pope III et al., 2002) and therefore, can have a direct influence on reduced life expectancy (Kampa and Castanas, 2007). Also larger particles have health effects. In dust samples after WTC twin towers collapse (Lioy et al., 2002) a complex mixture of coarse particles and fibers consisting of relatively larger particles (> 90% of dust particle mass was > 10 µm in diameter) was found. Once inhaled, particles > 2.0 µm in diameter are most commonly deposited in the upper airways, causing significant irritation. Among firefighters working in ground zero area increased incidence of upper airway symptoms (nasal congestion/drip, throat irritation, cough, and gastro esophageal reflux) occured (Fireman et al., 2004).

Atmospheric particles affect health when they enter the respiratory system. Depth of penetration and deposition of particles depends on the size of particle, the defense capabilities of the respiratory tract and the respiratory pattern (Godish, 2004). Godish (2004) also mentioned that particles of aerodynamic diameter of 10 µm are large enough to be retained by nose hairs and the defense system of upper respiratory tract. According to Stropnik (1994) particles with aerodynamic diameter larger then 15 µm can not penetrate in deeper lungs, therefore have no direct influence on health. According to Bilban (1999) the upper airways path excluded especially larger or very small dust particles due to inertia on the bends. Particles larger than 5 µm hit the wall and adhere to the mucus. Such particles together with mucus are excreted through the nasal cavity. Protective system of the upper respiratory tract is the least effective for the dust particles with aerodynamic diameter from 0.25 up to 5 µm. These particles thus represent the greatest health impact.

The health effects of particulate matter (PM) depend on their mass concentration and where they are deposited in the respiratory tract. An international harmonization of particle size-selective sampling criteria defined by the American Conference of Governmental Industrial Hygienists (ACGIH), International Organization for Standardization (ISO), and the Comité Européen de Normalisation (CEN) was adopted (Park et al, 2009). These criteria were defined as inhalable, thoracic, and respirable with their 50% cutoff sizes at an aerodynamic equivalent diameter (AED) of 100 µm, 10 µm, and 4 µm, respectively. These PM size fractions deposit in a particular region of the respiratory tract: the inhalable fraction entering the upper airways beyond the nose and mouth, the thoracic fraction depositing beyond the larynx and the respirable fraction reaching the airspace deep in the lungs (alveoli).

Depending on the ability of penetration and deposition in respiratory system Tran and Kuempel (2007) divided aerosols into three groups as inhalable, thoracic and respirable. The respirable particles size distribution includes the ultrafine or nanoparticles (<0.1 µm), fine particles (<2.5 µm) and coarse particles (<10 µm).

Stropnik (1994) distinguished two types of aerosols; inhalable and respirable aerosols. Particles smaller than 15 µm and greater than 2.5 µm (inhalable aerosols) are generally retained in the upper parts of respiratory system, nose, throat and esophagus. Respirable aerosols represent particles that have aerodynamic equivalent diameter of less than 2.5 μm and therefore penetrate deeper in the respiratory system all the way to pulmonary vesicles, where they may be retained for several days or even months.

The most exposed group in the population to air particles are children, because the particles penetrate deeper in their lungs as compared to adults becouse children they breathe deeper and faster, they spend more time outdoor and they are more active (Likar, 1998). The polluted air slows down the development of pulmonary functions in children (Gauderman et al., 2000; Gauderman et al., 2004). Senior citizens, especially those with a weakened cardiovascular and respiratory system, are a high risk group too (Vallero, 2008). Another risk group is patients with chronic pulmonary emphysema, asthma or cardiovascular diseases (Vallero, 2008).

However, epidemiological studies on large populations have been unable to identify a threshold concentration below which ambient PM has no effect on health. It is likely that within any large human population, there is such a wide range in susceptibility that some subjects are at risk even at the lowest end of the concentration range(WHO, 2003).

Coal

Coal has been described as the most significant pollutant of all fossil energy sources producing important polluting compounds as sulfur dioxide and its derivatives and many other impurities. Different manipulation with coal therefore can cause air pollution. Exposure to coal is considered as an important non-cellular and cellular source of reactive oxygen species that can induce DNA damage as shown for wild rodents in an open coal mining area (Leon et al., 2007). In addition, spontaneous combustion can occur in coal stockpiles resulting in releasing combustion by-products (polycyclic aromatic hydrocarbons - PAH) in environment. Several of these PAH exhibit well-known mutagenic and carcinogenic activity.

Coal particles belong according to the categorization of the International Agency for Research on Cancer (IARC) in group 3 - the agent is not classifiable as to its carcinogenicity to humans, which means that there were not enough studies made to confirm carcinogenicity, however it is not excluded (IARC, http://monographs.iarc.fr/ENG/Classification/crthalllist.php). Coal particles are, due to their chemical structure and their morphology, capable of binding with diverse pollutants, causing synergistic effects between various substances (Vallero, 2008).

Few if any studies regarding these phenomena have been reported. When a particle such as coal gets into the lungs, it reacts with the pulmonary cells, irritates them and releases the pollutants bound to it (Vallero, 2008). Coal particles can cause allergic reactions in upper respiratory tracts and lungs (Potkonjak, 1979; Zawisza, 1982). That is why its toxicity is connected mainly to the size of the particles and the presence of other pollutants in the air. Additionally Huang et al. (1993), Dalal et al. (1995) and Smith et al. (1998) support idea that presence of iron in coal is reason for reactive oxygen species (ROS) formation and therefore influence on health.

Long exposure to coal dust can lead to so called black lung disease, also known as coal workers' pneumoconiosis (http://en.wikipedia.org; Bilban, 1999). It is a common affliction of coal miners and others who work with coal, similar to silicosis from inhaling silica dust and to the long-term effects of tobacco smoking. Inhaled coal dust progressively builds up in the lungs and is unable to be removed by the body; that leads to inflammation, fibrosis, and in the worst case, necrosis. Coal workers' pneumoconiosis, in its most severe state, develops after the initial, milder form of the disease known as anthracosis (anthrac - coal, carbon). This is often asymptomatic and is found to at least some extent in all urban dwellers (Cotran et al., 1999 in http://en.wikipedia.org) due to air pollution. Coal dust can also increase the risk of developing chronic obstructive pulmonary disease. Both (black lung and chronical obstructive pulmonary disease) can be linked with working in a coal mine, coal trimming (loading and stowing coal for storage), mining or milling graphite, manufacturing carbon electrodes and carbon black. The severity of pneumoconiosis depends on the type of coal and the dust conditions in the working (http://www.webmd) and living environment.

Metals

Kodavanti et al. (2008) established a connection between metals in small particulate matters (particularly zinc) and the phenomenon of pulmonary inflammation in laboratory animals. Pulmonary inflammation in most cases resulted in the damage of the cardiac muscle. Authors concluded that the fine particles in outdoor air contain significant concentrations of various metals, in most cases also significant concentration of zinc. Beside zinc in particulate matter deposition a considerable amount of other metals, such as lead and iron is present (Vallero, 2008). Iron oxide is a potentially dangerous substance because it is a catalyst for the reaction according to Fenton's chemistry (Dalal et al, 1995; Evans, 2000). In this reaction hydrogen peroxide, which is a normal metabolite in pulmonary cells, in the presence of iron forms a hydroxyl radical, which is the most active and most aggressive free radical. Hydroxyl radicals directly destroy cells, degrade cellular membranes, proteins and cellular deoxyribonucleic acid (DNA) and cause mutations. In the legislation, iron oxide is not yet declared as toxic. However, the latest studies support the above mentioned mechanism of action (Smith et al., 1998; Evans, 2000; Reilly and Aust, 2000). Also in the case of iron oxide the size of the particles has the main role in determining its danger for health (Smith et al., 1998).

Chronic inhalation of high concentrations of iron oxides fumes or iron dust might result in deposition of iron in tissue and therefore development of pneumoconiosis, called siderosis. Causative agent can be iron oxide present in welding material, foundries and iron ore mining; also it can be caused by powdered hematite (http://en.wikipedia.org). The iron ore in EET depot is mostly hematite, the mineral form of iron (III) oxide (Fe_2O_3) (Topič, 2009).

Slovenia - Koper

Analysis of the epidemiological study made by the Institute of Public Health Celje (Eržen et al., 2003) on the health status of the residents in the Municipality of Koper shows an increase of chronic respiratory diseases and allergic illnesses among children. Also an increase in the number of women with lung cancer, which is 1.6 times higher than the Slovenian average, a result of the pollution load on the study area, was detected. Both observations indicate on the air pollution as the causative agent.

1.4 Particulate matter - PM

Particulate matter is a common physical classification for particles found in air (atmosphere) such as dust, dirt, soot, smoke and liquid droplets. Unlike other pollutants (O_3, CO, SO_2, NO_x, Pb etc.) particulate matter is not a specific chemical entity. Rather it's a mixture of particles of different origin, that differ in size, composition and chemical or physical properties (WHO, 2003; Vallero, 2008). The term aerosol is often used synonymously with PM (Bolte et al., 2007; Baron and Willeke, 2005; Vallero, 2008). An aerosol can be suspension of solid or liquid particles in air and includes particles as well as vapor or gas phase components of air.

Atmospheric particles (alternatively referred to as particulate matter - PM) are tiny particles of solids or liquids suspended in air. These particles vary in size and density (EPA, 2008). They originate as a result of processes on the surface of the earth and in the atmosphere (Bolte et al., 2007). They may be either emitted directly into the atmosphere or formed there by chemical reactions (Finlayson Pitts and Pitts, 2000). Particles may be emitted naturally or have an anthropogenic origin. Therefore, some naturally occurring particulates originate from volcanoes, dust storms, forest and grassland fires, living vegetation and sea spray. Human activities, such as the burning of fossil fuels in vehicles, power plants and various industrial processes also generate significant amounts of aerosols. The main problem of pollution represents anthropogenic sources; however, natural pollution is not negligible. Large scale natural pollution (such us volcanic eruptions (Tambora, Krakatao, Mt. St. Helen, El Chinchón, Pinatubo) and large scale fires may lead to regional or global effects (Bizjak, 2009). According to the origin and specific characteristics particles differ in size, mass, density, morphology, chemical composition and have various chemical and physical properties (Godish, 2004; Baron and Willeke, 2005). Finlayson Pitts and Pitts (2000) state that size is the most important characteristic since it is related to their (particles) effects on health, visibility and climate. According to their properties particles settle out from the atmosphere in matter of minutes if they are small and dense or remains suspended for days, even weeks, also depend on weather conditions. According to Stropnik (1994) the majority of particles in air represent size fraction from 0.01 to 10 μm. Also Godish (2004) refers that particles smaller than 20 μm because of their aerodynamic properties are those of special concern since they may remain suspended in air and depending on size and density settle out slowly.

Atmospheric particles can be primary or secondary according to their origin and formation process. Primary particles in the air are the result of direct emissions in the atmosphere from different natural or anthropogenic sources (Bolte et al., 2007). However, secondary particles occur in air as a result of different chemical reactions among particles, gases, H_2O and vapor (Godish, 2004). Emission of primary particles can occur from stationary sources (such as factories, power plants etc.) or from moving vehicle (mobile sources). Such particles could be emitted directly from moving vehicle (internal combustion engine) or indirectly when particles are re-suspended due to movement of the vehicles. Also non-point or areas sources are known when the sources represent larger areas (construction sites, large open stockpiles, open-pit mining, quarry...) (Vallero, 2008).

Shape

Particles vary in shape from simple sphere or different cubes to many irregular shapes. Shape is often determined by particle's chemical composition and the process under which particle was formed (Godish, 2004) and have important influence on various factors such as drag force, light scattering, electrical charging, or in some cases even toxicity (Murphy, 1984).

As particles are often irregular non-spherical (for example, asbestos fibers), there are many definitions of particle size (Baron and Willeke, 2005). The most widely used definition is the aerodynamic diameter or aerodynamic equivalent diameter (AED) (Godish, 2004; Baron and Willeke, 2005). Particulate aerodynamic behavior is expressed in terms of the diameter of an idealized sphere. A particle with an aerodynamic diameter of 1 micrometer moves in a gas like a sphere of unit density (1 gram per cubic centimeter or 1000 kg/m^3) with a diameter of 1 micrometer.

The aerodynamic properties of particles determine how particles will be transported in the atmosphere, how they can be removed from it and their behavior in gas suspension (Baron and Willeke, 2005). These properties also govern how far they get into the respiratory system.

The sampling and description of particles is based on this aerodynamic diameter, which is usually simply referred to as ‘particle size’. Particles having the same aerodynamic diameter may have different dimensions and shapes.

It is convenient to classify particles by their aerodynamic properties because:
- these properties govern the transport and removal of particles from the air
- they also govern their deposition within the respiratory system
- they are associated with the chemical composition and sources of particles (WHO, 2003).

Size

The size of a particle is determined by how a particle is formed. Combustion, for instance generates very small particles, while coarse particles are usually formed via mechanical processes (Vallero, 2008). Atmospheric particles differ in size over many orders of magnitude from <0.005 nm to several hundreds µm (Murphy, 1984; WHO, 2003; Godish, 2004).

According to size atmospheric particles are divided into two major fractions, course particles and fine particles (Godish, 2004; Vallero, 2008). Coarse particles are particles with aerodynamic diameters larger than 2.5 μm and fine particles are smaller than 2.5 μm. Fine particles can be further classified on the basis of accumulation modes, Aitken nuclei and ultrafine particles (Godish, 2004). Most of the total mass of airborne particulate matter is usually made up of fine particles ranging from 0.1 to 2.5 μm. Ultrafine particles often contribute only a few percent to the total mass, though they are the most numerous, representing over 90 % of the number of particles (http://en.wikipedia.org). Many of them can harm our health, especially very small particles that can enter deep into the lungs.

Most coarse particles are in the size from 2.5 to 10 μm, but they could be as large as several tens of micrometers or even more. Fine particles as well as course particles with diameter up to 10 μm tend to remain suspended in the atmosphere for long period of time and are described as suspended particles. Larger particles with aerodynamic diameter larger than 100 μm tend to settle out fast and therefore are described as settleable particles (Godish, 2004). Large particles are generally of less concern since they rarely travel long distances. Therefore, they are usually measured only if a large particulate emitting source (e.g. coal mine etc.) is nearby (Vallero, 2008). Large particles (also known as dust or grit) are therefore a major cause of nuisance, but can also be a cause of health and other problems, either from direct inhalation or ingestion or through secondary pathways after they have deposit (Hall et al., 1993).

The largest particles or coarse fraction are mechanically produced by the break-up of larger solid particles. These particles can include wind-blown dust from agricultural processes, uncovered soil, unpaved roads or mining operations. Traffic produces road dust and air turbulence that can stir up road dust. Near coasts, evaporation of sea spray can produce large particles. Pollen grains, mould spores, and plant and insect parts are all in this larger size range. The amount of energy required to break these particles into smaller sizes increases as the size decreases, which effectively establishes a lower limit for the production of these coarse particles of approximately 1 μm. Fine fraction of particles are largely formed from gases. The smallest particles, less than 0.1 μm, are formed by nucleation (condensation of low-vapor-pressure substances formed by high-temperature vaporization or by chemical reactions in the atmosphere) to form new particles (nuclei). Four major classes of sources with equilibrium pressures low enough to form nuclei mode particles can yield particulate matter:

heavy metals (vaporized during combustion), elemental carbon (from short C molecules generated by combustion), organic carbon and sulfates and nitrates. Particles in this nucleation range grow by coagulation among two or more particles to form a larger particle or by condensation of gas or vapor molecules on the surface of existing particles (WHO, 2003).

Chemical composition

The composition of aerosol particles depends on their source. Particles in air are aggregates of many molecules, sometimes of similar ones but usually of dissimilar ones (Vallero, 2008). Therefore particles suspended in the atmosphere contain hundreds of different chemical compound due to large number of sources of primary particles, formation of secondary particles in air by atmospheric chemistry, growth of atmospheric particles and sorption of gas phase substances (Godish, 2004). Chemical composition of particles in air differs and is dependent on origin, production processes and atmospheric history of individual particle. However, the chemical composition of particles is very important and highly variable. The chemical composition of tropospheric particles includes inorganic ions, different metals, elemental carbon, organic compounds and crustal (carbonates and compounds of alkali and rare earth elementals) substances (Vallero, 2008). Therefore wind-blown mineral dust tends to be made of mineral oxides and other material blown from the Earth's crust. Sea salt is considered the second-largest contributor in the global aerosol mass and consists mainly of sodium chloride originated from sea spray. In addition, sea spray aerosols may contain magnesium, sulfate, calcium, potassium and organic compounds, which influence their chemistry (http://en.wikipedia.org).

Secondary particles derive from the oxidation of primary gases such as sulfur and nitrogen oxides into sulfuric acid (liquid) and nitric acid (gaseous). The precursors for these aerosols may have an anthropogenic origin (from fossil fuel combustion) and a natural biogenic origin. In the presence of ammonia, secondary aerosols often take the form of ammonium salts; i.e. ammonium sulfate and ammonium nitrate (both can be dry or in aqueous solution); in the absence of ammonia, secondary compounds take an acidic form as sulfuric acid (liquid aerosol droplets) and nitric acid (atmospheric gas) (http://en.wikipedia.org)

Organic material in the atmosphere may either be biogenic or anthropogenic. Organic compounds found on or in particles are more complex in urban region then in remote places. As a consequence of higher pollution such particles in urban regions contain, in addition to organic compound from biogenic emissions, complex compounds emitted directly from sources of anthropogenic pollution (Godish, 2004). Particles can additionally function as "vehicles" for transporting and transforming chemical contaminants. Highly sorptive compounds (large organic carbon adsorption coefficient) can use particles as a long range transport. Also different charges of ions could be another option for contaminants transport on atmospheric particles (Vallero, 2008).

Another important aerosol is constituted of elemental carbon (also known as black carbon, BC, carbon black, elemental carbon). BC, often called soot, is one of the most important absorbing aerosol species in the atmosphere (includes strongly light-absorbing material).

Various factors influence the elevated concentration of pollutants, such as climatic characteristics, meteorological phenomena, physical-chemical processes of transformation of substances in the air and the topographical structure of the area (Žlebir et al., 2007).

Particle deposition

Atmospheric deposition poses significant ecological concerns. According to the process of deposition particles can be deposited at the earth's surface in two ways, dry deposition or wet deposition, depending on the phase in which a species strikes the earth's surface and is taken up (Finlayson Pitts and Pitts, 2000). Dry deposition is characterized by direct transfer of gas phase and particulates from air to ground, vegetation, water bodies and other Earth surfaces. This transfer can occur by sedimentation, impaction, diffusion to surfaces or in case of plants by physiological uptake. In the absence of precipitation dry deposition plays mayor role in removing pollutants from atmosphere (Finlayson Pitts and Pitts, 2000). Wet deposition includes rain, snow, fog, cloud, dew formation and washout the atmosphere (Godish, 2004; Vallero, 2008). Rain out therefore means process in the clouds, where the occurrence of droplets on solid particles (condensation nuclei) happened. In such way disposal of pollutants by rain, snow etc. occurs. On the other hand, wash out is the process by which pollutants are removed from the atmosphere by being absorbed in or adsorbed on water droplets.

If two particles in air collide they tend to adhere to each other due to their attractive surface forces. Therefore particles become larger and larger by agglomeration. Larger particles have greater mass and therefore a greater possibility for falling to the ground rather than to stay airborne. Such process of removing particles from atmosphere is called sedimentation (Vallero, 2008).

1.5 Particle sampling and method of analysis

A variety of sampling methods and devices are used for atmospheric particles measurements. They range from sample collection on a filter for later analysis to complex direct reading instruments that detect airborne particles in real time and display size distribution and chemical composition (Baron and Heitbrink, 2005). The selection of the method depends on parameter to be measured; total mass, concentration, size distribution, chemical composition. It is also important whether the collection of samples is required for further analysis or not, the coast of the study and calibration and operation characteristic of chosen method (Murphy, 1984). According to Murphy (1984) selection of a particle sampling instrument depends on objectives of the study. For size selective collection of particles inertial separation can be used; filtration is used for collection of particles; using electrostatic precipitation or electric mobility separation precipitation of particles on a collection surface or limitation of particles passage through the system based on the electrical mobility can be achieved; using optical particles counting the total particles concentration or size selective particle count can be achieved; condensation nuclei counting is used for submicron particles count; diffusion separation method separate particles according to diffusion characteristics; thermal precipitation is collection method which produce a gentle precipitation of particles on a collection surface.

Bizjak (2009) divided sampling devices (from a technological point of view) to 3 groups:
1. First generation represents simple, inexpensive and less reliable samplers without the driving elements.
2. Sampling devices of the second generation represent devices with driving parts (pump) that enable filtering and washing of the wet gases.
3. The third generation represents automated machines that perform continuous measurements and have the option of reading the current data and the possibility of data transmission.

Passive devices (dry, wet, sticky collectors) are intended for sediment sampling. They are simple and robust, however less reliable. Suspended particulate matter could be measured using high volume samplers, low volume samplers and filters (Bizjak, 2009).

The most common collection techniques involves the use of different filters for collections of particles from air. Usually sampling devices are designed for specific applications and are therefore different. Beside simple collectors (collecting all particles that entering the sampling device) measurement devices for classifying particles in two or more fractions are used (inertial separation devices like cyclones and impactors) (Baron and Heitbrink, 2005).

For the larger particles (also known as total suspended particles - TSP) sedimentation method with gravity are used. This method does not obtain data on the content of particles in 1 m^3, but the quantity or mass of particles per m^2 of the surface in time as mg/m^2 day. The amount of particulate matter deposition is dependent on the direction, current speed and movement of air and precipitation (fog, rain, snow). For small particles, which are deposited by diffusion or retained on sampling gauge due to collision, the deposition depends on air flow at the surface and sampling gauge micro-porosity and adhesions (Stropnik, 1994).

Particulate matter deposition

Atmospheric dust (large or coarse particles) has traditionally been considered mainly as a cause of nuisance or of health effects due to secondary pathways following its deposition to the ground. Particulate matter deposition is therefore measured using simple passive devices (dry, wet, sticky sampling devices). Two kind of measurements of dust, mainly for nuisance purposes, are commonly made using passive samplers, of deposition and of the horizontal flux of particles past a sampling station (Hall et al., 1993). However, these methods have some deficiencies due to the aerodynamic characteristics of the sampling gauge. Wind induced flows around the gauge either prevent the entry of particles into the gauge opening or removes them (after deposition) due to a wind generated circulation inside the gauge (Hall et al., 1993). Due to exposure to various disturbances such measurement are less reliable. The strong dependency of gauge performance on wind speed and particle size leads to unrepresentative sampling results (Hall et al., 1993). Never the less with some improvements of the measuring device results are indicative and therefore useful.

The results of such measurement are expressed in g/m^2 (or mg/m^2) in the unit of time; times of collection are usually different (Bizjak, 2009). Basic principle of such measurements is gravitational force which is proportional to particle mass and gravitational acceleration and force particle to settle.

Deposition is the process by which aerosol particles collect or deposit themselves on solid surfaces and thus decreasing the concentration in the air.

The rate of deposition or the deposition velocity is faster for particles of a large size. Very large particles will settle out quickly through sedimentation (settling) or impaction processes, while Brownian diffusion has the greatest influence on small particles.

According to the process of deposition two different types of deposition exist - dry and wet. Dry deposition is caused by gravitational sedimentation, interception, impaction, diffusion or Brownian motion, turbulence and other processes, such as thermophoresis, diffusiophoresis and electrophoresis. Wet deposition includes some atmospheric phenomena which scavenge aerosol particles - rain, snow, fog, cloud, dew formation and washout the atmosphere (Godish, 2004; Vallero, 2008).

The amount of dust released to atmosphere increases with increasing wind speed, with the handling of powdery materials in the open etc. A similar situation occurs with dust carried away from stockpiles. The nature of saltation process which lifts particles from the surface is such that below a critical wind speed there is no loss, while above it there is a very rapid increase in the flux of airborne dust with small further increase in wind speed (Hall et al., 1993).

In particle dust sampling deposit gauges are used at points of complaint or other areas where information on deposition is required (Hall et al., 1993).

1.6 Legislation

The basis of the Slovene legislation in the field of ambient air quality is the Environmental Protection Act (2002) and its subsequent Decrees. The particulate matter deposition and its limit values were regulated by the Decree on limiting values, alert thresholds and critical emission values for substances into the atmosphere (1994). The mentioned decree has provided maximum value for the monthly and annual deposition as well as the content of selected metals in deposition (Table 3).

Table 3: Limiting value for particulate matter deposition (Decree, 1994)

	time period	**Limiting value (calculated on daily deposition)**
particulate matter deposition	1 month	350 mg/m^2 day
particulate matter deposition	1 year	200 mg/m^2 day
Pb		100 µg/m^2 day
Cd		2 µg/m^2 day
Zn		400 µg/m^2 day

In year 2002 in the field of air protection the Decree on sulphur dioxide, nitrogen oxides, particulate matter and lead in ambient air (2002) was adopted. This decree annulled its prior Decree on limit values, alert thresholds and critical emission values for substances into the atmosphere (1994). However, limiting values regarding particulate matter deposition from the annulled decree were still in use (according to interpretation of ARSO) until July 2007. On July 27th 2007 (Decree, 2007) those limiting values were finally annulled. Therefore the dust deposition limiting values are used by the annulled decree as recommended values.

1.6.1 Legislation regarding ambient air quality in Slovenia

- Rules on the setting up of ambient air quality monitoring and methods for its implementation (Pravilnik o monitoringu kakovosti zunanjega zraka), Uradni list RS 36/07
- Decree on arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air (Uredba o arzenu, kadmiju, živem srebru, niklju in policikličnih aromatskih ogljikovodikih v zunanjem zraku), Uradni list RS 56/06
- Decree on national emission ceilings for atmospheric pollutants (Uredba o nacionalnih zgornjih mejah emisij onesnaževal zunanjega zraka), Uradni list RS 24/05 and 92/07
- Decision on the designation of areas and level of pollution caused by sulphur dioxide, nitrogen oxides, particulates, lead, benzene, carbon monoxide and ozone in ambient air (Sklep o določitvi območij in stopnji onesnaženosti zaradi žveplovega dioksida, dušikovih oksidov, delcev svinca, benzena, ogljikovega monoksida in ozona v zunanjem zraku) Uradni list RS 72/03

- Decree on ozone in ambient air (Uredba o ozonu v zunanjem zraku), Uradni list RS 8/03
- Decree on benzene and carbon monoxide in ambient air (Uredba o benzenu in ogljikovem monoksidu v zunanjem zraku), Uradni list RS 52/02
- Decree on sulphur dioxide, nitrogen oxides, particulate matter and lead in ambient air (Uredba o žveplovem dioksidu, dušikovih oksidih, delcih in svincu v zunanjem zraku), Uradni list RS 52/02, 18/03 and 121/06
- Decree on measures for maintaining and improving ambient air quality (Uredba o ukrepih za ohranjanje in izboljšanje kakovosti zunanjega zraka), Uradni list RS 52/02

The particulate matter in ambient air regulated in the Decree on sulphur dioxide, nitrogen oxides, particulate matter and lead in ambient air (2002) applies to the regulation only of fine particles PM_{10} and $PM_{2.5}$. It does not regulate particulate matter deposition. Therefore the recommended values for the dust deposition continues to use the values specified in the annulled decree (1994).

1.6.2 EU legislation

The Treaty on European Union (Treaty, 1992) on the environment is based on the precautionary principle and on the principles that preventive action should be taken, that environmental damage should as a priority be rectified at source and that the polluter should pay. The policy on the environment follows preserving, protecting and improving the quality of the environment and protecting human health.

The change of the Slovene regulations is a consequence of the harmonization of the Slovene legislation with the legislation of the EU. Legislation relating to air pollution with particulate matter, primarily address the following three directives:

- Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management; Official Journal L 296, 21/11/1996 P. 0055-0063,
- Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen and oxides of nitrogen, particulate matter and lead in ambient air; Official Journal L 163; 29/06/1999 P. 0041-0060,
- Council Directive 2004/107/EC of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air; Official Journal L 23, 26/1/2005 P. 0003-0016.

The general aim of the Directive on ambient air quality assessment and management (1996) is to define and establish objectives for ambient air quality in the Community designed to avoid, prevent or reduce harmful effects on human health and the environment as a whole, to assess the ambient air quality on the basis of common methods and criteria, to obtain adequate information on ambient air quality and ensure that it is made available to the public and to maintain ambient air quality where it is good and improve it in other cases. According to this Directive (1996) among other air pollutants also fine particulate matter such as soot (including PM_{10}) and suspended particulate matter is taken into consideration in the assessment and management of ambient air quality.

The second EU Directive (Council Directive 1999/30/EC relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air, 1999) established limiting values for concentrations of pollutants in ambient air with intention to avoid, prevent or reduce harmful effects on human health and the environment as a whole, manage assessment for those pollutant concentrations on the basis of common methods and criteria, ensure that adequate information are available to the public and maintain ambient-air quality where it is good and improve it in other cases. According to this Directive "pollutant" shall mean any substance introduced directly or indirectly by man into the ambient air and likely to have harmful effects on human health and/or the environment as a whole, while "level" shall mean the concentration of a pollutant in ambient air or the deposition thereof on surfaces in a given time.

The objective of Council Directive 2004/107/EC relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air establishes target values for the concentration of arsenic, cadmium, nickel and benzo(a)pyrene in ambient air to avoid, prevent or reduce harmful effects on human health and the environment as a whole. Additionally, this Directive tries to set common methods and criteria for the assessment of those concentrations in ambient air as well as on the deposition of particulates. Another goal is to ensure that adequate information on concentrations of metals and polycyclic aromatic hydrocarbons in ambient air as well as on the deposition obtained from particulates and are available to the public. According to this Directive "total or bulk deposition" means the total mass of pollutants which is transferred from the atmosphere to surfaces (e.g. soil, vegetation, water, buildings, etc.) in a given area within a given time.

These directives are partly revised in Directive on ambient air quality and cleaner air for Europe (Directive, 2008). From 11th of Jun 2010 Directive on ambient air quality assessment and management (1996) and Directive relating to limit values for sulfur dioxide, nitrogen and oxides of nitrogen, particulate matter and lead in ambient air (1999) will be annulled and replaced by this Directive.

2 PURPOSE OF THE STUDY

In addition to being a nuisance, particulate matter deposition can also be a cause of health and other problems, either from direct inhalation or ingestion or through secondary pathways after particles have deposited. Inhabitants of Ankaran and its surroundings have been complaining for several years about dust deposition in their living environment (houses, backyards and gardens). They believe the major contributor of dust is the activities at the Port of Koper, especially activities in coal and iron ore stockpiles at EET. Until now no study of the contribution of particulate matter deposition from Port of Koper to surrounding area has been conducted.

The purpose of the study was to collect, analyze and characterize the air borne particulate matter deposited in the residential areas around the port of Koper with aim to correlate these particles with port activities, especially with activities on EET terminal (coal and iron ore manipulation).

Standard and modified methods for the collection of particulate matter deposition were employed. Some modifications were made in order to optimize the method, and other to maximize the number of sampling sites and minimize costs. Deposition was determined gravimetrically. In addition, further analysis of metals content in the samples, examination by electron microscopy and analysis of stable carbon isotopes were performed, all with aim to detect and characterize particles in deposition samples and attempt to correlate these particles with activities at EET. Budgetary constraints necessitated limiting analysis for metals, measurement of carbon isotope ratios and electron microscopic determination of chemical composition and morphology to only the annual composite samples.

Additionally, a new instrument for quick estimation of direction and quantity of airborne particulate matter and therefore determination of the main emission sources of dust particles in the observed area was developed as a result of this study.

The results of this investigation can be used for assessment of dust deposition in the Port of Koper surroundings. Additionally, on the basis of the obtained results the effectiveness of preventive measures undertaken by the Port of Koper for prevention of dusting in surroundings can be assessed.

Hypothesis

1. Coal and iron ore depot at EET terminal in Port of Koper represent one of the sources for particulate matter deposition in surrounding area.
2. Ankaran and its surroundings is heavily burdened with dust deposition from the Port of Koper.
3. Dust preventive measures undertaken by the Port of Koper lead to reduction of particulate matter deposition in surrounding areas.

3 MATERIALS AND METHODS

Pictures, used in master thesis work were taken by author during the time of the study (2005 - 2008). Also other figures (except those cited to source) are also authors work.

3.1 Time schedule

The results presented here are the outcome of two one year long studies where dust emissions around Port of Koper was investigated. The first (preliminary study) was conducted from 15th of October 2005 to 15th of October 2006. Samples were collected once per month. According to preliminary results from first study a new modified and upgraded study was prepared and conducted from 1st of December 2007 until 30th of November 2008. Samples were collected and analyzed twice per month (gravimetrically) on the 1st and 15th day of each month for a one year period.

3.2 Description and location of the sampling sites

The sampling collection sites used for identification of particulate matter deposition and estimation of influence of Port of Koper on total dust deposition on surrounding area were located around Port of Koper. Some of them were placed directly in the residential environment. The choice for sampling sites location on the micro level was based on the anticipated influence of emissions in the nearby area. Micro level means location of the measurement spot and influences on it by location (distance between the nearby buildings, trees etc.). The sampling gauge was placed 1.5 – 2 meters above the ground (the height of breathing zone of an adult person). No obstacles (that could have influence on the air flow passing the sampling gauge) where in close proximity of the sampling sites.

In the preliminary study six sampling sites in the area of Ankaran and its surrounding (Figure 5) were included. Some sites were chosen for their proximity to potential dust sources. Sites 1, 2, and 3 were located downwind from a dust source in order to estimate how distance influence on the dust sedimentation. The first five sampling sites were placed in the prevailing direction of the wind or in the direction toward the residential area. All of the sampling sites were in close proximity to the Port of Koper, oriented toward municipality of Ankaran. The sixth sampling site was used as a control sample of the background (located in the residential area of Hrvatini, where due to distance from Port of Koper and the height above sea level a negligible influence of the terminal of strewn cargo of the Port of Koper was expected).

Figure 5: Locations of sampling sites - preliminary study ***(geographical source: Google Earth - www.earth.google.com)***

During study from December 2007 to December 2008, ten sampling sites also in the area of Koper and Ankaran (Figure 6) were included. Eight sampling sites were placed around Port of Koper in prevailing wind directions or directions towards residential areas. Two sampling sites (6 and 7) were used as a control sample of the background. Sampling site 6 was located in the residential area of Hrvatini. Sampling site 7 was located on Debeli Rtič, place far away from Port of Koper.

***Figure 6: Location of sampling sites - study 2007/08** (geographical source: Google Earth - www.earth.google.com)*

Sampling sites 1, 2 and 3 were placed in linear line (Figure 7) in predominant wind direction (NE - SW). Samples collected in this manner would allow determination of the impact of distance from the coal and iron ore depot on the amount of dust deposition.

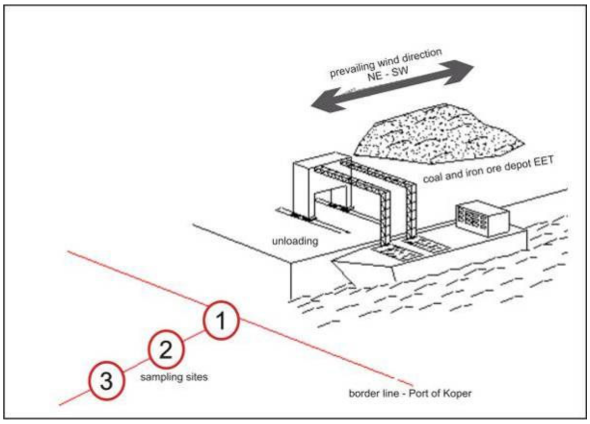


Figure 7: Linear direction of sampling sites 1, 2 and 3

Selection of the direction of the linear sampling sites 1, 2 and 3 in predominant wind direction (NE - SW) was based on predominant wind direction for the Port region for year 1996 (Kontič et al., 2001).

Appearance of the sampling sites and view from sampling sites toward coal and iron ore depot are given in the following figures (Figure 8 to Figure 27). Orientation of the sampling sites was given regarding to the starting point - EET depot. Geographical source for figures - a view from the air was Google Earth (www.earth.google.com).

Legend:

✴ coal and iron ore depot - EET

○ sampling site

Figure 8: Sampling site 1; at the Port of Koper fence, about 700 m away from the EET depot, direction NE

Figure 9: A view from sampling site 1 towards EET depot

Figure 10: Sampling site 2; At the house on the Železniška street 2, about 1100 m away from the EET depot, direction NE

Figure 11: A view from sampling site 2 towards EET depot

Figure 12: Sampling site 3; Residential house Andrioli, Jadranska c. 2, about 1500 m away from EET depot, direction NE

Figure 13: A view from sampling site 3 towards EET depot

Figure 14: Sampling site 4; Rožnik residential area, about 1100 m away from EET depot, direction NE

Figure 15: A view from sampling site 4 towards EET depot

Figure 16: Sampling site 5; residential house Ražman, Jadranska 19, about 1200 m away from EET depot, direction N

Figure 17: A view from sampling site 5 towards EET depot

Figure 18: Sampling site 6; residential house, Hrvatini 117, about 2600 m away from EET depot, direction NE (control)

Figure 19: A view from sampling site 6 towards EET depot

Figure 20: Sampling site 7; Debeli rtič, st. Jernej bay, about 3600 m away from EET depot, direction NW (control)

Figure 21: A view from sampling site 7 towards EET depot

Figure 22: Sampling site 8; center of Koper, Verger square, about 1800 m away from EET depot, direction SW

Figure 23: A view from sampling site 8 towards EET depot

Figure 24: Sampling site 9; Žusterna, beside swiming pool, about 3000 m away from EET depot, direction SW

Figure 25: A view from sampling site 9 towards EET depot

Figure 26: Sampling site 10; center of Ankaran, about 1800 m away from EET depot, direction N

Figure 27: A view from sampling site 10 towards EET depot

3.3 Collection of particulate matter deposition

The collection of particulate matter deposition was conducted with the standard Bergerhoff sedimentators (Figure 28) according to Commission Reinhaltung der Luft im VDI und DIN Guideline VDI 2119 part 2 (1996) - Measurement of Particulate Precipitations Determination of dust precipitation with collecting pots made of glass (VDI, 1996). The same method was applied also in the proposition of guidelines of the Association of clean air societies of Yugoslavia number 201 (SDČVJ, 1987). The stated method is used as the standard method for measuring the particulate matter deposition in Slovenia. On each sampling of the sites, there were placed three (during preliminary study 2005/06) and two (study 2007/08) Bergerhoff sedimentators according to VDI standard (1996).

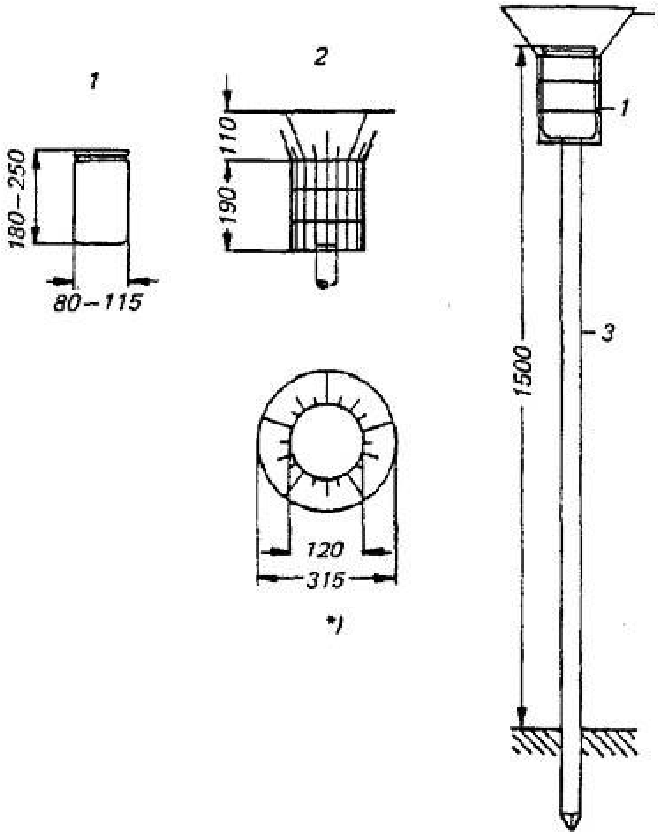


Figure 28: Components of a standardized measuring device type Bergerhoff (VDI, 1996) (Dimensions are in millimeters)

The method for collection of particulate matter deposition is not perfect, because it does not entirely include the wind contribution. When wind blows through the sampling gauge, majority of particles are not deposited on the ground or in the sampling gauge. They are blown away with the wind and precipitate when wind stop blowing or when hits the obstacle. That's why metal screen as obstacle oriented toward ore depot (EET) was added. That is the reason the method was modified by adding a metal screen (20 cm x 30 cm - sampling sites marked with letter B), which intercepted particulate matter depositions spread horizontally. The flow chart of sampling sites is shown in Figure 29. To improve method, distilled water was added to prevent the wind from blowing away the particulate matter deposition from the containers. The main purpose of the modification was to establish and quantify the particulate matter brought also by the wind from the observed directions.

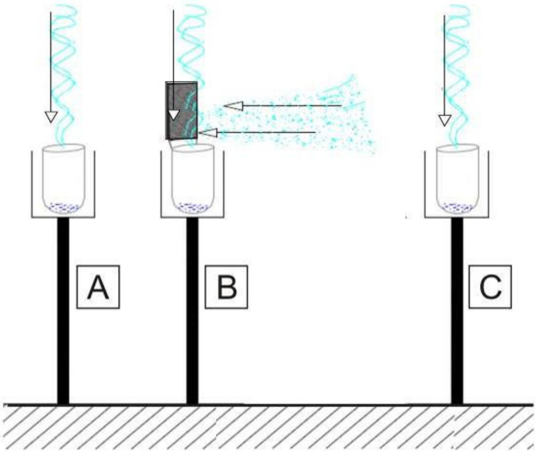


Figure 29: Appearance of sampling site A, B and C.

During preliminary study three sample collectors were placed at each sampling site (Figure 29 and Figure 30). The mass of material deposited in the first container, container A was determined monthly. The mass of material deposited in the second container, container C, was meant to be determined annually. The mass of material deposited in the third container, container B, from both (vertical deposition and additional horizontal contribution) was determined monthly. The yearly sample from container C was unusable because of the presence of decayed insects and plant leaves and contamination with algae. For this reason the yearly value of particulate matter deposition was calculated by the monthly values. Therefore during study 2007/08 third container (C) was omitted (Figure 31).

Figure 30: View from sampling site 5 (2005/06)

Figure 31: View from sampling site 5 (2007/08)

During preliminary study (2005/06) samples were collected and analyzed (gravimetrically) on the 15th day of each month for a one year period from October 2005 to October 2006. During study 2007/08 sample period was shortened to 15 days, samples were collected (and analyzed gravimetrically) twice per month on 1st and 15th each month from 1st of December 2007 to 30th November 2008.

3.4 Gravimetric analysis

The masses of particulate matter deposition on each sampling site were determined by gravimetric analysis. Each month, the glass collecting bottles from each sampling sites were taken to the laboratory. When insects or parts of insects, parts of leafs, etc. were observed to be present. These were removed prior to the analysis. The samples were analyzed by the gravimetric method and the amount of dust deposition was determined in mg/m^2 day. The samples were filtered through a previously dried (105°C ± 5°C) cellulose nitrate membrane filter of pore size 3 μm (ME 29 Scheilcher & Schuell and Sartorius 11302-47-N) using a vacuum filtering device. Collecting bottles were rinsed with distilled water to wash out all the particles. A modified procedure ISO 11923 (1997) was used. Three blank filters were carried through the procedure. The total volume of filtrate was measured, and 250 mL of the filtrate was transferred to a previously dried (105°C ± 5°C) cooled and weighed evaporating dish. contents of the dish were evaporated to dryness at a temperature of 80°C ± 5°C. Before analyzing the samples, blank filters and evaporating dish were thermo-stated for 60 minutes at 105°C ± 5°C. At the end, filter paper and evaporating dishes were weighted and the total dust amount was calculated. An analytical balance, capable of weighing with a precision of at least ± 0,1 mg was used (Mettler Toledo AT 261 and Sartorius ME 614 S). These data represent masses of the particles larger than 3 μm (mass on the filter) and the masses of the particles smaller than 3 μm (mass in the evaporating dish). After the gravimetric analysis of the sample, the amount of dust deposition was calculated and represent as mg/m^2 day using Equation 1 and 2.

Equation 1: $$m = \frac{(m_1 + m_2) \cdot f}{A \cdot t} \qquad (1)$$

Where the symbols mean the following:

m - mass of the particulate matter deposition (mg/m^2 day)
m_1 - mass of the sediment on the filter - particles larger than 3 μm (mg)
m_2 - mass of the particles in the filtrate - particles smaller than 3 μm (mg)
f - 10,000 cm^2/m^2 (conversion in m^2)
A - collecting area (cm^2)
t - sampling period (days)

Equation 2: $$m_2 = m_3 \cdot \frac{V_1}{V_2} \qquad (2)$$

Where the symbols mean the following:

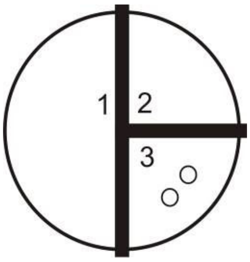
m_2 - mass of the particles in the filtrate - particles smaller than 3 μm (mg)
m_3 - mass of the particles in evaporating dish (mg)
V_1 - total volume of sample after filtration (mL)
V_2 - evaporated volume of sample after filtration (mL)

3.5 Preparation of the annual samples for different analysis - filters processing

During preliminary study (2005/06) samples were collected once a month. For electron microscopy, small fraction of filters from sampling period 15th February to 15th March 2006 were taken (Figure 32). For all other analysis entire filters were used. No other treatment of filters was made.

Figure 32: Filters prepared for electron microscopy (15.2.2006 - 15.3.2006)

During study 2007/08, samples for each sampling site were combined. For each analysis, part of original filter (Figure 33) was taken for further processing as described in detail for each method separately.



1 - Analyzes of metal content
2 - Aalyzes of the 12C/13C isotope ratio
3 - Electron microscopy

Figure 33: Appearance of template model for filter division

3.6 Identification of possible health risks

3.6.1 Chemical analysis of selected metals in deposited matter

Selected metals in particulate matter deposition was determined. During preliminary study 2005/06, chemical analysis for determination of metals was done once for each sampling location on 1 year sample (particulate matter deposition was collected for entire year before being analyzed) by atomic absorption spectrometry. The analysis was done in the laboratory of the Public Health Institute of Koper. In Table 4 methods for chemical determination of selected particles are presented.

Table 4: Methods for chemical determination of selected parameters

Parameter	**Method**
Iron	EPA7380
Aluminium	SIST EN ISO 15586:2003
Copper	SIST ISO 8288
Zinc	SIST ISO 8288
Cadmium	SIST EN ISO 15586:2003
Lead	SIST EN ISO 15586:2003
Total chromium	SIST EN ISO 15586:2003
Nickel	SIST EN ISO 15586:2003

For metal analysis of the samples collected in the 2007/08 study, half of each filter (Figure 33) was combined. The total annual sample therefore represent a 24 half-filters from each 15 day period. These analysis of metals was conducted in a laboratory for sanitary chemistry of the Public Health Institute of Celje. Samples were prepared by microwave digestion with the addition of 10 mL HNO_3 followed by dilution up to final volume of 500 mL. The measurement was carried out by ICP-MS and the results were given in μg of each metal in the sample, as follows:

- Measured values are calculated and given as μg of metal per sample.
- Annual sample for each sampling site represents a total of 24 samples collected twice per month during study 2007/08.
- Only half of the filters were used for the analysis of metals, remains of filters were used for other analyzes.
- For various reasons (vandalism, mechanical destruction of the sample, organic pollution) some of filters were discarded without making the analyses (Annex 1).
- The conversion of metals in the sample was carried out using Equation 3.

Equation 3:
$$m_m = \frac{m_{ms} \cdot 2}{\pi \cdot r^2 \cdot t} \qquad (3)$$

Where the symbols mean the following:

m_m - mass of the metal in yearly sample (μg/m^2 day)

m_{ms} - mass of the metal in sample (μg)

2 - factor 2 (using 1/2 of the filter)

π - 3,14 (Pi)

r - radius of collecting pot (m)

t - sampling period (days)

3.6.2 Gamma-ray emitter activity measurements in coal and iron ore samples

Because of the impurities coal could include some radio nuclides (Van Hook, 1979; Dowdall et al., 2004; Ward and Suárez-Ruiz, 2008) and thus represent health risk, the gamma-ray emitters activity was first measured in the samples of coal and iron ore. When the gamma ray emitters activity is found to be above background, further analyses of the samples of particulate matter deposition were performed.

The gamma-ray emitter activity in the sample of coal and iron ore was measured using high resolution gamma-ray spectrometry (HRG) following LMR-DN-10 (Korun and Glavič Cindro, 2003) procedure in the Jožef Stefan Institute. The reported uncertainties were calculated in accordance with GUM guidelines (1995). The results of the measurement of samples with gamma-ray spectrometer are the activities of all gamma-ray emitters present in the sample in concentrations exceeding their Minimum Detectable Activities. The measured activity of ^{40}K makes possible a comparison in concentration of this value with the result of a chemical analysis, offering a way for an independent check of activity measurements. The specific activity of ^{40}K measured in the sample of coal was 25 ± 4 Bq/kg corresponding to 780 ± 120 ppm of potassium. Specific activity of ^{40}K measured in the sample of iron ore was 35 ± 6 Bq/kg corresponding to 1100 ± 190 ppm of potassium. The activity of ^{226}Ra is determined from activities of short-lived radon progenies (^{214}Pb and ^{214}Bi). The factor describing the equilibrium between radium and radon progeny was calculated from the emanation rate of radon from the sample and the time interval between sample preparation and measurement. The activity of uranium is determined assuming that U-238 is in equilibrium with progenies ^{234}Th and ^{234m}Pa and that the ratio of concentrations of ^{235}U and ^{238}U equals its natural value.

Analyzes were performed only during preliminary study (2005/06) on samples of coal and iron ore gathered in the ore depot on the EET terminal in Port of Koper. Specific activities of gamma-ray emitters were calculated back to the date 25.8.2006. The sub-sample of 0.35 kg of coal taken from the 0.9 kg of original sample material and the sub-sample of 1.16 kg of iron ore taken from the 1,3 kg of original sample material were analyzed. Additionally a sample of soil (from uncultivated land area in Slovenia) was analyzed as example of normal amount of radio nuclides in the soil.

3.7 Application of SEM/EDXS (Scanning Electron Microsopy / Energy Dispersive X-ray Spectroscopy)

The presence of carbon in the samples could be analyzed using several techniques. However, problems occur whenever it is necessary to distinguish the individual sources of carbon. Organic and inorganic carbon can be determined in several ways.

However, problems are encountered when attempting to identify and quantify particles of coal in environmental samples containing plant fragments, insect fragments, pollen, et. cetera. For this reason SEM/EDXS (scanning electron microscope with energy dispersive X-ray spectroscopy) allowed the detection of the morphology structure of particles in particulate matter deposition as well as the determination of the chemical composition. The SEM/EDXS measurements were made in the Department for Nanostructured Materials at Jožef Stefan Institute.

Surface of samples were scanned using electron beam with high energy (20 keV). Upon irradiation with electrons, atoms that make up the sample produce a signal that contains information about the sample (surface topography, chemical composition and other properties such as electrical conductivity). More about SEM/EDXS methodology can be found in review by Goldstein et al. (2003), Russ (1984), Scott et al. (1995) and Heinrich et al. (1991).

During preliminary study only samples from sampling period from 15th of February to 15th of March 2006 were analyzed with electron microscopy since during this time period presence of high amount of coal in the filters were expected. Only a small fraction of each filter was taken from the original for analysis (Figure 32). In order to determinate coal and iron ore in samples of particulate matter deposition, originating from EET depot at the Port of Koper, shape, size and elemental chemical composition of collected particulate matter was determined. Additional sampling site at Beli Križ area in Portorož (Figure 34) was used for collection of particulate matter deposition in order to analyze it as a control for the electron microscopy.

***Figure 34: Location of additionally reference sampling site at Beli Križ** (geographical source: Google Earth - www.earth.google.com)*

For electron microscopy during 2007/08 study, samples from individual sampling period in one yearly sample for each sampling site were combined. For analysis, a part of original filter was to be processed further. Samples were analyzed qualitatively and quantitatively.

Samples were prepared by our own method, which was performed as described. Cellulose nitrate membrane filters (pore size of 3 μm) having an overall diameter of 47 mm and an effective diameter of 41 mm were used. From each 1/4 of filter (No.3 in Figure 33) the circle diameter of 6 mm (1/61 the surface of the sample) was cut. Due to various reasons (deliberate contaminated sample (sand, fire-cracker, etc..), organic polluted sample (leaves and the droppings of birds), the error in the process (spilled filter with alcohol, the occurrence of copper-oxide) and the occurrence of salts in the sample), it was necessary to eliminate from further analysis a few samples from individual monitoring sites throughout the year (Annex 1). Cut sections of the filter (2r = 6mm) were combined (in annual terms) and inserted into 50 mL test tubes.

For re-suspension in distilled water samples were treated by the following protocol:

1. Cut section of the filters was added 15 mL of distilled water

2. Homogenization on orbital shaker (Vibromix 10)
3. Treatment with an ultrasonic probe (cycle 0.9, amplitude 100%) for three minutes
4. 10 minutes break
5. Treatment with an ultrasonic probe (under the same conditions) for five minutes
6. Homogenization on orbital shaker (Vibromix 10) and visual assessment
7. 10 minute break
8. Treatment with an ultrasonic probe (under the same conditions) for five minutes
9. 30 minutes break
10. Treatment with an ultrasonic probe (under the same conditions) for one minute
11. Homogenization on orbital shaker (Vibromix 10)
12. Removal of washed cut section of the filters (2r = 6 mm)
13. In test tube distilled water was added up to 50 mL

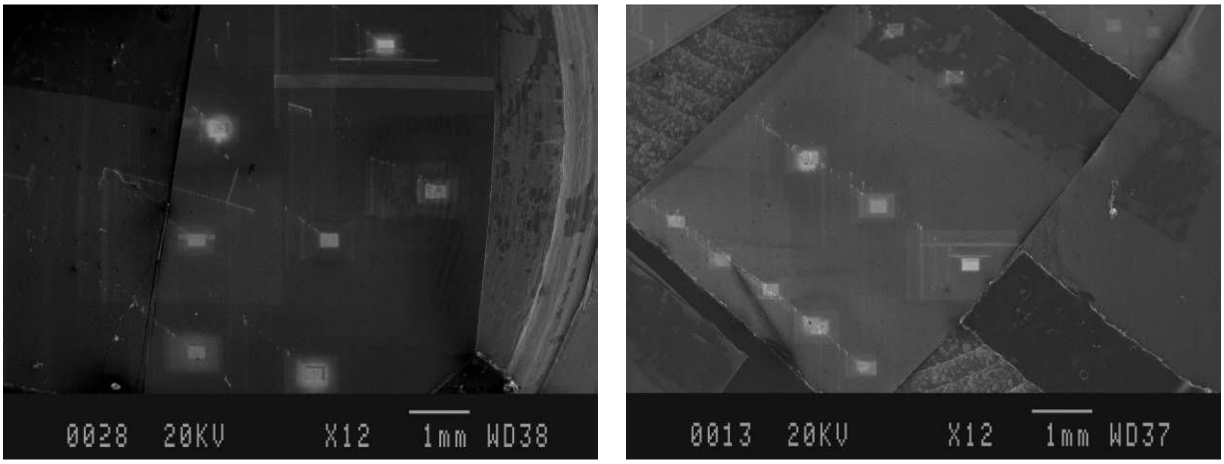
During this procedure yearly sample from each sampling site was prepared. From such prepared sample, 10 mL were taken out using automatic pipette and transferred to the Macherey Nagel polycarbonate membrane filter (pore size 0.4 μm, 2r = 47 mm) and filtered using a vacuum filtering device. Samples prepared in this way were transferred to Department for Nanostructured Materials at Jožef Stefan Institute, where the analyses were conducted.

A qualitative analysis for chemical composition, morphological appearance and size of individual particles was performed. Also quantitative stereological analysis was performed - the number of the particles were counted on a size known area. Results were given as number of particles on the filter surface.

From the pre-prepared polycarbonate filters (pore size 0.4 μm) approximately 5 x 5 mm parts were cut out in the center of the filter and prepared for processing in the SEM.

Pieces of filters were fixed on sample holder using double-sided self-adhesive conductive tape. Up to 14 filter samples were placed on one sample holder. Thin layer of carbon was deposited on filter samples with Balzers carbon coater. Sample holder was transferred to scanning electron microscope for further investigations.

The samples were investigated at 500x magnification. On each sample up to 12 areas were investigated as seen in Figure 35 and Figure 36. The results were given as average number of particles on the filter (number / cm^2).



Figures 35 and 36: SEM micrographs of filter sample where investigated areas could be seen (due to charge built-up those areas have bright contrast)

In the case of the control sample (blank cellulose nitrate filter pore size 3 µm) only small pieces of filter (Figure 37) were detected. No particles were found in control samples.

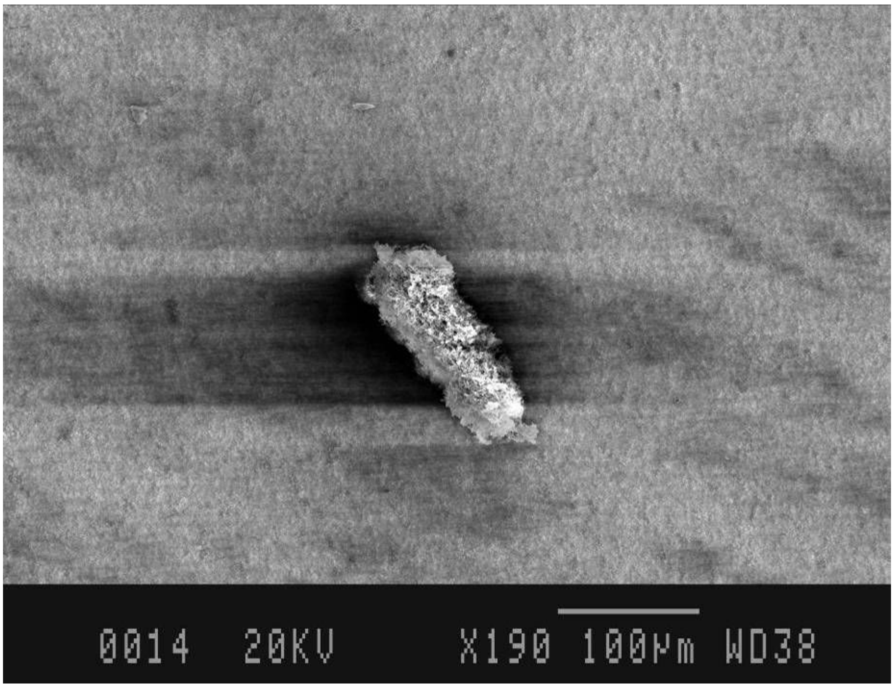


Figure 37: Piece of cellulose nitrate filter - control sample

The number of particles on each analyzed area (Figure 38) was calculated per cm^2 of the filter. On each sample several areas were used for counting of particles and average number of particles was calculated. The average number of particles has been multiplied by the number of 2551.02 (normalization to 1 cm^2). The result was given as the average number of particles per cm^2 of the filter.

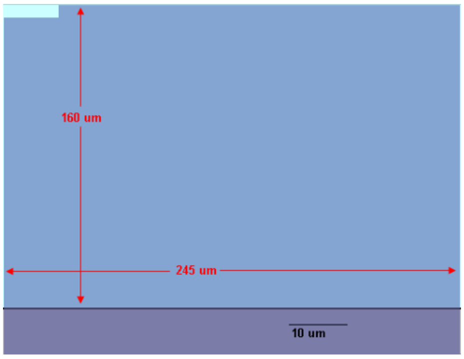


Figure 38: Schematic of an area of a SEM image taken at 500x magnification (observed area is 39200 µm^2)

3.8 The ratio of carbon isotopes $^{13}C/^{12}C$ measurement in the sample

Stable isotopes of light biogenic elements (including carbon) are ideal for monitoring the natural flux of biogeochemical and transport processes in different environments. Using ^{13}C, circulation of carbon in the environment can be monitored. In addition, the origin of organic carbon can be determined. Different sources of carbon in the environment have a specific ratio of carbon isotopes $^{13}C/^{12}C$. Analyzes of $^{13}C/^{12}C$ isotope ratio in samples of particulate matter deposition was therefore used for the estimation of the proportion of carbon in the samples which originated from the coal.

The ratio of stable carbon isotopes $^{13}C/^{12}C$ in different samples from the environment (water, biological material, soil, sediment) was determined with mass spectrometry. The isotopic composition or the ratio between the heavier and lighter isotopes of carbon is expressed as δ-value. δ-value represents the relative difference of isotopic composition of research sample (sa) according to the selected standard (st) and is expressed in ‰.

Equation 4: $$\delta^{13}C=\frac{R_{sa}-R_{st}}{R_{st}}*1000 \qquad (4)$$

Where the symbols mean the following:

R_{sa} - $^{13}C/^{12}C$ isotope ratio in the sample
R_{st} - $^{13}C/^{12}C$ isotope ratio in standard

International standards for isotopic measurements are provided by the International Atomic Energy Agency (IAEA) in Vienna. Standards are selected accordingly to similarity of the average prevalence of certain isotopes in nature. For carbon a carbonate standard V-PDB (Vienna Pee Dee Belemnite) is used with $R_{st} = 0.0112372$ (Craig, 1957).

The ratio of carbon isotopes $^{13}C/^{12}C$ was measured only in samples from study 2007/08. One quarter of each filter from different sampling period was used (No. 2 in Figure 33). For analyzes two filters from same month were combined. In this way for each sampling site 12 monthly samples (total 240 samples) were obtained. Sample was scraped from each quarter of the filter using surgical scalpel and placed in test tube (volume 10 mL). Further analysis of the samples was performed at the Department of Environmental Sciences of Jozef Stefan Institute. Each sample was inserted into the silver capsule (Sercon sc 0037, Pk of 250; Silver Capsules 5x9 mm) and analyzed using following procedure:

On samples in silver capsule first 3 M HCl for removing inorganic carbon was applied. Prepared sample was later dried in the sand bath at 60°C until the sample was completely dry. The sample size depends on the carbon content. For analysis minimum 200 µg of carbon is needed. Measurements of carbon isotopic composition was performed on mass spectrometer for analysis of light isotopes (Isotope Ratio Mass Spectrometry - IRMS) Europa Scientific 20-20 with preparation module for solid and liquid samples. Accuracy and precision of the measurements was monitored with the use of laboratory standards. For carbon urea C standard with $\delta^{13}C$ value of -30.6 ± 0.2‰ was used. Additionally the quality of the measurements were monitored using reference standards IAEA-NBS (oil), IAEA-CH-7 and IAEA-CH-6 with $\delta^{13}C$ values of -29.7 ± 0.2‰, -31.8 ± 0.2‰ and -10.4 ± 0.2‰, respectively. The precision of measurement was usually 0.2‰.

Under the same conditions the control sample and a sample of coal from EET landfill were analyzed. On the basis of the measured ratios of stable carbon isotopes $^{13}C/^{12}C$ in the monthly samples, control and coal from EET depot content of the coal in samples were calculated according to isotopic mass balance equations (Equation 5).

Equation 5:

$$\begin{aligned} \delta^{13}C_{sample} &= F_{coal} *\delta^{13}C_{coal} + F_{control} *\delta^{13}C_{control} \\ 1 &= F_{coal} + F_{control} \end{aligned} \qquad (5)$$

Where the symbols mean the following:

$\delta^{13}C_{sample}$	- isotopic composition of the sample
$\delta^{13}C_{coal}$	- isotopic composition of the coal
$\delta^{13}C_{control}$	- isotopic composition of control
F_{coal}	- the fraction of coal in the sample
$F_{control}$	- the fraction of control in the sample

3.9 Alternative method for quick estimation of direction and quantity of particulate matter deposition and impaction - particles counting

For a quick estimation of the direction and quantity of particulate matter and, therefore, the determination of the main sources of emissions of dust particles in the study area, a simple alternative measurement device based on deposition and/or adhesion was developed. The basic idea was to collect the particulate matter from air on adhesive material (medical Vaseline). This measurement device enabled collection of particles in both the horizontal and vertical directions. A plastic ball of 20 cm diameter, covered with medical Vaseline was used for the measuring device (Figure 39). It has hole at the bottom for wooden stick served as a carrier. Sampling devices were placed 1.5 to 1.7 m above the ground (the height of breathing of an adult person) and located around the coal and iron ore depot in Port of Koper.

The diameter of the ball - 20 cm (0.20 m)

Calculated area of the ball (the trap surface) = 1256 cm^2 (0.1256 m^2)

Figure 39: Sampling device 1

Sampling device type 1 was put on the sampling site 1, 2, 3, 4, 5 and 10 at different time intervals during the study 2007/08. On each ball, the points of the compass were marked. Sampling device 1 was installed beside the standard Bergerhoff sedimentators. Location of sampling sites marked with the direction of the ball, oriented towards EET depot and Port of Koper is shown in Figure 40.

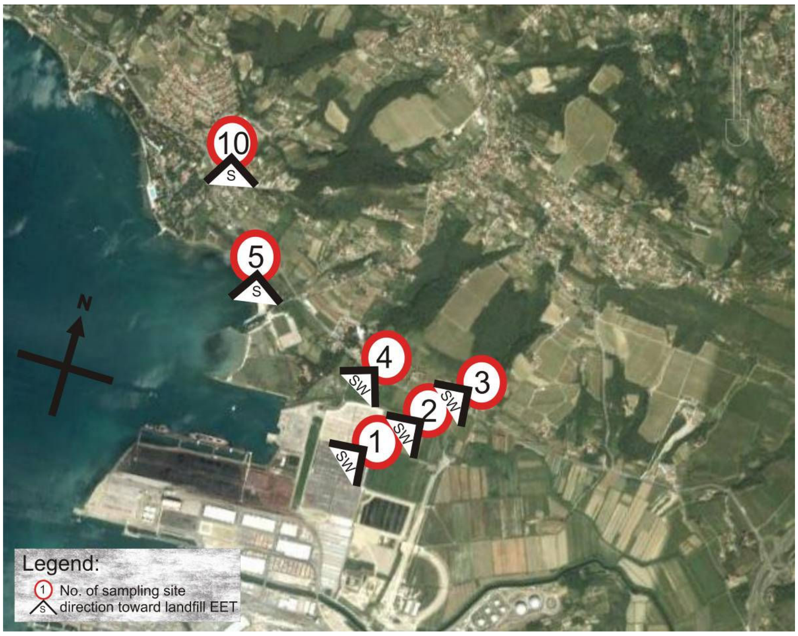


***Figure 40: Location of the measuring device type 1 - ball** (geographical source: Google Earth - www.earth.google.com)*

The diameter of the ball is 20 cm (0.20 m), calculated area of the ball (the trap surface) is 1256 cm^2 (0.1256m^2). Each ball on the measuring site was exposed for 1 month. After the exposure time, balls were analyzed in laboratory. Particles were counted manually using magnifier lenses on each main points of the compass (N, S, E and W) and further in the direction oriented towards EET ore depot. Particles on each side of the ball were counted 5 times on surface of 1 cm^2 using template model (Figure 41).

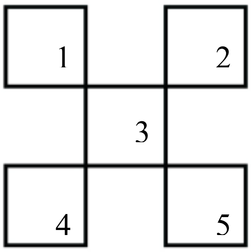


Figure 41: Appearance of template model for particles counting

Additionally, digital photography of each ball was taken with single-lens reflex camera Canon EOS 350D for further analyses. Pictures from 15th of October to 15th of November 2008 were processed and analyzed; as opposed to manual counting of particles, where six one-month average samples were analyzed.

Computer software IT 3.0 (Image Tool 3) was used for counting particles on the digital images. A computer program IT 3 version 3.0 is an open code program for the analysis and image processing. The program was developed by a group of experts Don Wilcox, Brent Dove Doss McDavid and David Greer from the University of Texas Health Science center in San Antonio (UTHSCSA). Program enables viewing, editing, analyzing, compressing, storing and printing images. The program may process different types of image formats, including BMP, PCX, TIFF, GIF and JPEG. Program enables automatic particle counting (black dots) in pre-prepared pictures. Results of counting were presented as number of particles per cm^2.

Additionaly scanning electron microscope with energy dispersive X-ray spectroscopy (SEM/EDXS) was used for detection of the morphology structure of particles trapped on sampling device (plastic ball) as well as the determination of the chemical composition. The SEM/EDXS measurements were made in the Department for Nanostructured Materials at Jožef Stefan Institute. The surface of 1 cm^2 were scraped and transferred on the Macherey Nagel polycarbonate membrane filter (pore size 0.4 µm, 2r = 47 mm) and examined by SEM/EDXS.

4 RESULTS

PART I - preliminary study

4.1 Results of preliminary study (15th October 2005 - 15 th October 2006)

4.1.1 Gravimetric analysis of particulate matter deposition - sampling site A

The monthly particulate matter deposition was collected on the 15th of each month for a one year period from October 2005 to October 2006. In Table 5 and Figure 42, the measured monthly deposition of particulate matter using standardized method of collection of particulates deposition (samples marked with letter A) at each sampling sites (in mg/m^2 day) are presented. Vertical deposition was differentiated from vertical plus horizontal deposition as A and B, respectively. Additionally masses of particles smaller than 3 µm are presented (Table 6). The particulate matter deposition and its limit values were regulated by the Decree on limiting values, alert thresholds and critical emission values for substances into the atmosphere (1994), which was annulled in July 2007, therefore for results from time period 2005/06 those limiting values were still used.

Table 5: Monthly mass of particulate matter deposition - sampling sites A (mg/m^2 day)

	1A	2A	3A	4A	5A	6A	limiting value **
15.10. - 15.11.2005	23	38	16	65	45	54	350
15.11. - 15.12.2005	24	66	29	20	51	168	350
15.12. - 15.01.2006	33	52	44	29	66	62	350
15.01. - 15.02.2006	34	14	35	85	13	13	350
15.02. - 15.03.2006	40	209	**390**	**1216**	**365**	255	350
15.03. - 15.04.2006	132	71	46	**357**	65	142	350
15.04. - 15.05.2006	145	203	164	327	313	279	350
15.05. - 15.06.2006	53	262	300	328	**537**	324	350
15.06. - 15.07.2006	128	**635**	288	344	**738**	201	350
15.07. - 15.08.2006	63	32	77	75	220	177	350
15.08. - 15.09.2006	*	182	168	210	102	154	350
15.09. - 15.10.2006	**1260**	213	**1201**	**4283**	**844**	166	350

* - sample was not analyzed (sample was destroyed)

** - limiting value according to Decree, 1994

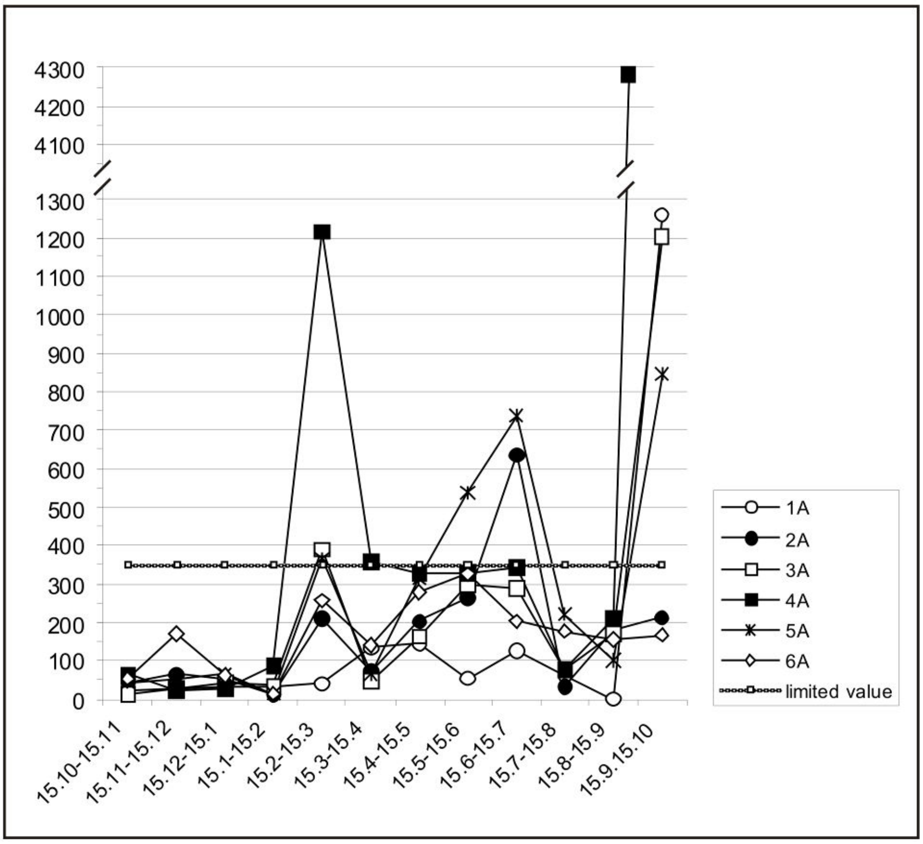


Figure 42: Monthly mass of particulate matter deposition - sampling sites A (vertical deposition collected by standardized method).

Table 6: Monthly mass of particulate matter deposition - sampling sites A - particles smaller than 3 µm (mg/m^2 day)

	1A	2A	3A	4A	5A	6A
15.10. - 15.11.2005	18	28	5	54	37	31
15.11. - 15.12.2005	15	48	13	5	30	97
15.12. - 15.01.2006	28	25	39	23	49	52
15.01. - 15.02.2006	13	5	24	39	5	5
15.02. - 15.03.2006	35	198	365	329	341	245
15.03. - 15.04.2006	115	53	25	125	42	110
15.04. - 15.05.2006	129	178	122	146	247	176
15.05. - 15.06.2006	45	229	291	301	498	279
15.06. - 15.07.2006	115	625	265	311	712	149
15.07. - 15.08.2006	50	23	56	34	152	148
15.08. - 15.09.2006	*	68	149	180	79	53
15.09. - 15.10.2006	1228	207	1094	4157	828	148

* - sample was not analyzed (sample was destroyed)

During the sampling period from October 2005 to October 2006, the total amount of particulate matter deposition at all sampling sites in the area of the municipality of Ankaran and surroundings exceeded the emission limit value of 350 mg/m^2 a day eleven times, corresponding to 15 % of all measurements.

The highest monthly values were measured in the period from 15.9.2006 to 15.10.2006. During this period, the monthly emission limit value was exceeded at nearly all of the sampling sites. A similar increase of particulate matter deposition values was observed in the period from 15.2.2006 to 15.3.2006 and in the period from 15.6.2006 to 15.7.2006.

Maximum monthly value was measured at the sampling site 4 (Rožnik residential area) in time period 15.9. - 15.10.2006 (4283 mg/m^2 day). At the same sampling site extremely high values were observed also during time period 15.2 - 15.3.2006 (1216 mg/m^2 day). In sampling sites 1, 3 and 5 very high values were observed during time period 15.9. - 15.10.2006. The highest values of dust deposition were therefore measured particularly in the period 15.9.2006 to 15.10.2006. These could be attributed to strong wind, which blew from the direction of the sea across the ore storage pile toward the residential area for a short time (a few hours). The consequences were reported also by the local residents as dust deposition seen on yards, gardens and facades. Figure 3 and 4 were taken in the proximity of the sampling site 4 in October 2006, in the period when the values of particulate matter deposition was extremely high.

4.1.2 Gravimetric analysis of particulate matter deposition - sampling site B

With the modification of the sampling device by adding a metal screen (20 cm x 30 cm) oriented towards the iron ore and coal storage piles, more dust (Table 7) was obtained in samples than was obtained with the standard method (see Figure 42 and Figure 43). With metal screen also the horizontal transport of the dust with wind could be collected. The addition of distilled water to the collection vessel prevented the loss of dry dust sample by the action of strong wind. It is important to emphasize that the limiting value was set for collection of particulate matter deposition using standardized measuring device and not for modified one. Limiting values in case of sampling sites B are presented as orientation values.

Table 7: Monthly mass of particulate matter deposition - sampling sites B (mg/m^2 day)

	1B	2B	3B	4B	5B	6B	limiting value **
15.10. - 15.11.2005	**803**	71	59	69	37	137	350
15.11. - 15.12.2005	38	49	12	53	100	*	350
15.12. - 15.01.2006	94	91	17	54	8	49	350
15.01. - 15.02.2006	104	16	96	37	42	14	350
15.02. - 15.03.2006	270	201	233	**782**	304	218	350
15.03. - 15.04.2006	153	102	74	114	154	151	350
15.04. - 15.05.2006	**816**	127	336	**633**	**459**	**456**	350
15.05. - 15.06.2006	**711**	**999**	**1521**	**942**	**637**	**603**	350
15.06. - 15.07.2006	257	326	**1341**	346	**650**	307	350
15.07. - 15.08.2006	159	94	31	194	190	261	350
15.08. - 15.09.2006	113	**663**	168	30	142	240	350
15.09. - 15.10.2006	**1193**	**640**	**1329**	**5743**	**1072**	91	350

* - sample was not analyzed (sample was destroyed)

** - limiting value according to Decree, 1994

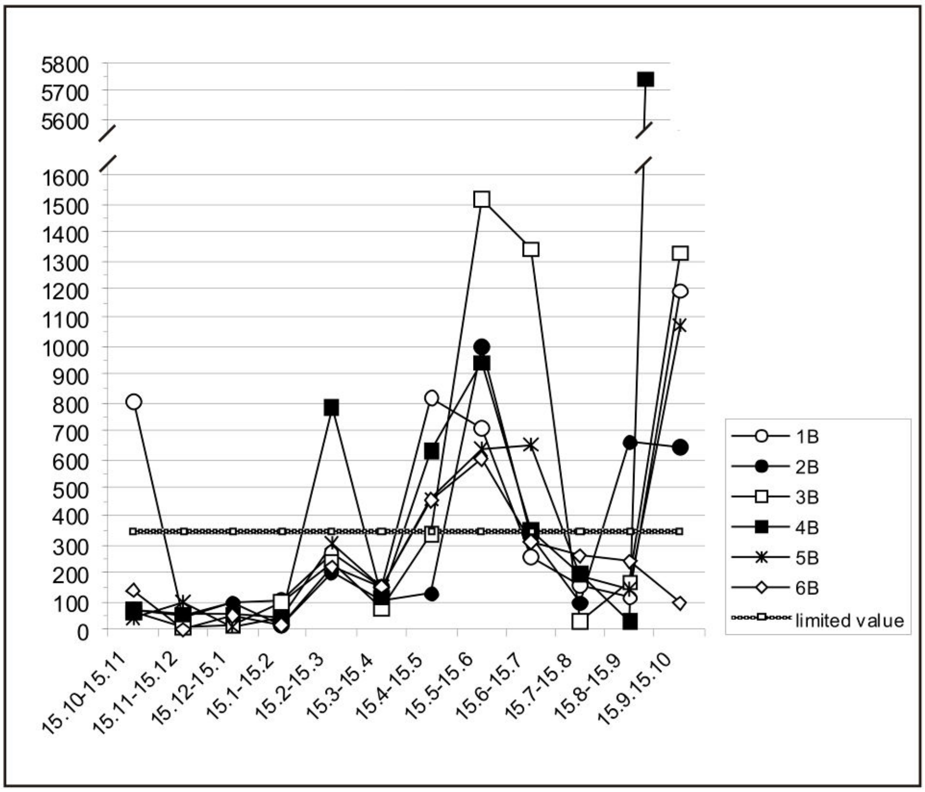


Figure 43: Monthly mass of particulate matter deposition - sampling sites B (vertical plus horizontal deposition collected by modified method).

Table 8: Monthly mass of particulate matter deposition - sampling sites B - particles smaller than 3 µm (mg/m^2 day)

	1B	2B	3B	4B	5B	6B
15.10. - 15.11.2005	88	57	32	54	18	117
15.11. - 15.12.2005	23	15	5	45	46	*
15.12. - 15.01.2006	64	81	12	47	5	16
15.01. - 15.02.2006	78	8	77	19	24	5
15.02. - 15.03.2006	165	171	203	419	281	139
15.03. - 15.04.2006	92	63	49	70	113	85
15.04. - 15.05.2006	687	79	265	217	256	231
15.05. - 15.06.2006	613	916	1305	846	591	599
15.06. - 15.07.2006	222	290	1286	309	605	203
15.07. - 15.08.2006	108	75	20	160	140	234
15.08. - 15.09.2006	64	628	111	17	100	146
15.09. - 15.10.2006	1145	625	1317	5657	918	58

* - sample was not analyzed (sample was destroyed)

The results show considerable differences between individual months at both sampling sites, A and B. It seems that the quantity of particulate matter deposition is dependent on the weather, the wind and rain, the manipulation of the ore and the quantity of ore at the stockpiles on EET depot.

4.1.3 Particulate matter deposition - calculated yearly results

The average particulate matter deposition per year (Figure 44) was calculated from the results of the monthly sampling intervals. Only sampling sites A (vertical deposition) were comparable with the limiting value because the limiting value was set for measurements made by the standardize method. In any individual month as well as on an annual basis, the highest amounts were collected at the sampling site 4 – Rožnik, which lies approx. 1000 m north – north east from the EET storage piles. These elevated amounts could be attributed to the morphology of the terrain and the position of sampling site regarding the proximity of the coal and iron ore depot.

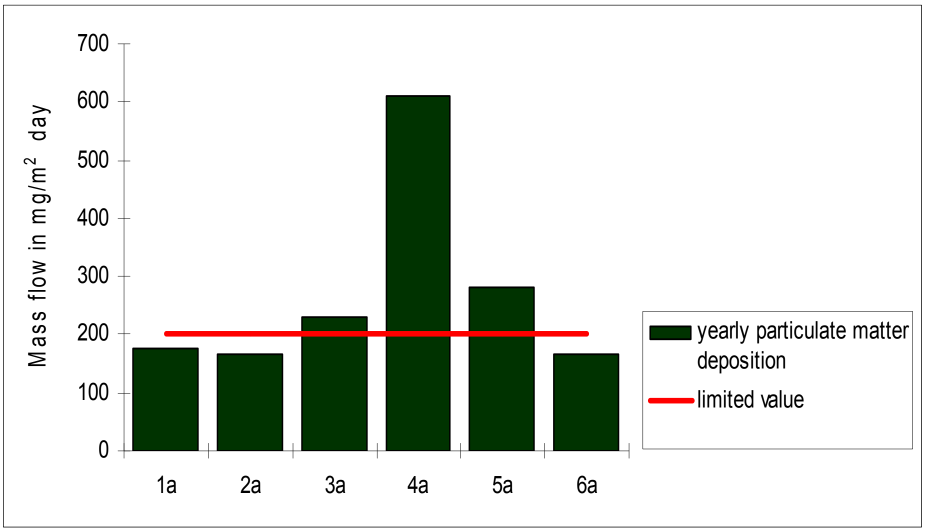


Figure 44: Mass of particulate matter deposition - sampling sites A - calculated yearly results (mg/m^2 day)

4.1.4 Comparison among sampling device A and B on each sampling sites

Higher values of particulate matter deposition in sampling sites B compared to the sampling sites A can be observed at almost all sampling sites with the exception of a few measurements during individual time periods (Figure 45 to Figure 50).

Spearman's (rho) correlation coefficient for sampling sites A and B are relatively high, only exception is sampling site 1, where no correlation were observed. For sampling site 2 A and B correlation is 0,84 (p=0.001), for sampling site 3 A and B is 0.797 (p=0.002), for sampling site 4 A and B is 0.699 (p=0.011) for sampling site 5 A and B is 0.902 (p=0.000) and for sampling site 6 A and B is 0.783 (p=0.003). Sampling sites B appear to consistently collect more particulate matter than sampling sites A.

In the case of dust carried by the wind (especially strong wind) dust particles are "released" when they hit an obstacle. In our case the obstacle is the metal screen on sampling device. In nature obstacles represent buildings, trees and other vegetation. Consequently, the amount of particulate matter deposition is higher in sampling sites B then A.

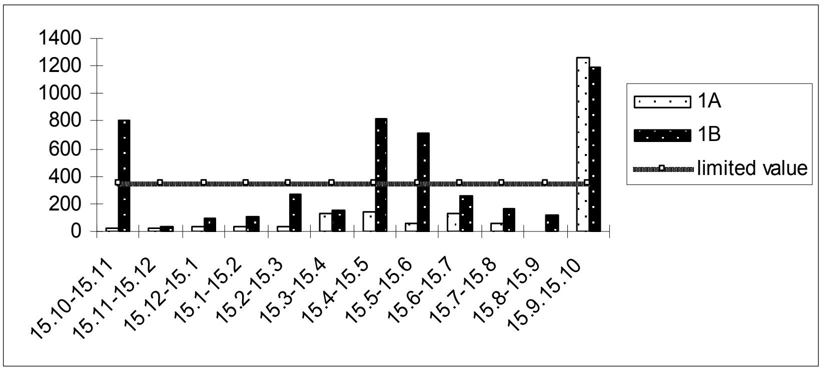


Figure 45: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 1)

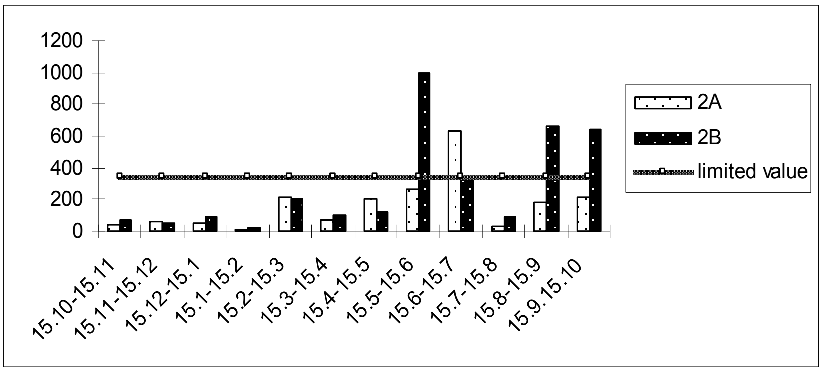


Figure 46: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 2)

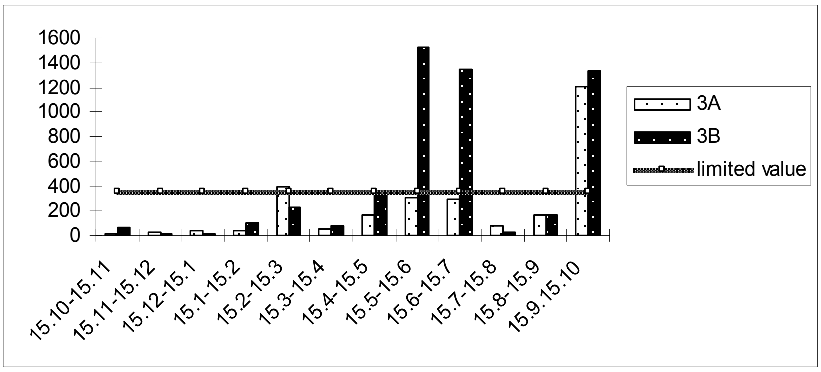


Figure 47: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 3)

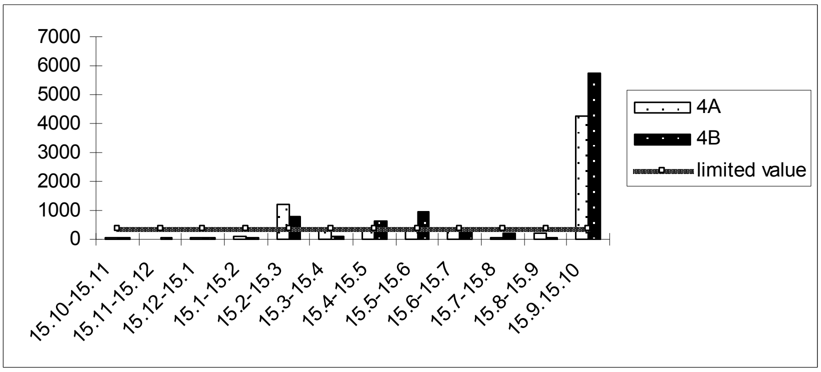


Figure 48: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 4)

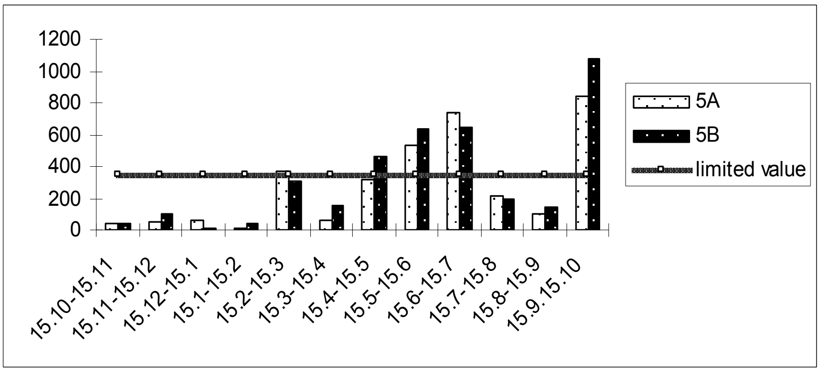


Figure 49: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 5)

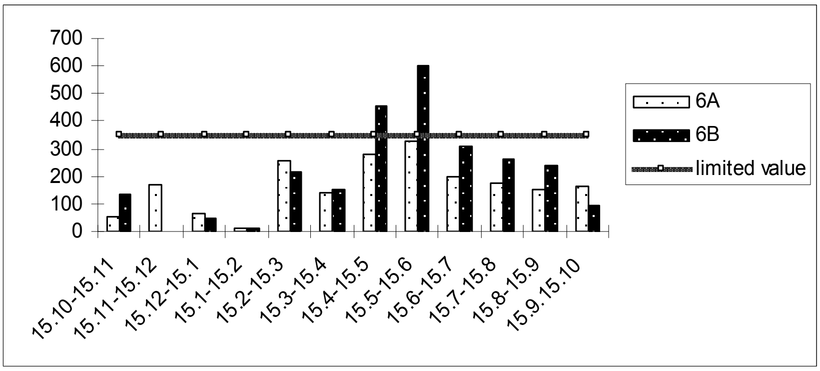


Figure 50: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 6 - control)

4.1.5 Meteorological data for the time period from 15.10.2005 to 15.10.2006

Meteorological data of wind direction and strength were obtained from Port of Koper Department of Environment and Occupational Health. Time interval of entire preliminary study was adopted to the time interval of acquired wind data (from 15th of the month to the 15th of next month). For further work only % of wind blowing across EET depot of coal and iron ore toward individual sampling sites were used (Table 9).

Table 9: % of wind blowing in direction toward sampling sites

	% of wind				
	1 (SW)	2 (SW)	3 (SW)	4 (SW)	5 (S)
15.10. - 15.11.2005	1.4	1.4	1.4	1.4	8
15.11. - 15.12.2005	2.4	2.4	2.4	2.4	12.6
15.12. - 15.01.2006	*	*	*	*	*
15.01. - 15.02.2006	1.3	1.3	1.3	1.3	9.7
15.02. - 15.03.2006	2.8	2.8	2.8	2.8	8.7
15.03. - 15.04.2006	3.2	3.2	3.2	3.2	5.8
15.04. - 15.05.2006	3.2	3.2	3.2	3.2	5.8
15.05. - 15.06.2006	2.8	2.8	2.8	2.8	6.4
15.06. - 15.07.2006	2.5	2.5	2.5	2.5	4.5
15.07. - 15.08.2006	2.1	2.1	2.1	2.1	6.8
15.08. - 15.09.2006	2.6	2.6	2.6	2.6	8.4
15.09. - 15.10.2006	*	*	*	*	*

* data was not available

Some additional meteorological data for preliminary study was acquired from ARSO. August 2006 was extremely wet month (Figure 51), specially in the coastal area (Figure 52). Weather conditions was probably also one of the reasons for low dust deposition during summer time.

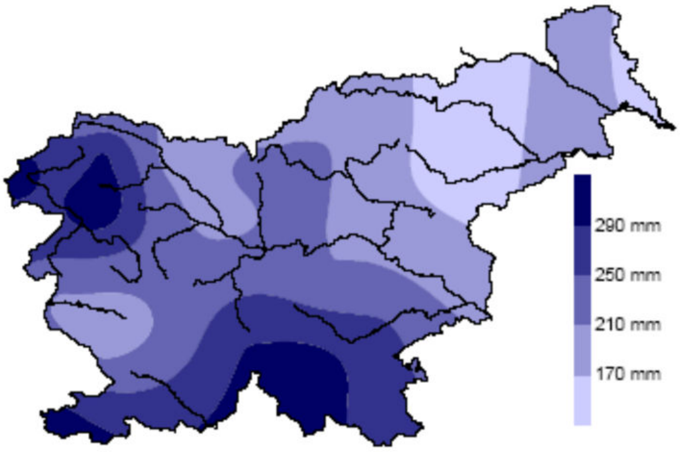


Figure 51: Precipitations in Slovenia - August 2006 ***(Source: ARSO, http://www.arso.gov.si/)***

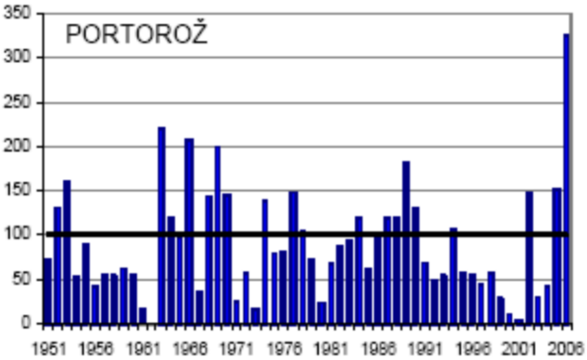


Figure 52: Precipitation in coastal area - Portorož (mm) ***(Source: ARSO, http://www.arso.gov.si/)***

Since a lot of gaps in meteorological data during preliminary study occur improvement in acquiring these data was one of the improvements for the study that follows.

4.1.6 Correlation among strength and direction of the wind and the particulate matter deposition

Data on wind direction and strength involved in the study were obtained from the meteorological station in Port of Koper, provided by their Department of Environmental and Occupational Health. Available data represent the direction and strength of the wind, expressed as % of frequency. Measuring interval represent the period from 15th of the current month to 15th of the following month. Wind speed is given in two intervals, first up to 1 m/s and second over 1 m/s. Data on the frequency of wind at individual directions regardless of strength were included in study. For each sampling site only frequency of winds blowing from the direction of EET toward individual sampling sites were taken into account.

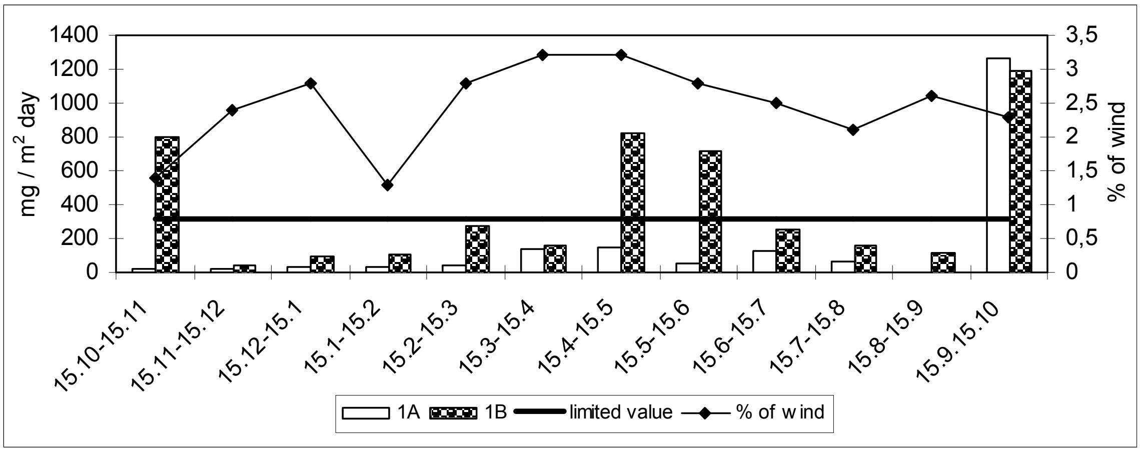


Figure 53: Correlation among particulate matter deposition and wind - sampling site 1

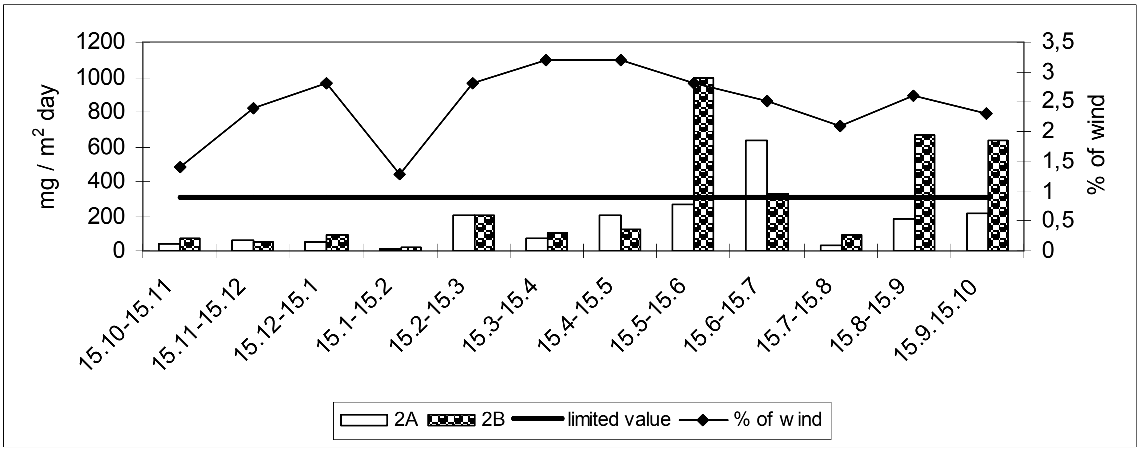


Figure 54: Correlation among particulate matter deposition and wind - sampling site 2

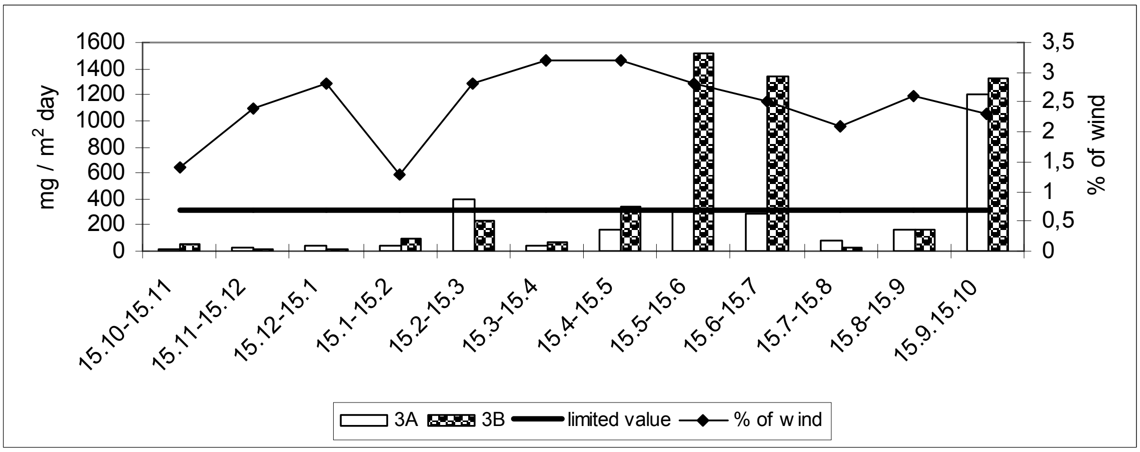


Figure 55: Correlation among particulate matter deposition and wind - sampling site 3

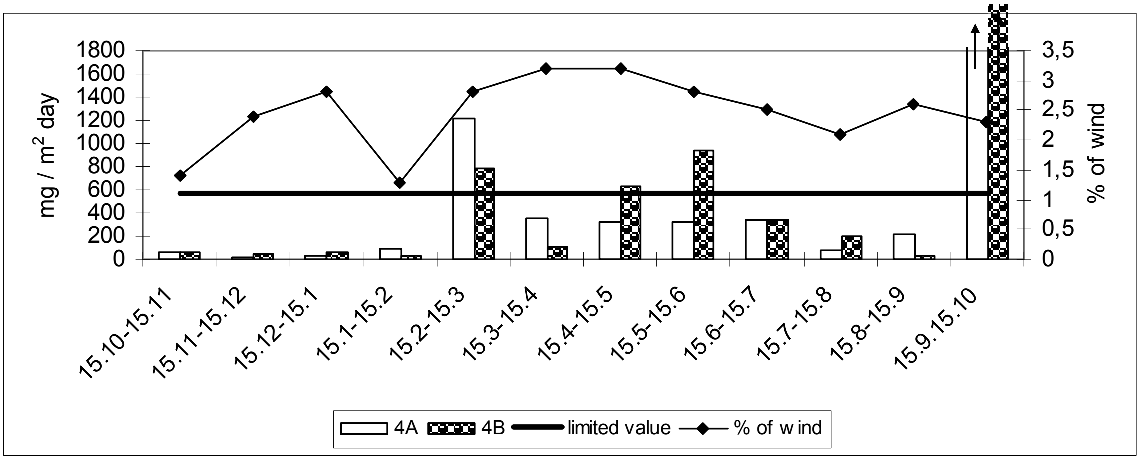


Figure 56: Correlation among particulate matter deposition and wind - sampling site 4

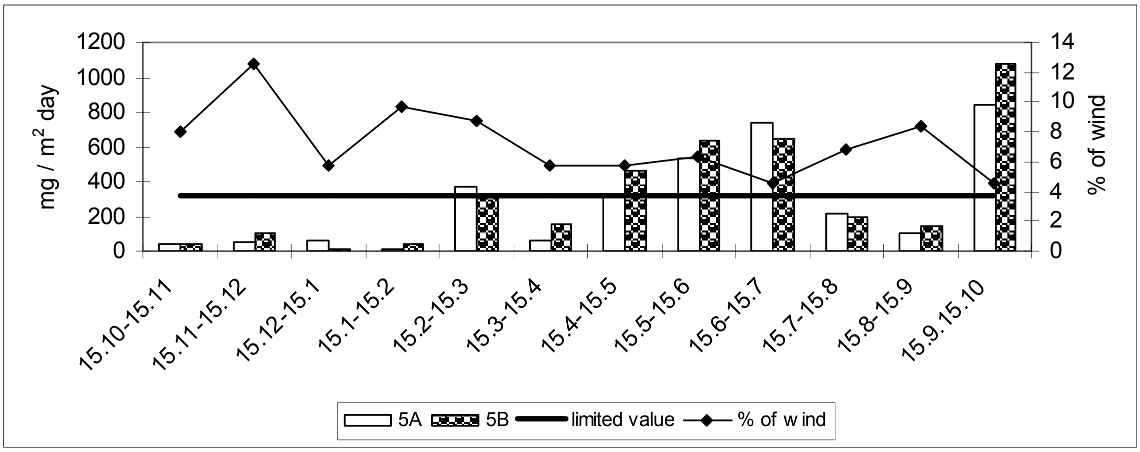


Figure 57: Correlation among particulate matter deposition and wind - sampling site 5

Correlations between the amount of dust deposition and frequency of wind from the direction of EET (Figure 53 to Figure 57) due to insufficient data of the wind speed (only information about the wind speed above and under 1 m/s) and too long measurement interval (1 month) can not be confirmed (highest Spearman's rho correlation is 0.48). Increased emission concentrations could be expected during strong winds blowing through the EET, therefore using selected method of data acquisition is not possible to detect the impact of the extremely strong wind that blows for only a very short period of time.

For the time period 15.9. - 15.10.2006, therefore, there is no correlation between the increased particulate matter deposition and the wind although the residents from Rožnik residential area detected increased deposition of dust in their living environment after the strong Mistral. During same time period also increased amount of deposition were measured, however increased levels of wind were not detected. For example if the wind blows 5 hours with high wind speed it represent only 0.5 % of wind frequency on monthly average data, although many dust particles can be transported from the landfill to surrounding environment during this short time event.

4.1.8 Comparison among particulate matter deposition and coal and iron ore manipulation at EET on each sampling site

Data about quantities of coal and iron ore manipulation on EET terminal in Port of Koper were provided by Department of Environmental and Occupational Health of Port of Koper. From the collected data correlation between amount of particulate matter deposition and ore manipulation at EET can not be confirmed (highest Spearman's rho correlation is 0.44). Data interval of ore manipulation were adjust to time intervals of other data (particulate matter deposition, wind speed and direction). Comparison among particulate matter deposition at each sampling site and coal and iron ore manipulation at EET is presented in Figures 58 to 62.

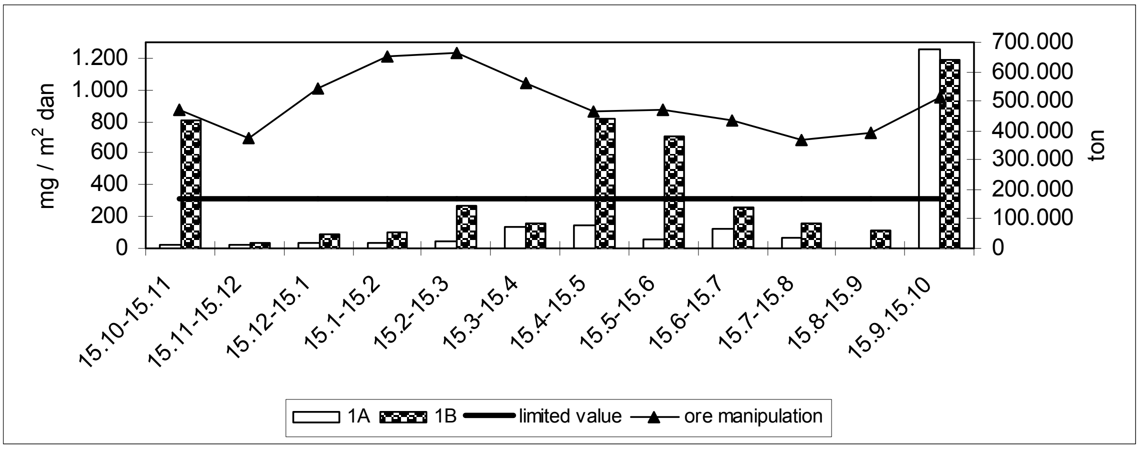


Figure 58: Comparison among particulate matter deposition and ore manipulation at terminal EET - sampling site 1A and 1B

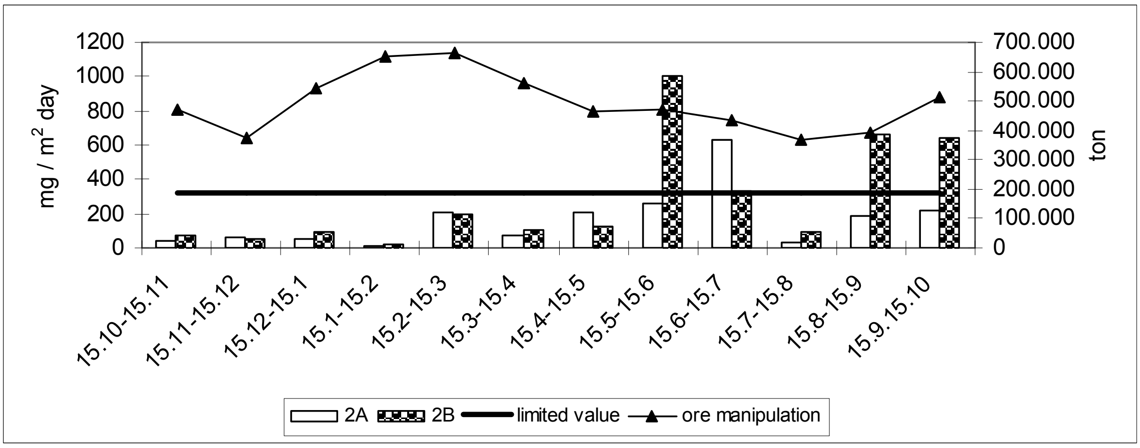


Figure 59: Comparison among particulate matter deposition and ore manipulation at terminal EET - sampling site 2A and 2B

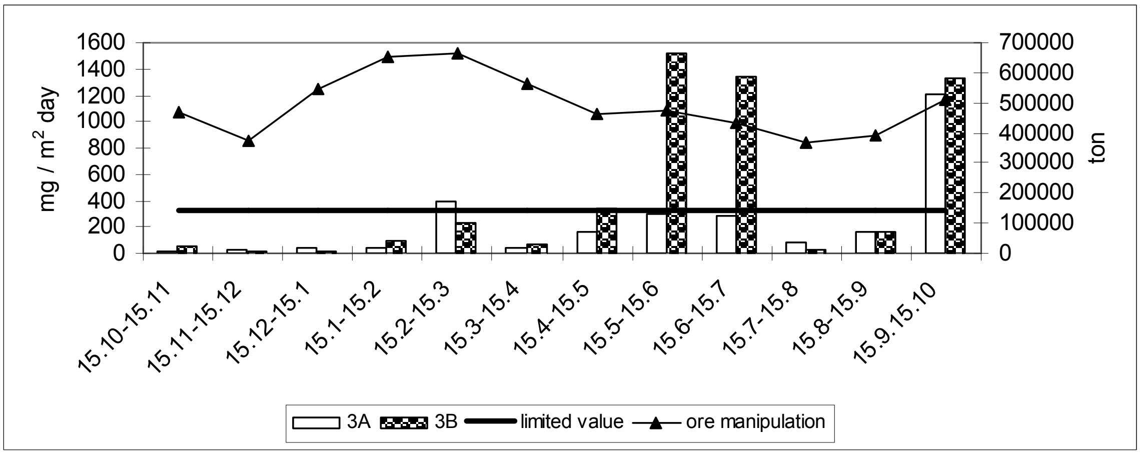


Figure 60: Comparison among particulate matter deposition and ore manipulation at terminal EET - sampling site 3A and 3B

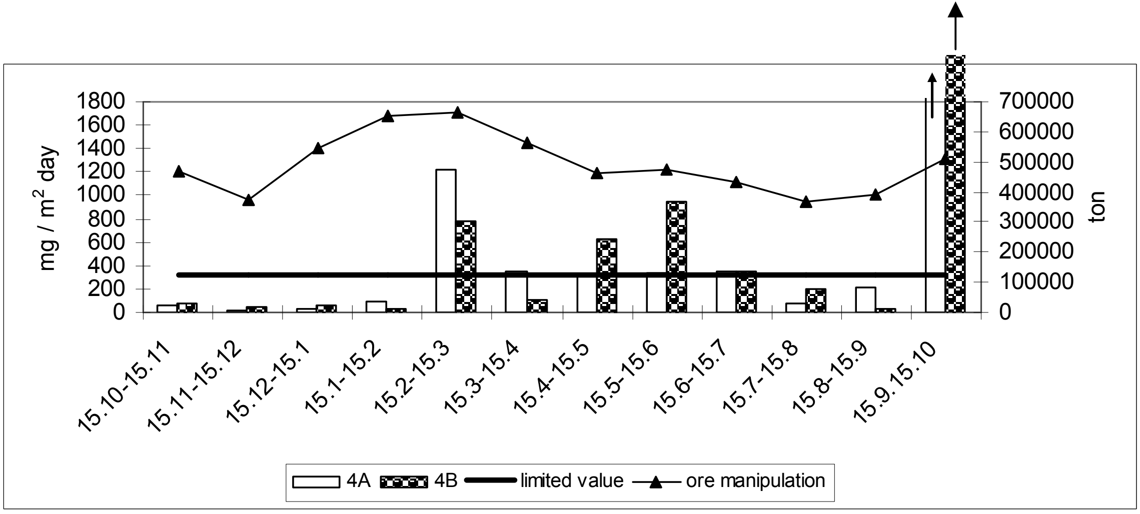


Figure 61: Comparison among particulate matter deposition and ore manipulation at terminal EET - sampling site 4A and 4B

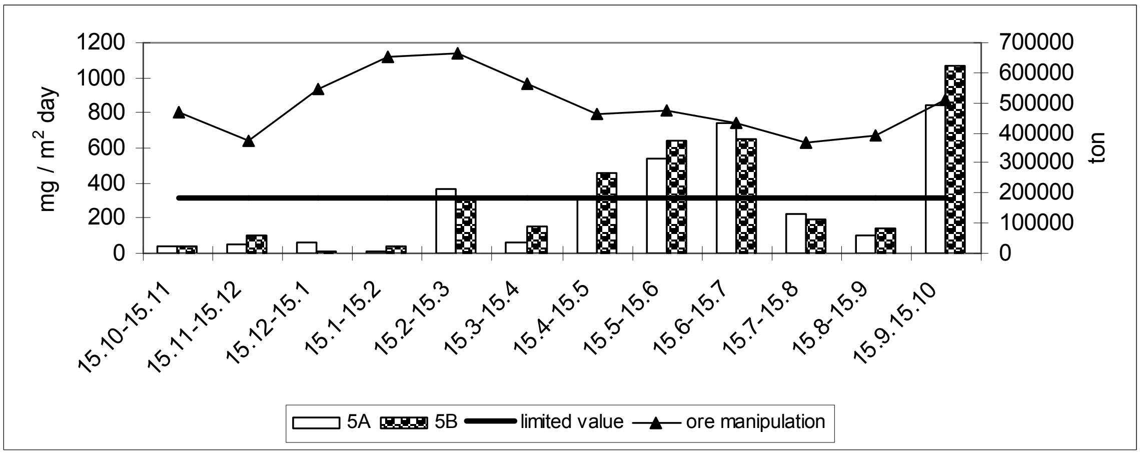


Figure 62: Comparison among particulate matter deposition and ore manipulation at terminal EET - sampling site 5A and 5B

Quantity of particulate matter deposition is higher during summer time. One of the reasons is probably dryness of surroundings and also strong winds, which blows from sea through landfill towards residential area of Roznik and Ankaran and it's probably not correlated with the unloading of coal and iron ore - because the amount of ore manipulation does decrease during summer.

However, the presence of iron in emission measurements of PM_{10} was confirmed in other studies. The proportion of iron in PM_{10} particles in the study "Measurements of air pollution in Ankaran from 28th of June to 11th of September 2005 " performed by ARSO (2005) varied between 6.6 and 13.9 mg/kg with high correlation between iron and PM_{10} concentration. Also the study, conducted by Žitnik et al. (2005) reported a correlation between the iron ore transfer in the EET and the iron concentration in PM_{10}. Perhaps the method for collecting particulate matter deposition is not accurate enough to detect such correlations, especially since the sampling interval is relatively long. According to results from study, conducted by Topič (2009), iron ore on the surface of stockpile developed a special film that prevents dusting to the surrounding area. Dusting occurs, therefore, mainly during manipulation with ore, which has been shown in other studies with correlation between iron ore manipulation and iron concentrations in air particles. Contrary to the situation with iron ore, coal storage and manipulation represent continuously source of dusting since coal on the surface of stockpiles does not develop some special films. In addition, coal must be continuously compressed in order to prevent spontaneous ignition. Therefore in case of strong wind, the coal stockpile represent possible source for airborne particles.

4.1.8 Influence of distance from the EET depot on amount of particulate matter deposition

Sampling sites 1, 2, 3 were placed in linear direction (Figure 7) in predominant wind direction (NE - SW) to evaluate the impact of distance from the EET depot for coal and iron ore on the amount of particulate matter deposition. The morphology of terrain is shown in Figure 63.

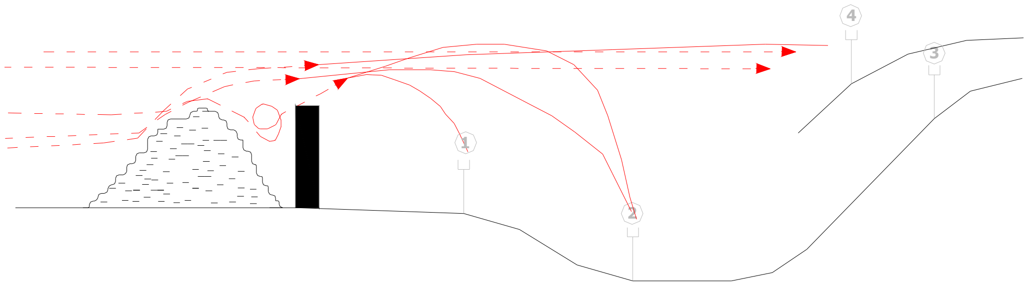


Figure 63: The potential transport of suspended particles from the EET depot towards sampling sites 1, 2, 3 and 4

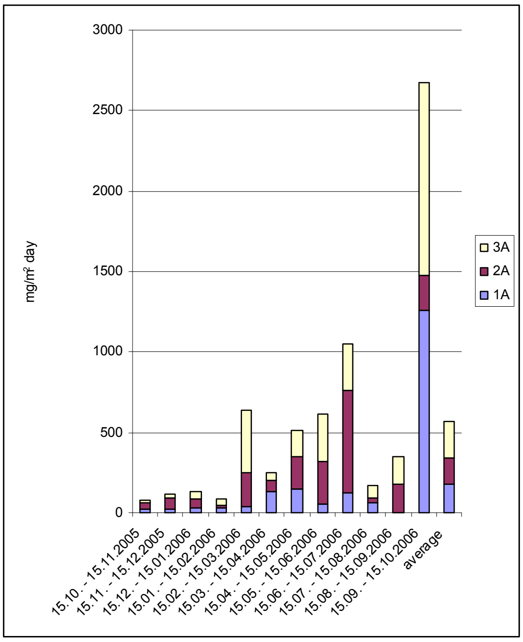


Figure 64: Amount of particulate matter deposition on sampling sites 1, 2 and 3 - sampling sites A

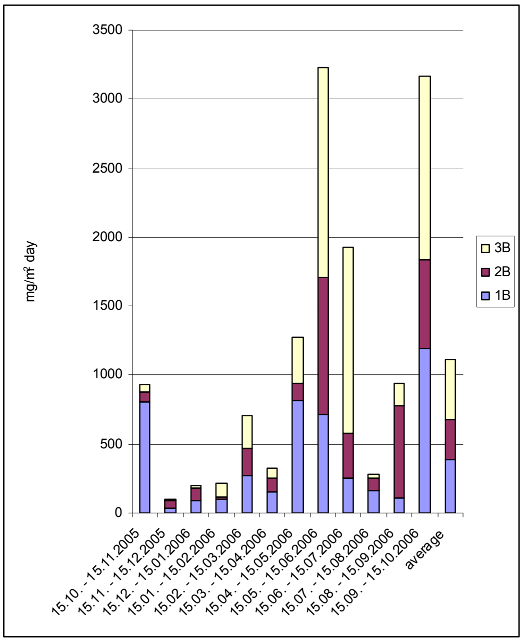


Figure 65: Amount of particulate matter deposition on sampling sites 1, 2 and 3 - sampling sites B

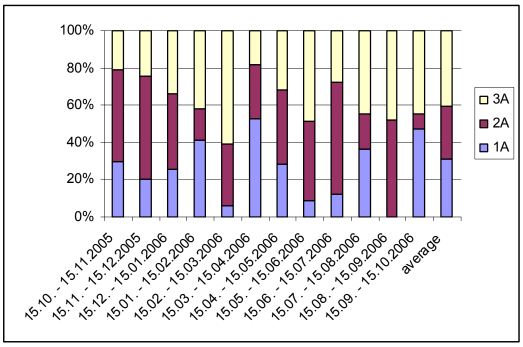


Figure 66: % of particulate matter deposition on sampling site 1, 2 and 3

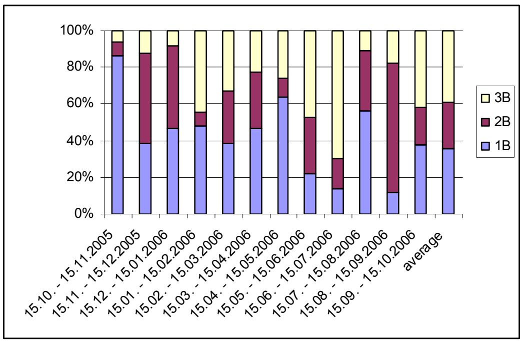


Figure 67: % of particulate matter deposition on sampling site 1, 2 and 3

According to results on sampling sites B (Figure 67) higher amount of particulate matter deposition were observed on sampling sites closer to EET depot (sampling site 1). Only in the case of extreme values of particulate matter deposition are values on sampling site 1 lower than in other two sampling sites. Otherwise, the share of total amount exceeded 40 %. On the sampling sites A this trend were not observed (Figure 66), the proportion of dust deposition at sites 1, 2 and 3 is approximately evenly spread (due to the fluctuations in different time periods). If there are no extreme wind conditions and therefore amount of particulate matter deposition is relatively low, on sampling sites B the trend that the proportion of dust deposition with distance from the landfill decrease (sampling site 1 > sampling site 2 > sampling site 3) can be observed.

Excluding last time interval (15.9.-15.10.2006) the median values shown (Figure 68) decrease mass of particulate matter deposition with distance from EET ore depot in case of sampling device B, however this trend did not appear in case of standardize sampling device A. Spearman's (rho) correlation coefficient for sampling site 2 and 3 are relatively high; for 2 A and B is 0.85 (p=0.001), for sampling site 3 A and B is 0.78 (p=0.004). No correlation was found for sampling site 1.

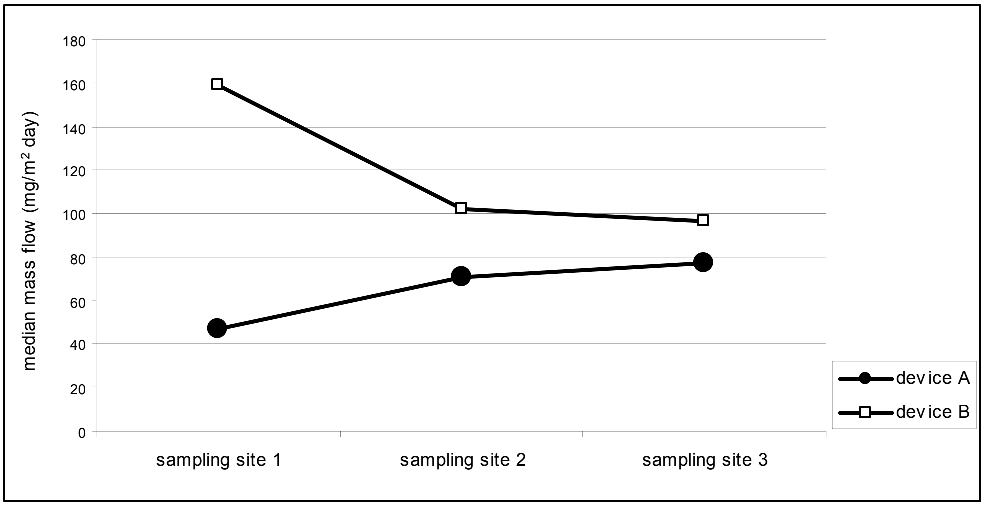


Figure 68: Trend in mass flow on different sampling sites

4.1.9. Chemical analyzes

4.1.9.1 Chemical analysis of coal, iron ore and soil

Heavy metals were determined in coal, iron ore and the surrounding soil. The results are shown in Table 10.

Table 10: The content of metals in coal, iron ore and soil

	COAL* **(mg/kg d.w.)**	**SOIL*** **(mg/kg d.w.)**	**IRON ORE*** **(mg/kg d.w.)**	**IRON ORE**** **(mg/kg d.w.)**
Fe	4800	29600	649000	558240
Al	9800	13500	3200	3150
Cu	8.9	46.9	41.1	40
Zn	15.1	116.8	18.7	16
Cd	<1	<1	<1	0.1
Pb	2.5	25.0	3.6	10
Cr	5.9	66.7	6.5	9
Ni	4.5	94.8	1.6	5

* - Public Health Institute Koper

** - Public Health Institute Celje

Analyses were made in Chemical laboratory of Public Health Institute Koper and Sanitary chemical laboratory of Public Health Institute Celje. According to results no significant amounts of specific metals other than iron and aluminum were found in iron ore or coal comparable to soil sample. High value of iron in sample of soil could contribute to fact that surrounding soil "terra rosa" is rich in iron.

4.1.9.2 Chemical analysis of different metals in deposited matter (Annual sample)

The results from the determinations of aluminum, cadmium, chromium, copper, iron, nickel and zinc in the one – year samples of particulate matter deposition show that the limit value of the metals for Zn, Cd and Pb (Decree, 1994) were not exceeded (Table 11). The only exception was the concentration of zinc at the sampling site 4A. The regulations do not specify limits for amounts of Al, Cr, Cu, Fe and Ni. Results also show increased values of Fe, Al, Cu, Zn and Pb at the sampling site 4. High values of metals in the deposition are present also on the control location (sampling site 6A).

It was not possible to distinguish the coal and iron ore originating from the Port of Koper from other organic sources of carbon (burning of fossil fuel, traffic, pollen, etc.) and iron compounds in the soil on the basis of the results from the metal determinations.

Table 11: Values of metals in the yearly sample of particulate matter deposition (µg/m^2 day).

sampling site	Fe	Al	Cu	Zn	Cd	Pb	Cr	Ni
1A	3054	2584	66	146	<0,3	25	27	14
2A	7740	7263	93	239	<0,3	35	39	26
3A	14433	16805	93	278	<0,3	40	90	35
4A	29450	31942	371	861	1,2	87	98	50
5A	6892	6110	80	93	<0,3	24	28	14
6A	13081	8748	172	324	<0,3	60	46	42
Limiting value	/	/	/	400	2	100	/	/

/ - limiting value is not determined

4.1.9.3 The content of iron in samples from 15.5. to 15.6.2006

The ignition residues of samples collected in time period from 15.5. to 15.6.2006 (particles <3 mm) was colored red. Therefore additional measurements were made to determine the iron content by flame AAS. Results are shown in Table 12 .

Table 12: Contents of iron in sample ignition residues from samples collected on 15.6.2006

sampling site	Fe (μg/m^{2}day)	Fe (mg/kg d.w.)
1A	15	18113
1B	1549	11690
2A	47	11337
2B	128	968
3A	51	2173
3B	191	1448
4A	13	2312
4B	219	1656
5A	6	695
5B	78	586
6A	9	1763
6B	255	1927

Figure 69: Red ignition residue

The results shows that the iron content during observed period of time is higher at sampling sites B (vertical plus horizontal deposition). Also higher amount of particulate matter deposition was obtained during same period of time, particularly on sampling sites B.

4.1.9.4 Determination of samples ignition residue

Many of dust particles collected as particulate matter deposition have organic origin, including pollen, plant parts, algae, small animals etc, as well as coal particles, soot... With determination of samples ignition residue (Table 13) the proportion of inorganic and organic part were identified.

Table 13: Ignition residue of deposition (particles smaller than 3 µm) - % of inorganic part

	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B	6A	6B
15.05. - 15.06.2006	*	13	*	4	*	1	*	7	*	2	*	1
15.06. - 15.07.2006	1	7	1	4	2	4	1	4	10	9	5	7
15.07. - 15.08.2006	*	*	*	*	*	*	<1	4	4	12	<1	13
15.08. - 15.09.2006	*	5	3	8	13	18	26	30	8	0	11	6
15.09. - 15.10.2006	10	10	3	4	4	11	10	12	12	10	6	1

* - no data available

Results shows that particulate matter deposition, smaller than 3 µm is composed mainly of organic matter. Inorganic represents from <1 to 30 % of the composition.

4.1.10 Results of gamma-ray emitter's activity measurements of iron ore, coal and sample of soil

In nature there are many natural radioactive isotopes, which could be as impurities present also in coal and iron ore (Van Hook, 1979; Dowdall et al., 2004; Ward and Suárez-Ruiz, 2008). For this reason representative sample of coal and iron ore from EET depot in Port of Koper was analyzed for gamma-ray emitters' activity (Table 14 and Table 15).

Specific activities of gamma-ray emitters were calculated back to the date 25.8.2006. The number following the ± symbol is numerical value of the combined standard uncertainty of the specific activity and corresponds to the confidence interval with a 68 % confidence. The number following the < symbol is numerical value of the minimal detectable activity for a given radionuclide and corresponds to the confidence interval with a 68 % confidence.

Table 14: Specific activity of gamma-ray emitters in coal sample

isotope	Specific activity (Bq/kg)
^{134}Cs	<0.07
^{137}Cs	<0.25
^{210}Pb	8.7 ± 2.8
^{214}Bì	10.2 ± 1.1
^{226}Ra	9.8 ± 1.1
^{228}Ra	7.7 ± 0.6
^{228}Th	7.9 ± 0.5
^{238}U	7.6 ± 2.1

Table 15: Specific activity of gamma-ray emitters in iron ore sample

isotope	Specific activity (Bq/kg)
^{134}Cs	< 0,04
^{137}Cs	< 0.04
^{210}Pb	19 ± 11
^{214}Bì	21 ± 2
^{226}Ra	21 ± 2
^{228}Ra	6.1 ± 0.3
^{228}Th	6.1 ± 0.2
^{230}Th	70 ± 34
^{238}U	14 ± 3

Table 16: Specific activity of gamma-ray emitters in soil sample

isotope	Specific activity (Bq/kg)
^{7}Be	2.1 ± 1.2
^{40}K	364 ± 36
^{137}Cs	32.4 ± 1,6
^{210}Pb	63 ± 40
^{214}Bi	39,0 ± 3,9
^{226}Ra	39.0 ± 2.7
^{228}Ra	30.1 ± 1,3
^{228}Th	29.0 ± 1,5
^{230}Th	<90.6
^{238}U	19.6 ± 5.3

For soil analyzes (Table 16) soil from Slovenia area (uncultivated land) as example of normal amount of radio nuclides in the soil were used (source: Jožef Stefan Institute). Among other radioactive isotopes ^{137}Cs is present in soil sample due to Chernobyl accident and also nuclear experiments, performed in atmosphere. That is the mayor difference between results of gamma-ray emitter's activity in coal and iron ore samples and results of gamma-ray emitter's activity in soil sample.

Because the activity of the gamma-ray emitters from sample of coal and iron ore was not significantly increased additional analyzes of samples of particulate matter deposition were not performed.

4.1.11 Results of electron microscopy

Electron microscopy of particulate matter deposition was used to confirm presence of coal and iron ore particles in particulate matter deposition collected around EET depot (Port of Koper). Presence of both coal and iron ore particles linked the dust deposition with the activity on the coal and iron ore depot. For purpose of preliminary study only samples from time period from 15th of February to 15th of March 2006 were analyzed. During that time presence of coal was detected with visual inspection of the filtered samples (Figure 70, Figure 71 and Figure 72), also higher particulate matter deposition was detected in all sampling sites, especially in sampling site 4. Presence of coal was confirmed with morphological and chemical analysis by electron microscopy (Figures 73 to 78) of the filters.

Figures 70, 71 and 72: Sample of particulate matter deposition - sampling site 4 - from 15th February to 15th March 2006

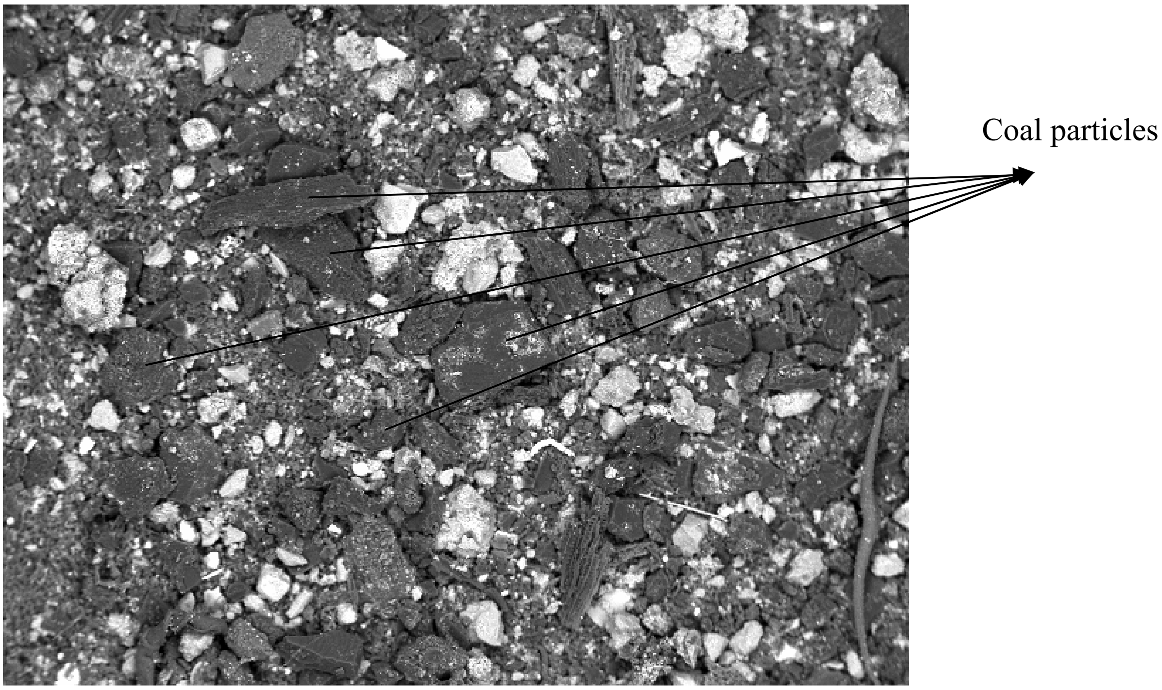


Figure 73: Sample 4A (85x magnification, image width 1.55 mm)

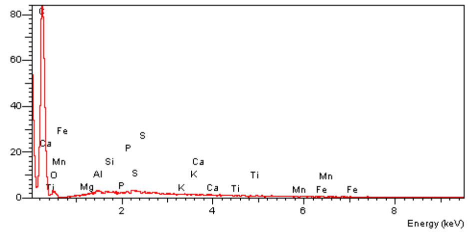


Figure 74: Typical EDXS spectrum of coal particle

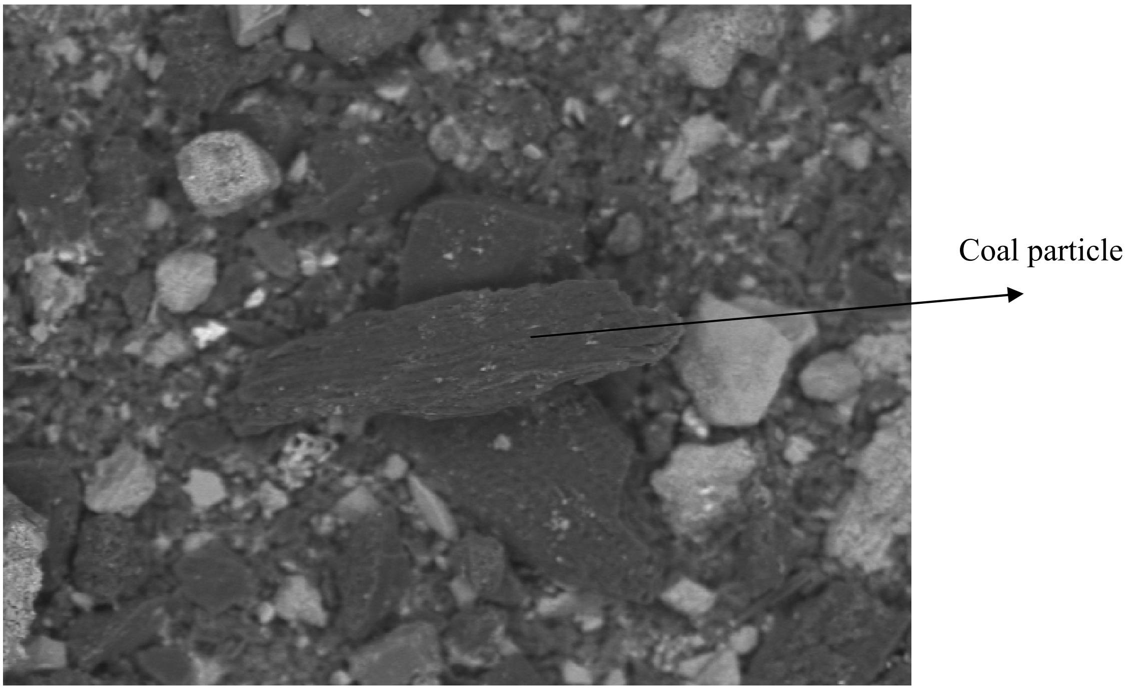


Figure 75: Sample 4A (220x magnification, image width 600 µm)

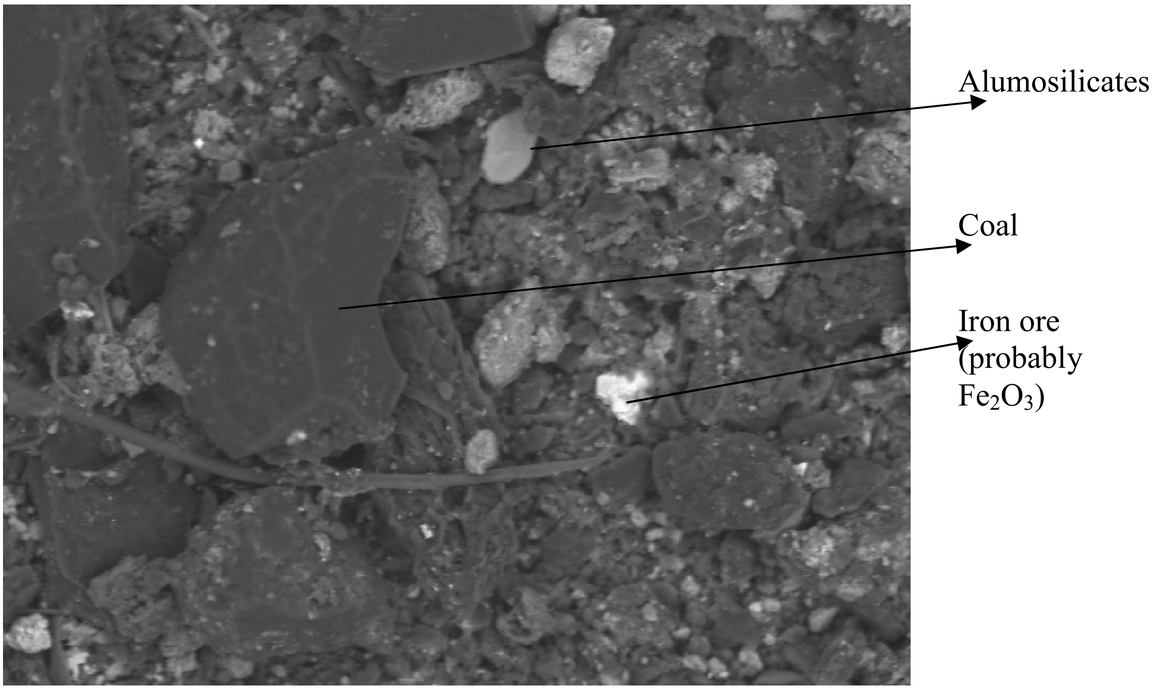


Figure 76: Sample 4A (330x magnification, image width 400 µm)

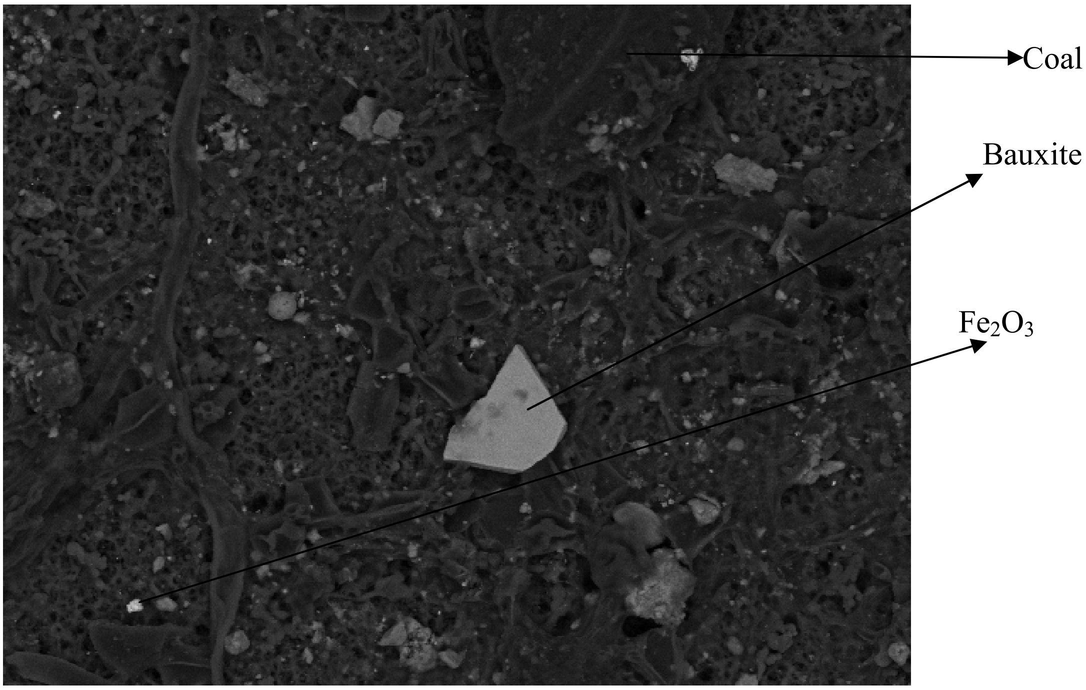


Figure 77: Sample 4B (350x magnification, image width 377 µm)

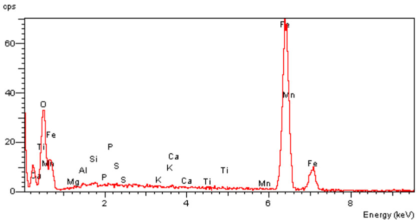


Figure 78: Typical EDXS spectrum of Fe_2O_3

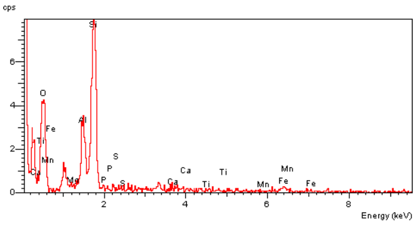


Figure 79: Typical EDXS spectrum of alumosilicates

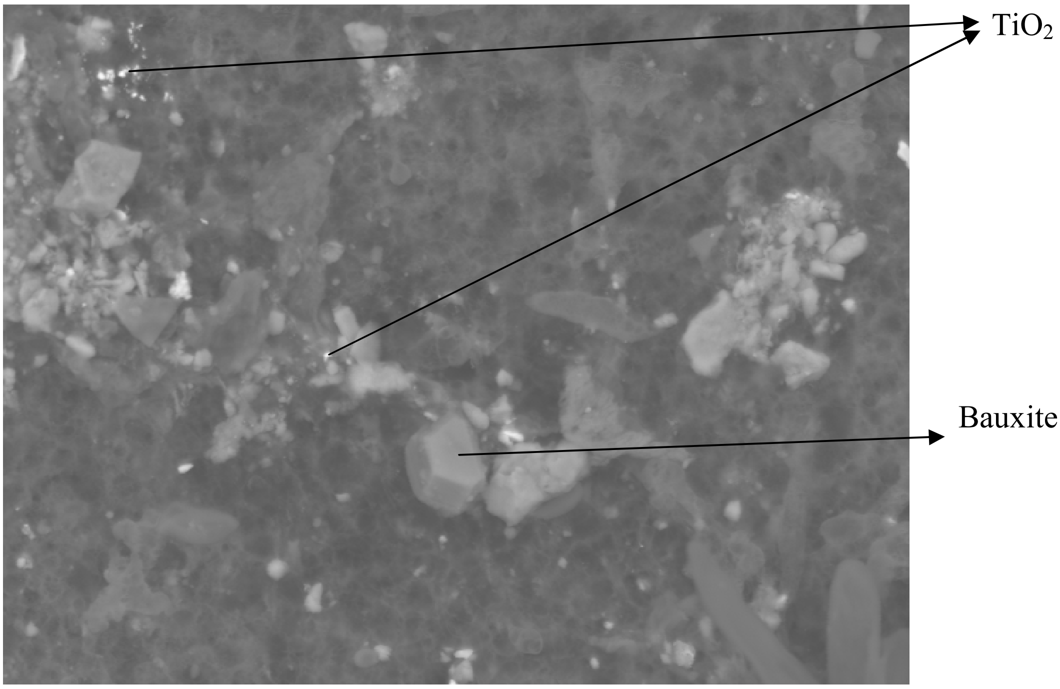


Figure 80: Sample 3A (750x magnification, image width 176 µm)

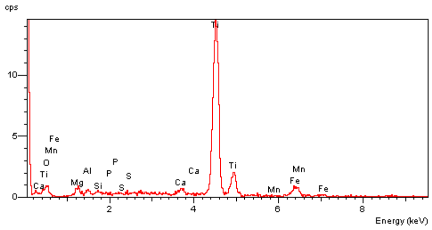


Figure 81: Typical EDXS spectrum of TiO_2

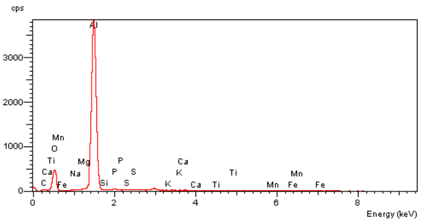


Figure 82: Typical EDXS spectrum of bauxite

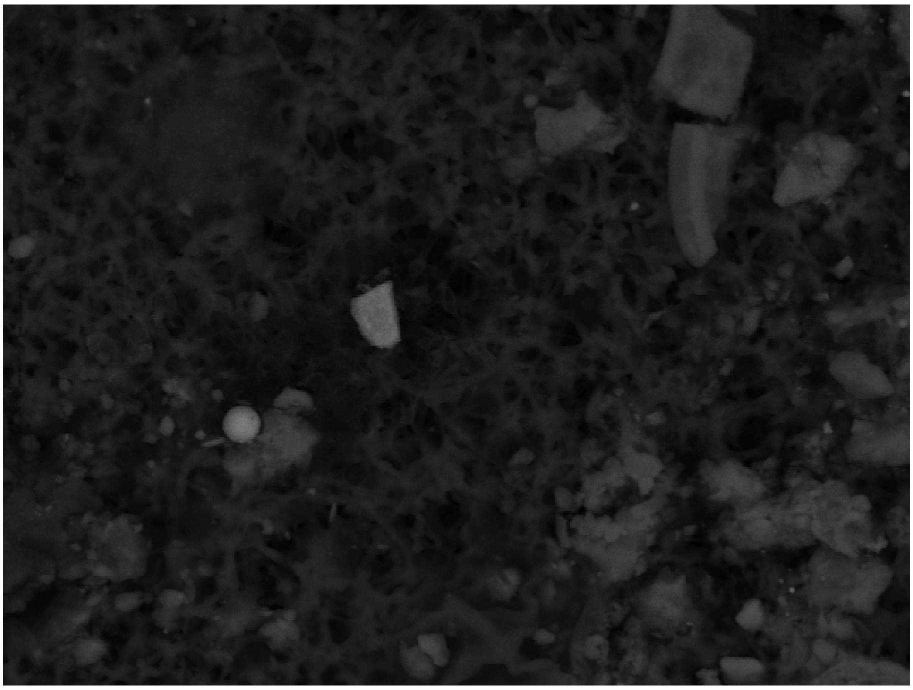


Figure 83: Sample 6A - control (1200x magnification, image width 110 µm)

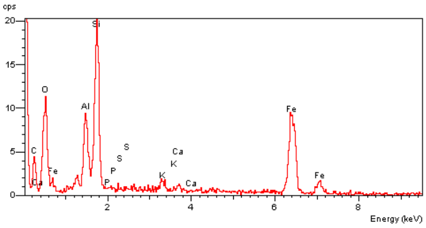


Figure 84: Typical EDXS spectrum of iron in the presence of silicon or aluminum

In reference sampling site in Beli Križ area (Portorož) SiO2, Ca and Mg carbonate were detected. No coal or iron ore were detected (Figure 85 and 86).

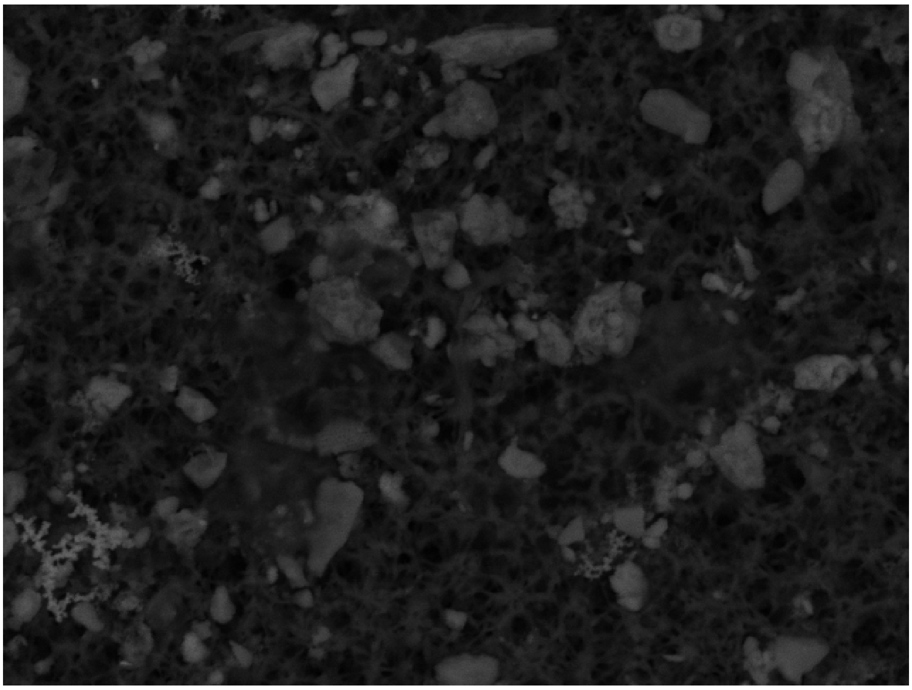


Figure 85: Reference sample (850x magnification, image width 155 µm)

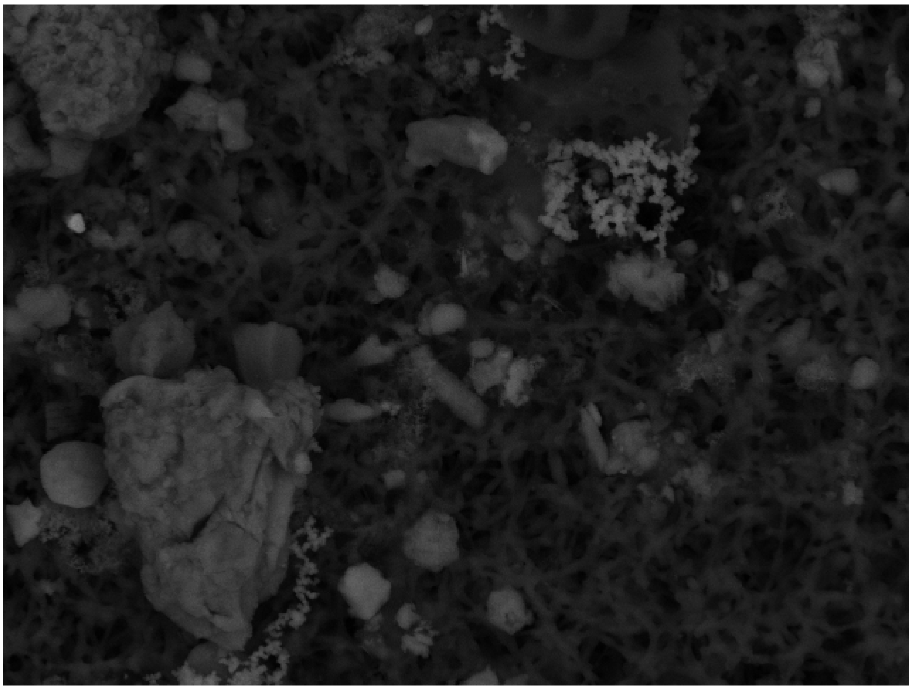


Figure 86: Reference sample (1200x magnification, image width 110 µm)

In samples of particulate matter deposition from time period 15.2.2006 - 15.3.2006 at sampling sites 1 to 5, iron oxide and coal particles were detected. In the sample at the sampling site 6, iron was also present, however not as Fe_2O_3 but always in the presence of silicon and alumina. Therefore it could be speculated that the origin of such iron is probably from the soil from the surrounding environment. Coal particles in the sample at sampling site

6 (control) were not detected. Also morphological characteristics of the rust (scale), which could contaminate the samples, were not detected. In the reference sample at the sampling site Beli Križ (Portorož area) iron and coal particles were not detected. Only SiO_2, Ca-carbonate and Mg-carbonate were found.

Figures 87 and 88: Wax cloth swimming pool coverage in Žusterna

Additionally analyzes were made on samples from the wax cloth swimming pool coverage (Figures 87 to 91) from Žusterna (Koper). Particles of bauxite and TiO_2 were detected.

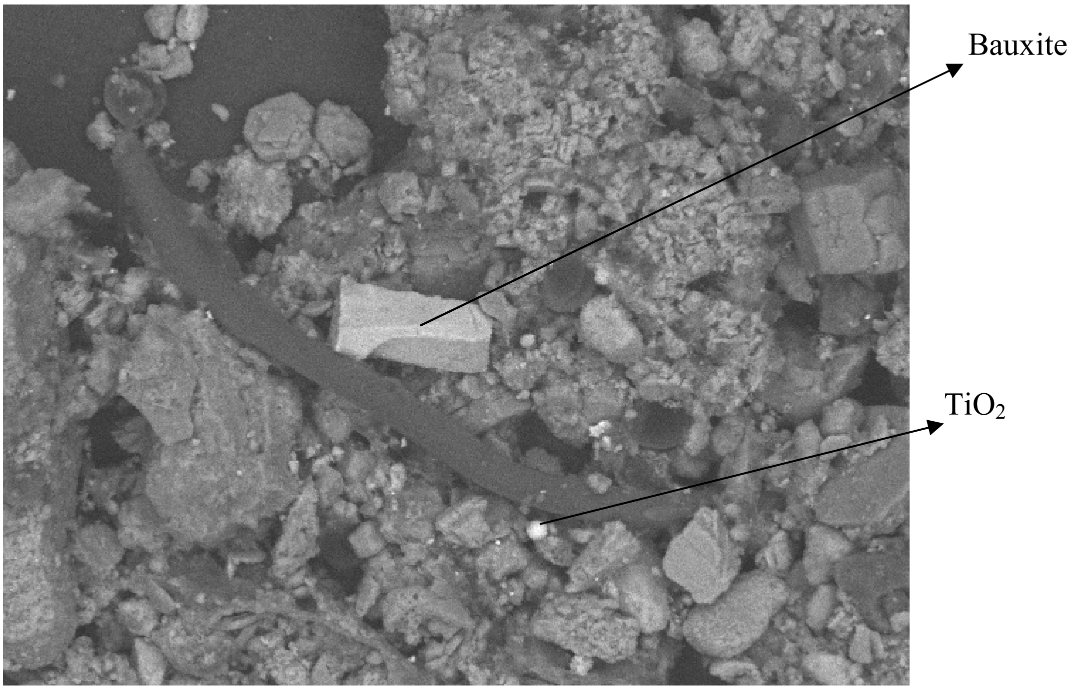


Figure 89: Swimming pool coverage (wax cloth) from Žusterna (450x magnification, image width 293 µm)

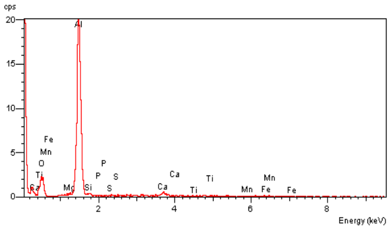


Figure 90: Typical EDXS spectrum of bauxite

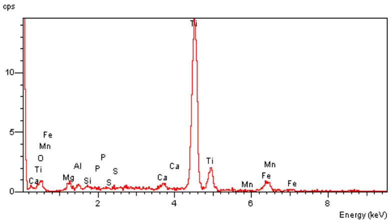


Figure 91: Typical EDXS spectrum of TiO_2

From results with SEM we can conclude that warehousing and handling with coal and iron ore on EET depot in Port of Koper have an influence on increased particulate matter deposition in surroundings. With analysis of morphology and chemical structure of particulate matter deposition using Electron microscope, the presence of coal and iron ore were confirmed. The quantitative analyzes could not be done with the samples collected because they were too concentrated.

PART II - study 2007/08

4.2. Results of study from 1st December 2007 - 30th November 2008

4.2.1 Gravimetric analyses of particulate matter deposition - measurement interval twice per month

Samples were collected and the depositions of airborne particulate matter were determined by gravimetric analysis at each sampling site on every 1st and 15th of each month. Values of particulate matter deposition in Table 17 are presented in mg/m^2 day for each sampling site using standardized method of collection of particulates deposition (samples marked with letter A).

Table 17: Mass of particulate matter deposition - sampling sites A (mg/m^2 day)

	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	recommended value
1.12.-15.12.2007	95	94	56	85	202	102	98	159	/ *	98	350
15.12.2007-1.1.2008	32	63	86	43	131	71	43	/ *	/ *	63	350
1.1.-15.1.2008	191	85	64	126	100	63	59	79	110	44	350
15.1.-1.2.2008	72	94	54	114	76	62	77	107	94	55	350
1.2.-15.2.2008	38	31	47	36	82	48	38	302	105	39	350
15.2.-1.3.2008	44	39	39	211	94	67	42	109	54	54	350
1.3.-15.3.2008	36	59	56	69	188	77	54	/ *	182	213	350
15.3.-1.4.2008	105	90	257	217	225	123	129	133	/ *	70	350
1.4.-15.4.2008	57	63	95	71	139	230	42	150	235	65	350
15.4.-1.5.2008	75	78	60	96	189	59	71	129	80	94	350
1.5.-15.5.2008	21	46	29	28	159	75	69	92	29	46	350
15.5.-1.6.2008	123	176	156	177	**389**	130	269	210	123	141	350
1.6.-15.6.2008	61	61	86	48	296	78	145	92	65	67	350
15.6.-1.7.2008	/ *	126	84	75	310	97	159	88	69	93	350
1.7.-15.7.2008	70	157	92	105	324	305	205	146	129	90	350
15.7.-1.8.2008	100	111	124	276	147	74	157	111	72	94	350
1.8.-15.8.2008	57	311	128	167	/ ***	213	241	59	/ **	**364**	350
15.8.-1.9.2008	80	77	51	46	186	66	149	97	152	65	350
1.9.-15.9.2008	77	102	106	95	213	95	131	113	/ *	146	350
15.9.-1.10.2008	15	54	18	20	33	56	34	/ *	49	20	350
1.10.-15.10.2008	56	88	105	83	105	88	52	116	54	59	350
15.10.-1.11.2008	119	114	92	130	/ ***	174	130	180	123	102	350
1.11.-15.11.2008	62	75	67	169	/ ***	59	71	134	75	46	350
15.11.-1.12.2008	56	58	38	43	349	**369**	49	99	/ **	63	350

* - sample was not analyzed (sample was destroyed)

** - high values due to presence of NaCl or Cu compounds

*** - high values due to presence of organic pollution of sample (decay parts of plants or insects, algae)

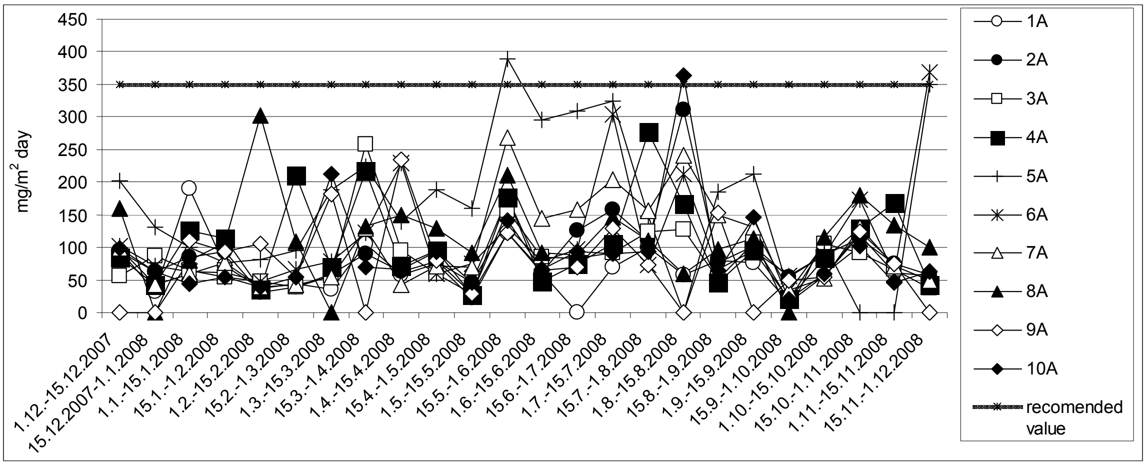
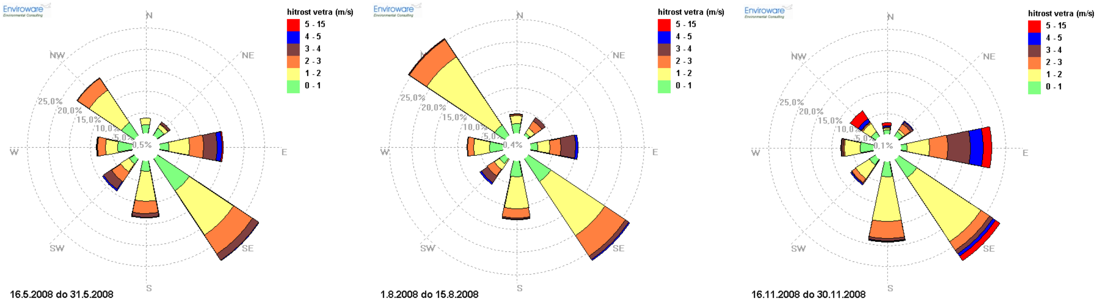


Figure 92: Mass of particulate matter deposition - sampling sites A

The recommended values of 350 mg/m^2 day for particulate matter deposition was established in the annulled Decree on limit values, alert thresholds and critical emission values for substances into the atmosphere (1994). It is still in use. During entire monitoring period, only four from 240 samples approached or exceeded the recommended value. They are the sampling site 5A during the period 15.5. - 1.6., the sampling site 10A during the period 1.8. to 15.8. and sampling sites 5A and 6A during the period 15.11. - 1.12. In all of these periods, the wind blew with increased intensity (longer period of time as well as higher speed) in the direction of S and SW - from the EET depot towards the sampling site 5 and 10 (wind-roses for observed periods - Figure 93, Figure 94 and Figure 95). However, it is important to emphasize that the mass of monthly particulate matter deposition were considerably lower and does not exceed the recommended values in any case (see Table 23 and Figure 107).



Figures 93, 94 and 95: Wind-roses for time period of 16.5. to 31.5., 1.8. to 15.8. and 16.11. to 30.11.2008

In the following tables and figures, the masses of particulate matter deposition at the sampling sites A (as well as in sampling sites B) are shown separately for the particle size below and above 3 µm. The particles are divided into major and minor fractions on the basis of the analytical method. Cellulose nitrate membrane filter of pore size 3 µm were used for filtration. Therefore particles were split to those remaining on the filter (particles larger than 3 µm) and particulate matter in the filtrate (the smaller particles and the dissolved substances). During such division some particles, smaller then 3 µm could remain on filters due to filters pore saturation. However, results are still indicative enough for the purpose of this study.

The concentration of particles larger than 3 µm in sampling sites A rarely exceed values of 80 mg/m^2 daily while the values for particles smaller than 3 µm usually ranging between 50 and 200 mg/m^2 per day.

Dust particles smaller than 3 µm (Table 19 and Figure 97) make a greater contribution to the total particulate matter deposition than do particles larger than 3 µm (Table 18 and Figure 96). The smaller particles are also in terms of impact on the health more problematic because they are able to penetrate deeper into the respiratory system upon inhalation.

Table 18: Mass of particulate matter deposition - sampling sites A - particles larger than 3 µm (mg/m^2 day)

	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A
1.12.-15.12.2007	46	36	16	29	49	41	38	49	/ *	36
15.12.2007-1.1.2008	8	23	28	18	20	31	15	/ *	/ *	25
1.1.-15.1.2008	31	26	15	41	33	13	16	20	26	3
15.1.-1.2.2008	12	25	8	15	9	6	12	23	20	6
1.2.-15.2.2008	10	10	13	13	23	18	11	61	15	20
15.2.-1.3.2008	4	2	0	21	11	9	5	18	0	7
1.3.-15.3.2008	7	15	13	23	56	23	18	/ *	88	118
15.3.-1.4.2008	11	5	29	25	31	15	14	14	/ *	8
1.4.-15.4.2008	31	34	41	28	39	103	28	67	36	38
15.4.-1.5.2008	26	25	18	33	25	8	18	48	25	38
1.5.-15.5.2008	5	18	5	8	56	26	28	28	13	23
15.5.-1.6.2008	45	69	74	74	9	41	40	80	46	68
1.6.-15.6.2008	8	11	15	5	52	18	48	16	7	20
15.6.-1.7.2008	/ ***	43	36	26	95	29	51	18	11	34
1.7.-15.7.2008	21	48	34	38	72	79	34	23	34	25
15.7.-1.8.2008	8	15	14	28	31	31	29	32	12	14
1.8.-15.8.2008	13	90	18	34	/ ***	36	29	25	/ **	26
15.8.-1.9.2008	18	15	14	11	48	20	5	8	11	14
1.9.-15.9.2008	15	31	39	23	41	13	20	31	/ *	33
15.9.-1.10.2008	2	11	7	11	7	21	15	/ *	2	13
1.10.-15.10.2008	7	8	20	7	3	3	8	15	5	7
15.10.-1.11.2008	26	17	6	22	/ ***	35	12	14	31	26
1.11.-15.11.2008	29	29	33	36	/ ***	26	31	33	29	20
15.11.-1.12.2008	5	11	8	10	44	82	7	28	/ **	15

* - sample was not analyzed (sample was destroyed)

** - high values due to presence of NaCl or Cu compounds

*** - high values due to presence of organic pollution of sample (decay parts of plants or insects, algae)

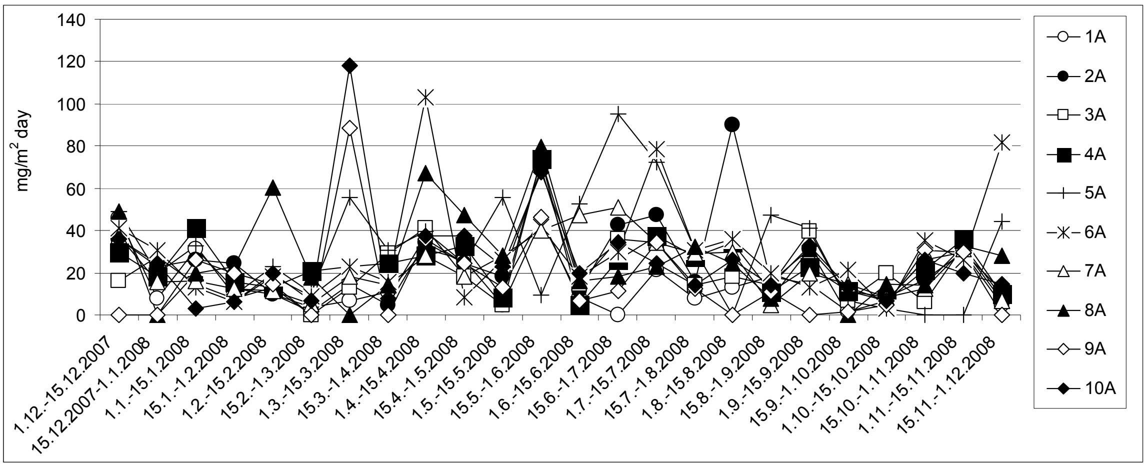


Figure 96: Mass of particulate matter deposition - sampling sites A - particles > 3 µm

Table 19: Mass of particulate matter deposition - sampling sites A - particles smaller than 3 µm (mg/m^2 day)

	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A
1.12.-15.12.2007	50	58	39	56	152	61	60	110	/ *	62
15.12.2007-1.1.2008	25	40	58	25	111	40	28	/ *	/ *	38
1.1.-15.1.2008	160	59	49	85	67	50	43	60	84	40
15.1.-1.2.2008	60	69	46	99	67	56	65	84	74	49
1.2.-15.2.2008	28	21	34	23	59	29	27	242	90	20
15.2.-1.3.2008	40	37	39	190	84	58	37	91	54	47
1.3.-15.3.2008	29	44	43	46	133	55	35	/ *	94	95
15.3.-1.4.2008	94	86	228	193	194	108	115	119	/ *	63
1.4.-15.4.2008	26	29	54	43	100	127	14	83	199	28
15.4.-1.5.2008	49	53	42	63	165	51	53	82	55	56
1.5.-15.5.2008	16	28	25	20	103	49	41	64	16	23
15.5.-1.6.2008	78	107	82	103	379	89	229	130	77	74
1.6.-15.6.2008	52	50	71	43	243	60	98	76	58	47
15.6.-1.7.2008	/ *	84	48	49	215	67	108	70	57	59
1.7.-15.7.2008	49	110	57	67	252	226	170	123	94	66
15.7.-1.8.2008	92	95	111	249	117	43	127	78	60	80
1.8.-15.8.2008	44	221	110	133	/ ***	177	211	34	/ **	337
15.8.-1.9.2008	61	61	37	35	138	46	144	89	141	51
1.9.-15.9.2008	62	70	67	72	172	82	111	82	/ *	113
15.9.-1.10.2008	13	43	11	8	26	34	20	/ *	48	7
1.10.-15.10.2008	49	80	85	76	102	85	44	102	49	52
15.10.-1.11.2008	93	97	86	108	/ ***	138	118	166	92	76
1.11.-15.11.2008	32	46	34	133	/ ***	33	40	101	46	26
15.11.-1.12.2008	51	47	29	33	305	287	43	72	/ **	49

* - sample was not analyzed (sample was destroyed)

** - high values due to presence of NaCl or Cu compounds

*** - high values due to presence of organic pollution of sample (decay parts of plants or insects, algae)

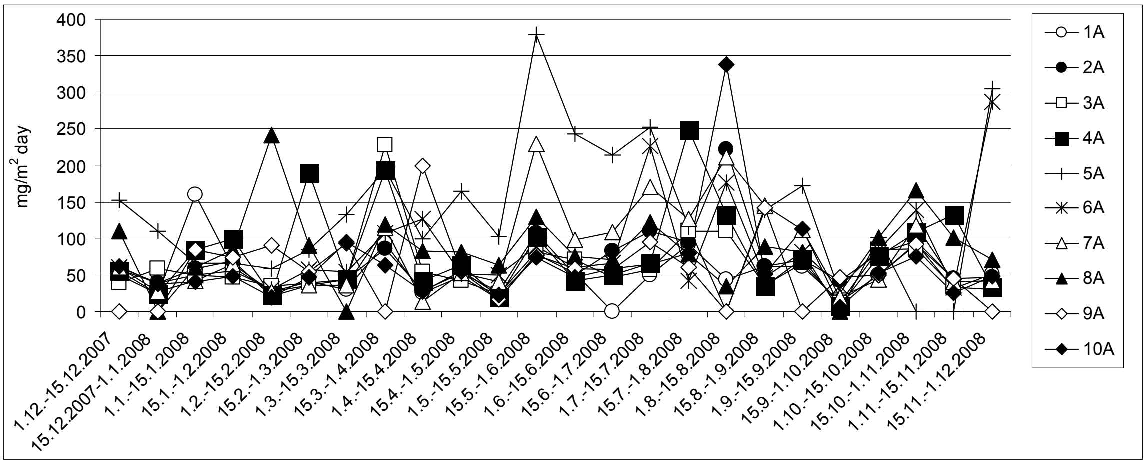


Figure 97: Mass of particulate matter deposition - sampling sites A - particles < 3 µm

Particulate matter deposition at sampling sites B, reflecting both vertical and horizontal input of dust (especially contribution with wind) was measured by gravimetric analysis. Results show that the mass of particulate matter deposition ranged from 80-250 mg/m^2 day and rarely reach or exceed the recommended value of 350 mg/m^2 day (Table 20 and Figure 98).

Table 20: Mass of particulate matter deposition - sampling sites B (mg/m^2 day)

	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	recommended value
1.12.-15.12.2007	128	118	90	84	269	138	98	278	/ *	111	350
15.12.2007-1.1.2008	40	69	8	45	66	78	89	/ *	/ *	83	350
1.1.-15.1.2008	140	121	52	91	125	89	94	108	48	246	350
15.1.-1.2.2008	66	103	57	100	91	96	76	147	227	98	350
1.2.-15.2.2008	41	139	62	80	82	141	43	206	/ **	66	350
15.2.-1.3.2008	109	42	72	119	95	146	49	/ *	95	90	350
1.3.-15.3.2008	79	43	57	102	159	151	168	/ *	/ **	164	350
15.3.-1.4.2008	323	122	136	145	240	137	181	204	219	85	350
1.4.-15.4.2008	233	109	107	177	/ ***	101	145	197	196	107	350
15.4.-1.5.2008	**384**	86	80	83	174	100	140	132	54	119	350
1.5.-15.5.2008	46	51	46	72	143	149	111	139	49	41	350
15.5.-1.6.2008	213	157	/ *	217	/ ***	180	230	268	180	187	350
1.6.-15.6.2008	74	101	99	298	**400**	134	122	129	120	92	350
15.6.-1.7.2008	147	102	69	67	/ ***	164	136	141	97	110	350
1.7.-15.7.2008	128	/ *	108	249	**431**	116	**359**	/ *	213	133	350
15.7.-1.8.2008	247	160	91	98	198	58	160	**367**	126	65	350
1.8.-15.8.2008	259	88	131	/ *	/ ***	293	262	/ **	/ **	172	350
15.8.-1.9.2008	190	138	35	89	149	78	/ *	349	207	60	350
1.9.-15.9.2008	87	206	121	131	177	139	197	167	/ *	102	350
15.9.-1.10.2008	28	67	20	41	34	129	48	/ *	95	57	350
1.10.-15.10.2008	123	84	80	84	136	157	69	200	66	92	350
15.10.-1.11.2008	160	85	78	94	/ ***	165	178	167	138	125	350
1.11.-15.11.2008	85	67	107	117	151	73	92	141	111	47	350
15.11.-1.12.2008	85	66	46	189	**516**	109	110	/ *	/ **	155	350

* - sample was not analyzed (sample was destroyed)

** - high values due to presence of NaCl or Cu compounds

*** - high values due to presence of organic pollution of sample (decay parts of plants or insects, algae)

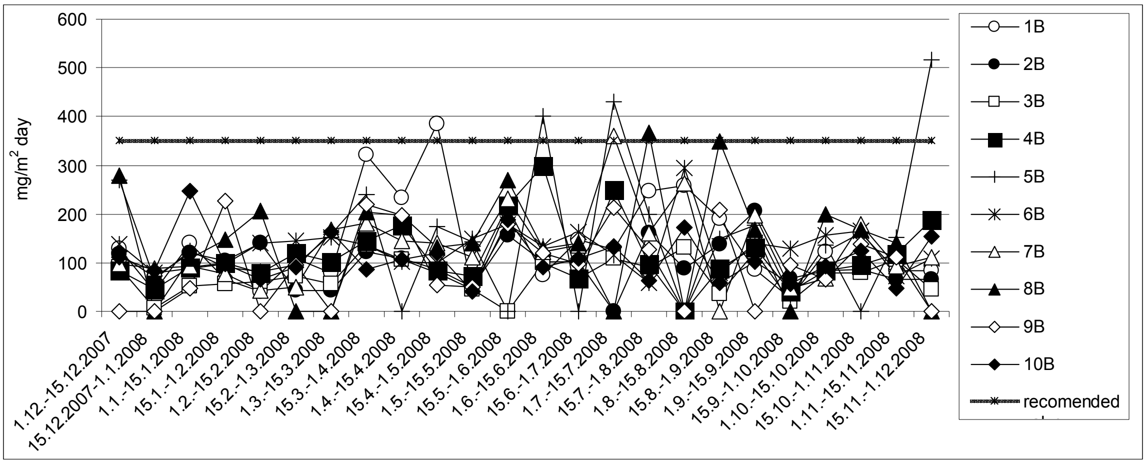


Figure 98: Mass of particulate matter deposition - sampling sites B

In most samples with particles larger than 3 µm (Table 21) the values of particles deposition were between 10 and 100 mg/m^2 day, while the value of the particle smaller than 3 µm (Table 22) were between 60 and 200 mg/m^2 day. It appears that even in the case of sampling sites B the majority of particles represent fine particles smaller than 3 µm. Maximum measured value for particles on filters (larger than 3 µm) was 167 mg/m^2 day in time period from 15.4. to 1.5.2008 in sampling site 1 while maximum value for smaller particles in filtrate was 460 mg/m^2 day in time period 15.11.to 1.12.2008 in sampling site 5.

Table 21: Mass of particulate matter deposition - sampling sites B - particles larger than 3 µm (mg/m^2 day)

	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B
1.12.-15.12.2007	38	38	34	34	7	46	43	111	/*	33
15.12.2007-1.1.2008	17	17	12	18	29	9	28	/*	/*	34
1.1.-15.1.2008	29	34	16	38	34	18	41	34	0	49
15.1.-1.2.2008	8	31	9	14	11	18	12	40	37	18
1.2.-15.2.2008	26	13	10	25	23	59	15	92	/**	31
15.2.-1.3.2008	19	7	23	23	14	47	4	/*	7	19
1.3.-15.3.2008	36	16	23	39	44	87	69	/*	/**	82
15.3.-1.4.2008	74	14	23	48	51	45	37	66	6	15
1.4.-15.4.2008	116	56	56	51	/***	33	74	90	46	57
15.4.-1.5.2008	167	33	28	25	8	10	61	43	25	49
1.5.-15.5.2008	15	21	21	25	48	69	43	54	26	20
15.5.-1.6.2008	63	57	/*	98	/***	40	97	95	65	86
1.6.-15.6.2008	15	23	29	51	57	33	13	28	11	25
15.6.-1.7.2008	36	36	20	18	/***	66	38	46	21	44
1.7.-15.7.2008	41	/*	38	98	61	56	70	/*	49	59
15.7.-1.8.2008	26	22	28	14	72	14	35	46	25	18
1.8.-15.8.2008	121	25	39	/*	/***	75	39	/**	/**	54
15.8.-1.9.2008	51	49	6	37	45	37	0	78	25	26
1.9.-15.9.2008	21	136	52	72	43	62	39	82	/*	36
15.9.-1.10.2008	20	18	16	15	15	72	29	/*	34	39
1.10.-15.10.2008	8	15	10	11	13	15	5	2	7	16
15.10.-1.11.2008	15	11	3	22	/***	55	18	18	20	18
1.11.-15.11.2008	38	31	46	41	25	31	38	52	29	20
15.11.-1.12.2008	18	13	10	51	56	36	26	/*	/**	43

* - sample was not analyzed (sample was destroyed)

** - high values due to presence of NaCl or Cu compounds

*** - high values due to presence of organic pollution of sample (decay parts of plants or insects, algae)

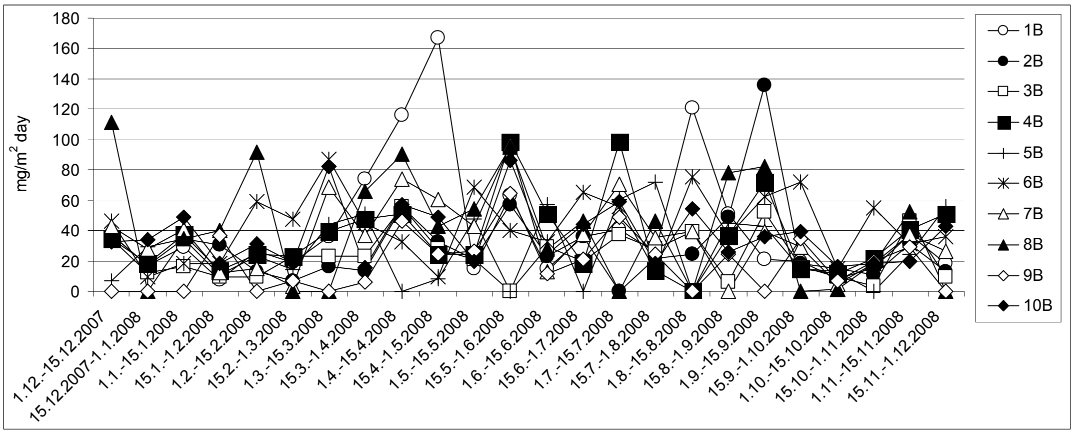


Figure 99: Mass of particulate matter deposition - sampling sites B - particles > 3 µm

Table 22: Mass of particulate matter deposition - sampling sites B - particles smaller than 3 μm (mg/m^2 day)

	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B
1.12.-15.12.2007	90	80	56	49	262	92	56	167	/*	79
15.12.2007-1.1.2008	23	52	-5	26	37	69	61	/*	/*	49
1.1.-15.1.2008	111	86	36	53	90	71	53	73	48	197
15.1.-1.2.2008	58	73	48	86	80	78	64	107	190	80
1.2.-15.2.2008	15	126	52	56	59	82	28	115	/**	34
15.2.-1.3.2008	90	35	49	97	81	98	46	/*	88	70
1.3.-15.3.2008	43	26	34	62	115	64	99	/*	/**	82
15.3.-1.4.2008	249	108	113	97	190	92	144	138	213	70
1.4.-15.4.2008	117	53	52	126	/***	68	72	107	150	50
15.4.-1.5.2008	217	53	52	59	165	90	79	89	29	70
1.5.-15.5.2008	31	29	25	48	95	80	69	85	23	21
15.5.-1.6.2008	151	100	/*	118	/***	140	133	173	115	101
1.6.-15.6.2008	59	78	69	248	342	101	109	101	108	67
15.6.-1.7.2008	111	66	49	49	/***	98	98	95	75	66
1.7.-15.7.2008	87	/*	70	151	370	61	289	/*	164	74
15.7.-1.8.2008	221	138	63	84	126	45	124	321	101	46
1.8.-15.8.2008	138	64	92	/*	/***	218	223	/**	/**	118
15.8.-1.9.2008	140	89	29	52	104	41	/*	270	183	34
1.9.-15.9.2008	66	70	69	59	134	77	157	85	/*	66
15.9.-1.10.2008	8	49	3	26	20	57	18	/*	61	18
1.10.-15.10.2008	115	69	70	72	123	143	64	198	59	75
15.10.-1.11.2008	144	74	75	73	/***	110	160	148	118	106
1.11.-15.11.2008	47	35	61	76	126	42	55	88	81	27
15.11.-1.12.2008	67	52	36	138	460	73	84	/*	/**	112

* - sample was not analyzed (sample was destroyed)

** - high values due to presence of NaCl or Cu compounds

*** - high values due to presence of organic pollution of sample (decay parts of plants or insects, algae)

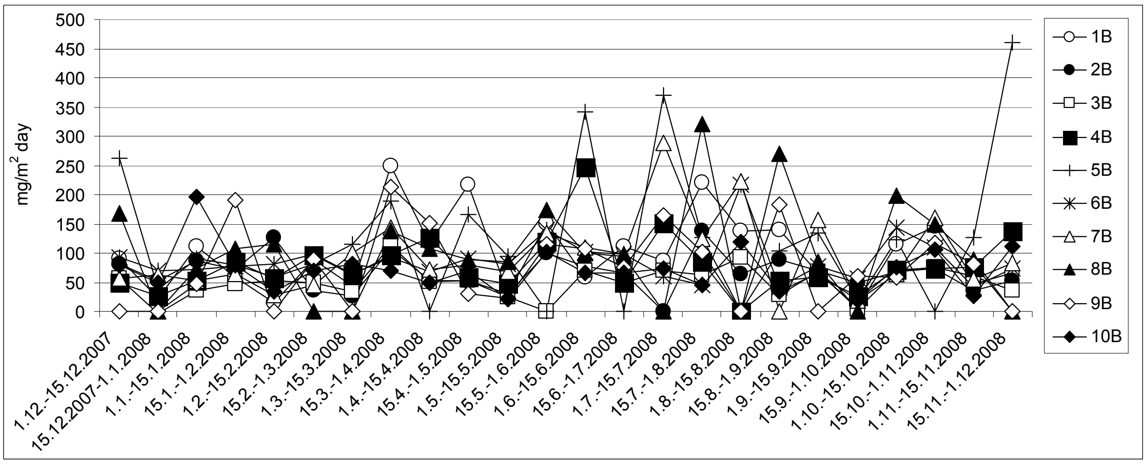


Figure 100: Mass of particulate matter deposition - sampling sites B - particles < 3 μm

4.2.2 Particulate matter deposition - trend at various sampling sites

Results of particulate matter deposition are well correlated (Figure 101 and Figure 102) at some sampling sites. On others sites correlation among different location is not so great, it's rather negative (Figure 103 and Figure 104).

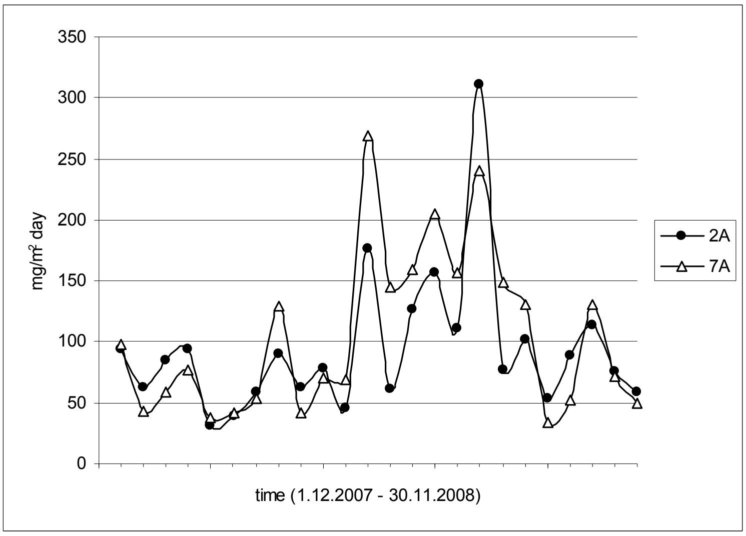


Figure 101: Particulate matter deposition - correlation among sampling sites 2A and 7A

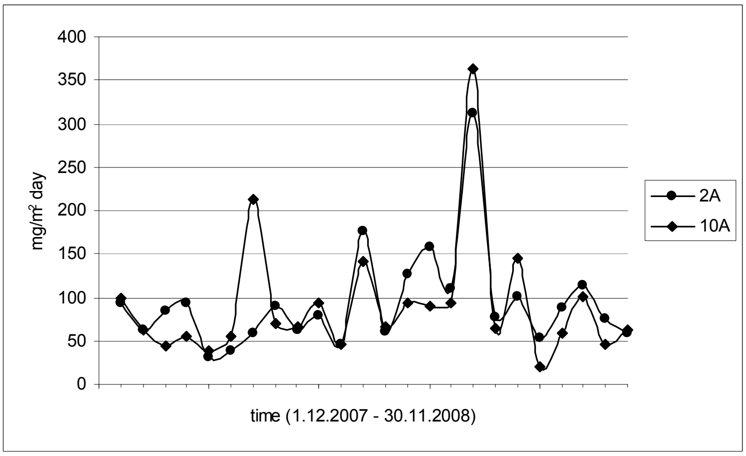


Figure 102: Particulate matter deposition - correlation among sampling sites 2A and 10A

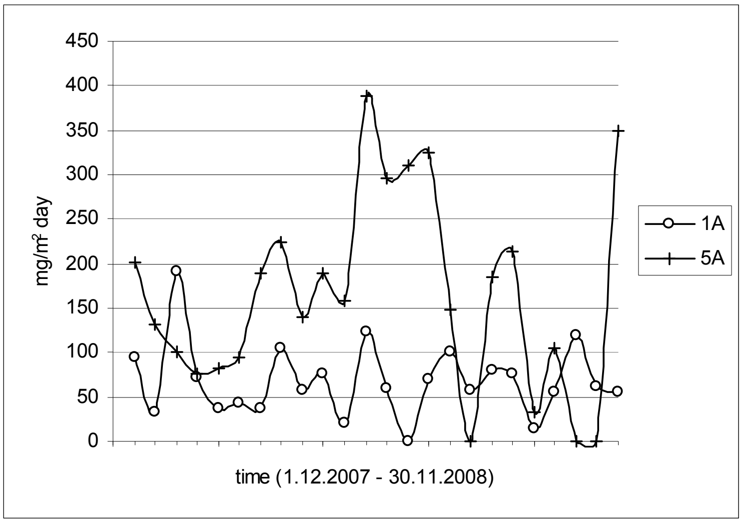


Figure 103: Particulate matter deposition - correlation among sampling sites 1A and 5A

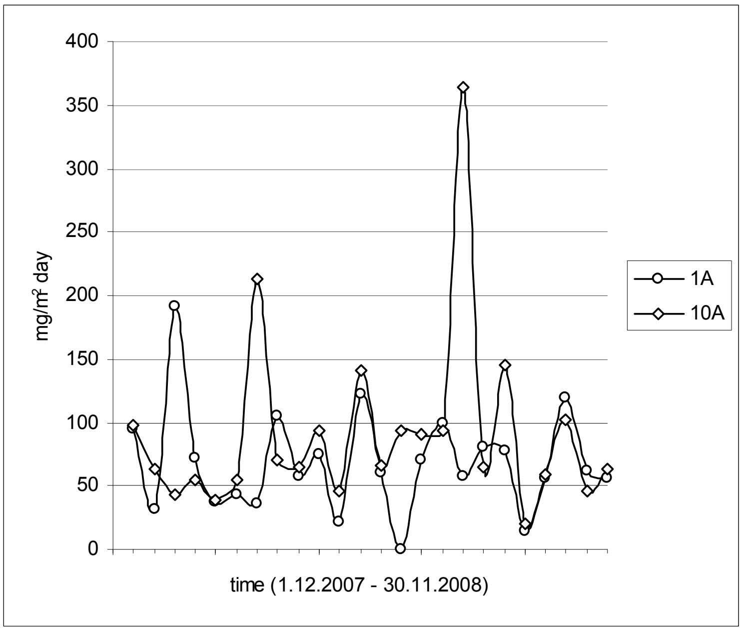


Figure 104: Particulate matter deposition - correlation among sampling sites 1A and 10A

If trends of the particulate matter deposition at sampling sites 1, 2 and 3 are compared, correlation at sampling sites A (standardized method) is very good (Figure 105). However, in the case of the sampling sites B (modified sampling gauge) there is no longer correlation among results from individual sites (Figure 106). Possible explanation could be fact that screen of modified sampling device were oriented in direction toward EET and Port of Koper. If predominant wind blows from any other direction, sampling gauge was practically protected from such influence (while sampling site A was not).

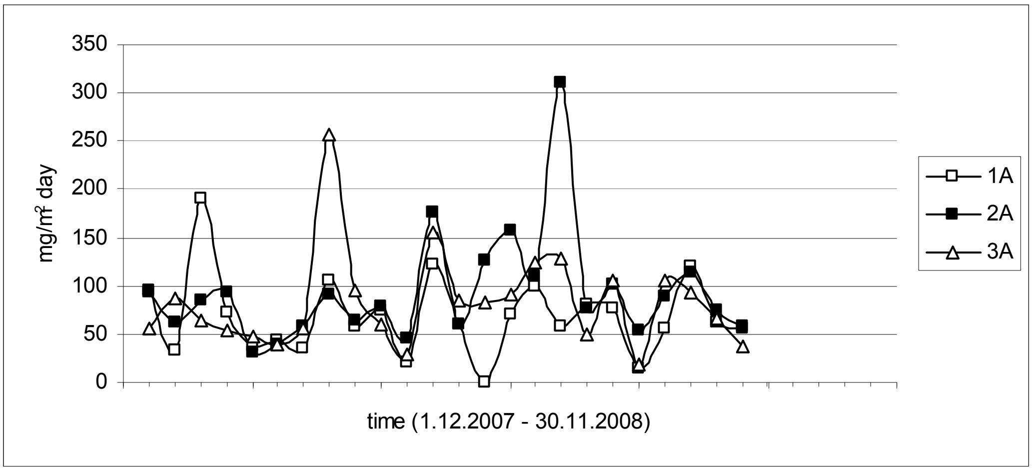


Figure 105: Trends of the particulate matter deposition at sampling sites 1, 2 and 3 - standardized method

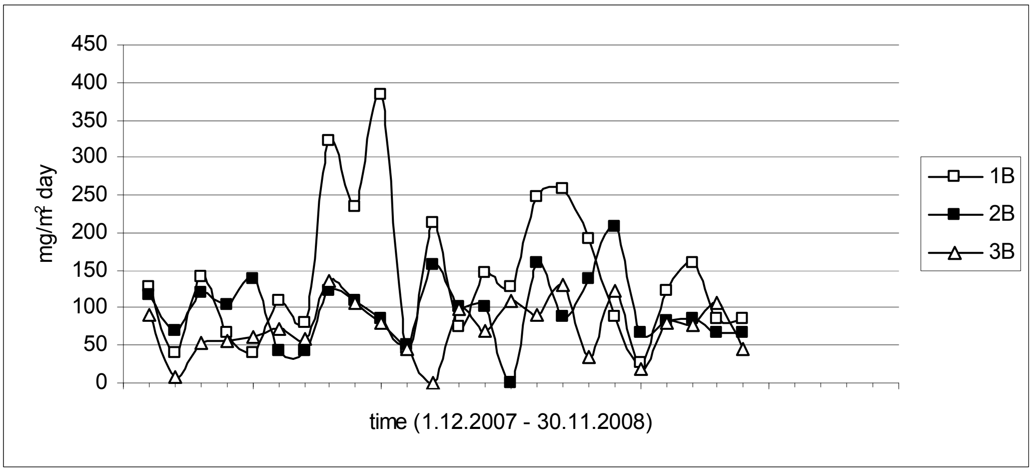


Figure 106: Trends of the particulate matter deposition at sampling sites 1, 2 and 3 - modified sampling gauge

4.2.2 Gravimetrical analyses of particulate matter deposition - calculated monthly results

The results of particulate matter deposition were calculated as monthly results as shown in Table 23 and 24. Mass of particulate matter deposition at the sampling sites A, calculated on a monthly time period during entire monitoring interval from December 2007 to November 2008 has never exceeded the recommended value of 350 mg/m^2 day.

Table 23: Mass of particulate matter deposition - sampling sites A - monthly results (mg/m^2 day)

	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	recommended value
December 2007	63	78	71	63	165	86	70	159	/*	80	350
January 2008	130	89	59	120	87	62	68	94	102	49	350
February 2008	41	35	43	120	88	57	40	209	80	47	350
March 2008	72	75	160	145	207	101	92	133	182	139	350
April 2008	66	71	77	83	164	144	56	140	157	79	350
May 2008	74	113	95	105	278	104	172	153	78	95	350
Jun 2008	61	94	85	62	303	87	152	90	67	80	350
July 2008	86	133	109	193	233	186	180	128	100	92	350
August 2008	69	190	88	105	186	137	193	78	152	209	350
September 2008	46	78	62	57	123	75	83	113	49	83	350
October 2008	89	101	98	107	105	132	92	149	90	81	350
November 2008	59	67	52	106	349	214	60	117	75	55	350

* - sample was not analyzed (sample was destroyed)

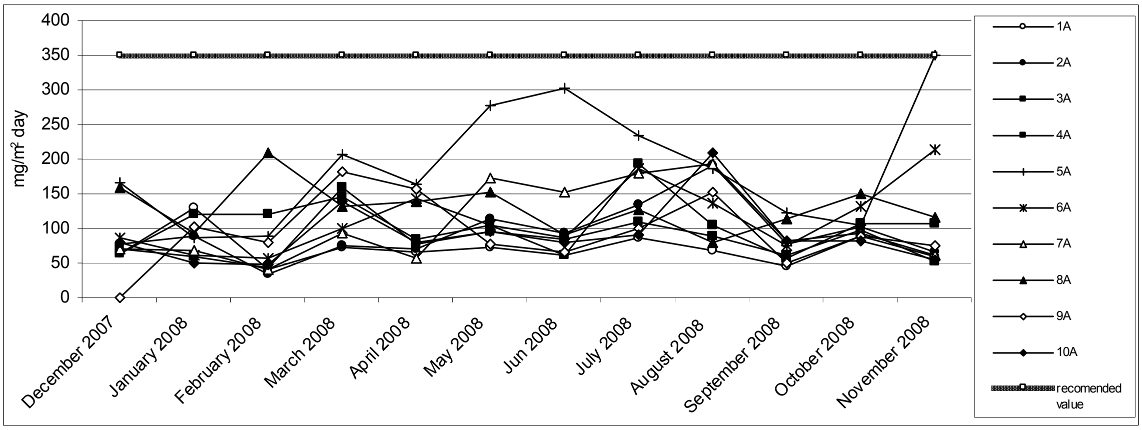


Figure 107: Mass of particulate matter deposition - sampling sites A - monthly results

Table 24: Mass of particulate matter deposition - sampling sites B - monthly results (mg/m^2 day)

	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	recommended value
December 2007	83	93	48	63	164	107	94	278	/ *	97	350
January 2008	102	112	55	96	107	93	85	128	140	170	350
February 2008	74	92	67	99	88	143	46	206	95	77	350
March 2008	205	83	98	124	201	143	174	204	219	123	350
April 2008	309	98	94	130	174	101	142	165	125	113	350
May 2008	132	105	46	147	143	165	173	206	117	117	350
Jun 2008	111	101	84	183	**400**	149	129	135	108	101	350
July 2008	182	168	91	151	301	101	229	**358**	148	94	350
August 2008	224	114	82	89	149	182	262	349	207	114	350
September 2008	57	137	70	86	106	134	122	167	95	79	350
October 2008	142	84	79	89	136	161	125	183	103	109	350
November 2008	85	66	76	153	333	91	101	141	111	101	350

* - sample was not analyzed (sample was destroyed)

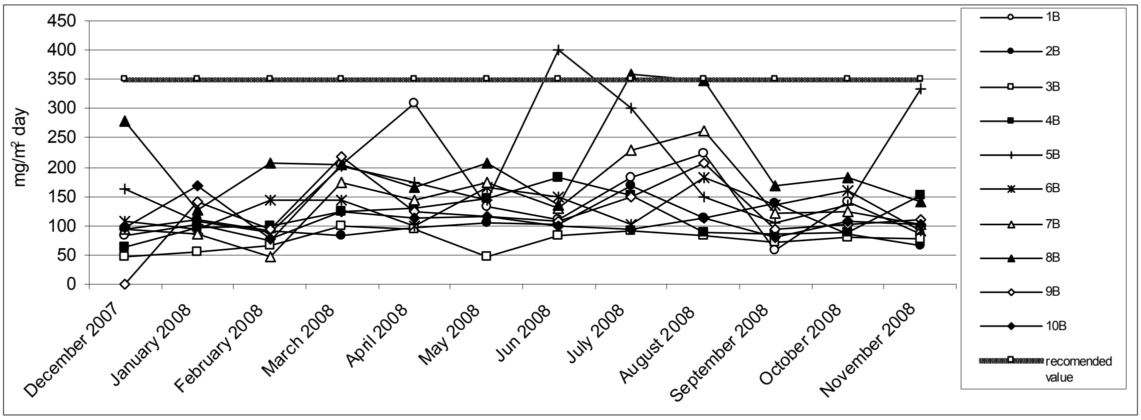


Figure 108: Mass of particulate matter deposition - sampling sites B - monthly results

According to monthly results, seasonal fluctuations of particulate matter deposition in study area are present. The mass of particulate matter deposition was observe to increase during hot dry periods. Since the correlation between the humidity in the soil and the amount of dust were not determined future monitoring of the moisture in the soil is recommended. Comparison among sampling device A and B on each sampling sites are presented in Section 4.2.6.

4.2.3 Particulate matter deposition - calculated yearly results

The Decree (1994), which was subsequently annulled, provided for annual limit lower threshold value (200 mg/m^2 day) than required for the monthly values of 350 mg/m^2 day. These value were not exceeded over the entire sampling period on any location (Figure 109). High concentrations were measured in sampling site 5A and 5B (probably due to the presence of organic impurities in the sample) and sampling site 8B (most likely due to the influence of strong NE wind - Bora) (Table 25). In all cases, with the single exception of sampling site 3, the amount of dust deposition is lower in sampling gauge A (vertical deposition) than in the sampling gauge B (vertical deposition and horizontal wind contribution). Such results were expected due to additional contribution from the wind.

Table 25: Mass of particulate matter deposition - sampling sites A and B - calculated yearly results (mg/m^2 day)

sampling site	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B	
particulate matter deposition (mg/m^2 day)	71	142	94	101	83	76	105	120	187	191	
sampling site	6A	6B	7A	7B	8A	8B	9A	9B	10A	10B	recommended value
particulate matter deposition (mg/m^2 day)	116	130	105	137	129	197	100	132	91	109	200

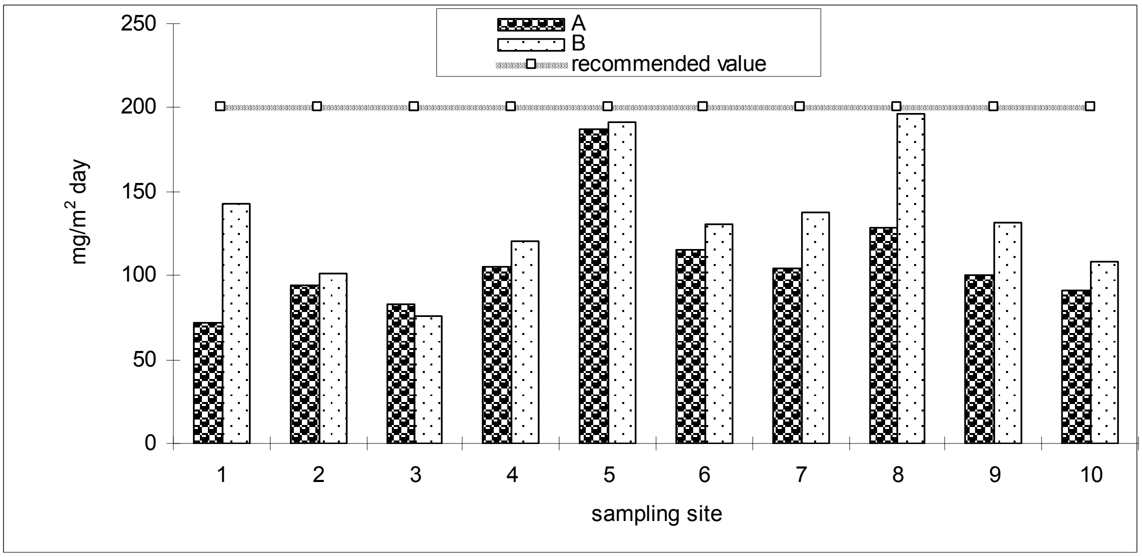


Figure 109: Mass of particulate matter deposition - sampling sites A and B - calculated yearly results (mg/m^2 day)

4.2.4 Chemical analysis of different metals in deposited matter (Annual sample)

Selected toxic metals were determined in particulate matter deposition. Annulled Decree (1994) set limiting values for only three metals, lead, cadmium and zinc. The limiting values regulated in this decree remains as recommended values. None of the three metals approached these recommended maximum value in any samples of particulate matter deposition collected during entire study.

EU Directive 2004/107/EC of the European Parliament and of the Council from 15th of December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air (2004) expects monitoring of these elements in fine particles (PM_{10}) as well as in particulate matter deposition. One of the objective of Directive is also to ensure that adequate information on concentrations of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air as well as on the deposition of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons is obtained and ensure that it is made available to the public. For the analysis of particles deposition, specific standard (Air Quality - Ambient Air - Determination of lead, nickel, arsenic and cadmium in atmospheric depositions; oSIST prEN 15841:2008) was enforced. This standard specifies the method of sample collection and analysis. However, limiting or target values for metals in deposition have not yet been set by the EU, nor have limiting values been promulgated in Slovenia. Never the less all four metal mentioned in Directive as well as some others were analyzed.

Among all metals analyzed (Table 26 and Figure 110) highest values were observed for iron and aluminum; possible source or reason for high values could be natural composition of the surrounding soil, however high values of iron could be linked also to the impact of iron ore in the ore depot at EET in Port of Koper. Increased levels of copper may result from leaching of copper in the sample from a copper wire, added into the collecting tank for algae growth prevention. In addition to the metals mentioned, presence of TiO_2 was detected (see the results of electron microscopy), however titanium was not analyzed.

Table 26: Results of different metals in the annual sample at each sampling site (µg/m^2 day)

sampling site	**Cr**	**Pb**	**Cd**	**As**	**Ni**	**Zn**	**Cu**	**Fe**	**Al**
1A	1.4	4.2	<0.1	0.1	1.4	37.9	313.1	654.4	407.2
1B	2.7	2.7	<0.1	0.1	<1	31.0	165.6	544.0	447.0
2A	10.8	6.7	<0.1	0.3	5.4	52.5	255.8	2688.9	723.1
2B	1.3	4.0	<0.1	0.1	1.3	33.7	245.1	659.8	356.8
3A	1.5	4.6	<0.1	0.2	1.5	55.5	337.4	859.7	579.3
3B	<1	1.3	<0.1	<0.1	<1	21.5	246.4	263.9	164.3
4A	2.7	2.7	<0.1	0.1	1.3	33.7	368.9	735.2	542.6
4B	1.5	3.1	<0.1	0.2	<1	20.0	436.0	480.7	278.9
5A	3.6	3.6	<0.1	0.2	1.8	23.4	444.7	777.7	511.3
5B	2.7	4.0	0.1	0.1	2.7	78.1	228.9	933.1	519.7
6A	1.3	4.0	<0.1	0.1	1.3	33.7	210.1	514.4	320.5
6B	2.8	2.8	<0.1	0.1	1.4	25.3	130.6	883.2	421.3
7A	7.0	4.2	<0.1	0.1	2.8	36.6	228.1	1437.8	650.6
7B	1.4	2.8	<0.1	<0.1	<1	16.9	200.8	415.6	254.2
8A	1.7	3.4	<0.1	0.2	1.7	27.2	295.9	588.4	363.9
8B	1.3	1.3	<0.1	<0.1	<1	22.9	344.7	246.4	130.6
9A	1.4	2.8	<0.1	0.1	1.4	26.8	247.8	501.3	364.7
9B	1.9	3.8	<0.1	0.2	1.9	26.5	351.6	776.9	604.9
10A	1.9	3.8	0.2	0.2	1.9	32.3	341.6	698.3	491.5
10B	1.3	1.3	<0.1	0.1	<1	14.8	160.2	421.5	325.9
recommended value		100	2			400			

< 1; < 0,1 - value of each metal below the detection limit

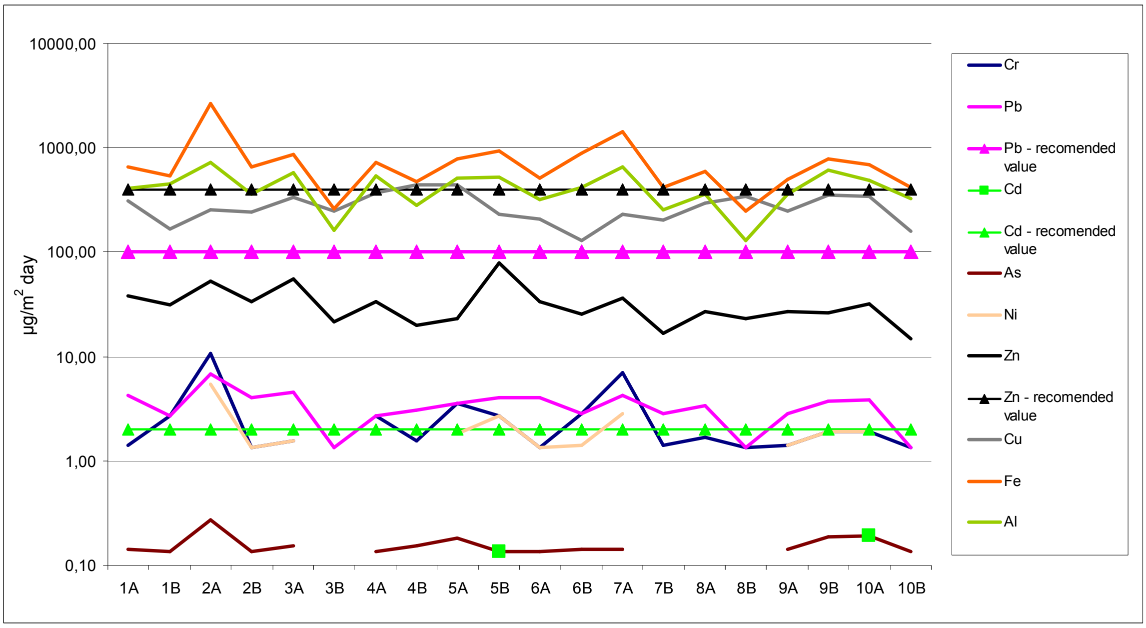


Figure 110: Portion of individual metal in the annual sample at each sampling site

4.2.5 The carbon isotopes $^{13}C/^{12}C$ ratio results

Table 27: The values of $^{13}C/^{12}C$ isotope ratio of coal and blank filter

sample	$\delta^{13}C$(‰)
coal	-28.2
control - blank filter	-25.0

Table 28: $\delta^{13}C$ values determined in particulate matter deposition

	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B	6A	6B	7A	7B	8A	8B	9A	9B	10A	10B
December	-26.4	-26.6	-26.0	-26.4	-25.5	-26.5	-25.7	-25.9	-26.7	-25.4	-26.4	-26.2	-25.9	-26.5	-25.8	-26.7	-	-	-26.1	-25.8
January	-26.2	-26.3	-26.5	-25.8	-25.3	-25.3	-25.9	-26.2	-26.2	-25.2	-25.3	-29.4	-25.8	-25.4	-25.9	-26.4	-26.1	-26.2	-26.0	-25.3
February	-26.6	-27.1	-28.1	-27.4	-26.3	-27.1	-31.0	-26.7	-28.2	-27.6	-27.5	-28.0	-26.9	-26.0	-27.7	-26.7	-28.7	-25.9	-26.2	-26.1
March	-25.5	-28.4	-	-27.2	-25.1	-25.8	-25.7	-25.5	-25.2	-25.5	-	-25.4	-25.4	-25.9	-	-25.5	-25.1	-	-	-26.1
April	-28.9	-27.3	-27.6	-25.4	-28.2	-28.6	-34.8	-27.7	-29.9	-29.4	-25.9	-26.6	-29.1	-29.7	-31.7	-27.6	-26.5	-28.1	-21.5	-27.2
May	-25.1	-24.5	-26.0	-25.5	-26.9	-25.2	-22.5	-25.3	-25.9	-25.6	-25.0	-23.5	-26.7	-26.9	-25.8	-25.0	-25.7	-25.9	-26.7	-25.4
Jun	-	-25.6	-26.0	-25.4	-26.0	-25.0	-	-23.9	-25.7	-25.5	-	-26.0	-26.1	-26.1	-24.7	-25.4	-	-	-24.8	-26.4
July	-	-	-25.4	-25.2	-24.4	-25.2	-24.6	-25.3	-25.5	-26.0	-24.5	-26.3	-25.4	-25.9	-25.6	-25.5	-25.1	-25.5	-24.8	-25.5
August	-25.1	-26.0	-26.0	-25.2	-24.8	-25.2	-24.5	-24.4	-25.9	-25.4	-24.2	-24.7	-25.0	-25.0	-24.4	-25.9	-24.9	-25.1	-25.8	-25.0
September	-25.8	-25.7	-26.2	-26.2	-26.6	-23.5	-26.6	-26.3	-26.4	-26.2	-26.3	-26.9	-25.0	-26.3	-25.3	-26.9	-26.1	-26.9	-25.7	-26.1
October	-25.1	-24.7	-25.3	-24.8	-25.6	-23.6	-24.1	-24.7	-23.1	-24.7	-24.1	-24.8	-23.9	-25.2	-26.4	-24.1	-24.8	-25.1	-24.9	-25.7
November	-25.0	-26.6	-26.4	-25.8	-27.2	-26.2	-24.4	-26.0	-25.5	-25.4	-25.5	-26.4	-25.9	-26.6	-	-26.9	-	-29.0	-27.7	-28.7

🟨 - values of $^{13}C/^{12}C$ isotope ratio comparable to values in the coal
🟩 - control sampling sites (6 and 7)

Attempts were made to determine the presence of coal in samples of particulate matter deposition by measuring the ratio of carbon isotopes $^{13}C/^{12}C$. Coal from one source has more or less constant isotopic ratio of carbon isotopes and therefore the same $\delta^{13}C$ values. Analysis of coal from EET depot showed that $\delta^{13}C$ is -28.2 (Table 27). The results of isotope ratios of carbon isotopes $^{13}C/^{12}C$ from different sampling sites are presented in Table 28. With results from carbon isotopes ratio of each monthly sample and results from the coal and control the content of the carbon in samples which origin from coal was estimated (Figure 111 and Figure 112).

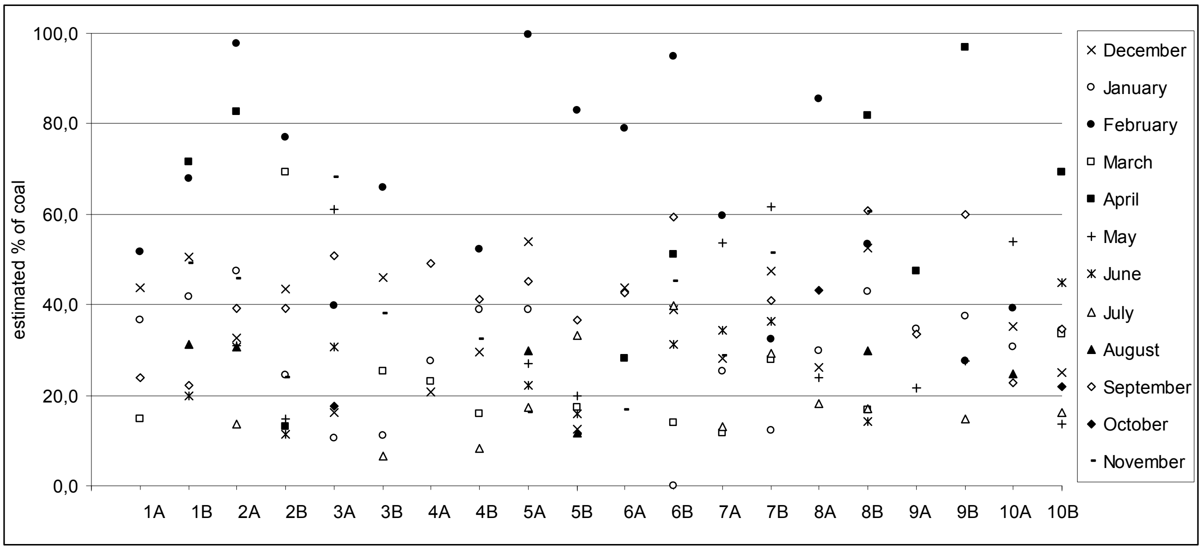


Figure 111: % of carbon determined in samples which probably originated from coal - results according to different sampling sites

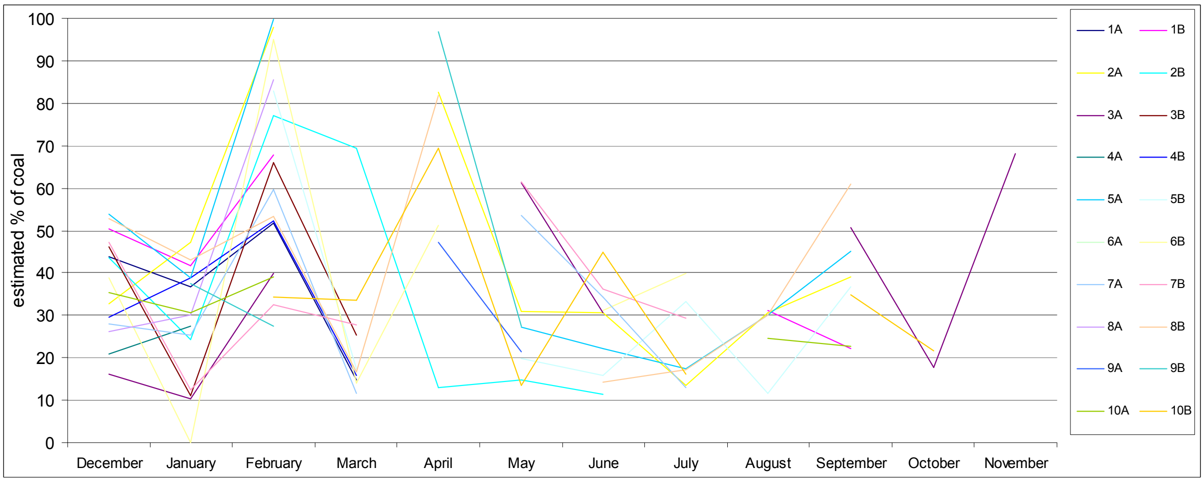


Figure 112: % of carbon determined in samples which probably originated from coal - results according to different sampling period

The conclusion drawn from these measurements is the largest amount of carbon in samples which could be associated with coal appears in the period of February and April 2008, especially in February almost in all sites. However, it is difficult to correlate results with the influence of wind or other weather parameters. In the observation time period (February 2008) prevailing N and NE wind (Bora) was noticed. But relatively low temperature (potential impact of the heating of dwellings using fossil fuels) was observed throughout the winter period in association with the lower $\delta^{13}C$ values indicating that carbon could originate from coal. Temperatures were practically the same during entire winter and were not lower during February. Therefore it is difficult to correlate the results with the amount of particulate matter deposition. Amount of dust deposition was relatively low during February, higher amounts were obtained during dry and hot summer period. However the amount of particulate matter deposition represents total suspended particles that settle to the ground as opposed to the observed measurements of carbon (which comes from coal) isotopic composition. At sites B (vertical plus horizontal deposition) higher amounts of carbon originating from the coal than in sites A were observed. Since all modified sampling devices were oriented toward EET and Port of Koper we can assume that source of coal could be coal depot at EET.

But it is necessary to point out that the chosen method represents new approach for assessing the source of carbon. The possibility of an error must be highlighted because the samples investigated were not homogeneous in composition and structure. Rather, they consisted of different particles from environment. Among others sources carbon could have originated from particles of coal, scrap of insects (parts of legs or skeleton), pollen, plant parts (decompose leaves in the sample), algae, soot (heating of buildings, cars, transport etc.) and others. The isotopic value ($\delta^{13}C$) is specific for each of these sources and in case of non-homogeneous sample measured $\delta^{13}C$ values could represent the average value of different sources, which may indicate the wrong conclusion about the origin. In addition, the assessment with which the proportion of carbon originating from coal was estimated was given in % of carbon in the sample. With the method, the amount of carbon in sample were not determined. Therefore, the correlation between the carbon in the sample, which probably originated from the coal at each sampling sites and the amount of particulate matter deposition (gravimetric analysis) can not be made with the data collected to date. For further investigation, therefore, quantification of carbon in samples as well as improving the method would be necessary.

4.2.6 Comparison between sampling device A and B on each sampling sites

Since method for collection of particulate matter deposition using standard Bergerhoff sedimentators according to VDI and DIN guideline (VDI, 1996) (detailed described in Section 4.2) may be flawed because it does not capture the entire amount of the horizontal wind contribution. The method was modified adding metal screen oriented toward EET depot on sampling devices marked with letter B. Results shows that the horizontal contribution of the wind (metal screen - sampling site B) significantly contributed to increased quantities of dust at the sampling site 1, which is the nearest to the landfill (Figure 113). Out of 24 observations, the masses of particulate matter deposition on sampling sites B were higher than the masses at the corresponding A sampling sites. The Spearman's (rho) correlation coefficient for sampling sites 1A and 1B is almost 0.7 with p value 0.000. A similar observation was detected on other sampling sites (Figures 114 to 122), on sampling sites 1, 2, 6, 7, 8 and 10 at least 15 out of 24 times, mass of particulate matter deposition on sampling sites B is higher than mass on sampling site A. Additionally, on all sampling sites at least in half of the time intervals (12 x) mass of dust deposition is higher in samplers B then in samplers A.

However, one of the reasons why in some cases amount of particulate matter deposition is higher in sampling sites A compared to sampling sites B could be relatively low amount of particulate matter deposition during entire period of monitoring; another reason could be good weather condition (low wind velocity in observed directions). Also modified sampling device were oriented in direction toward EET and Port of Koper. If predominant wind blows from any other direction, sampling gauge was practically protected from such influence (while sampling site A was not).

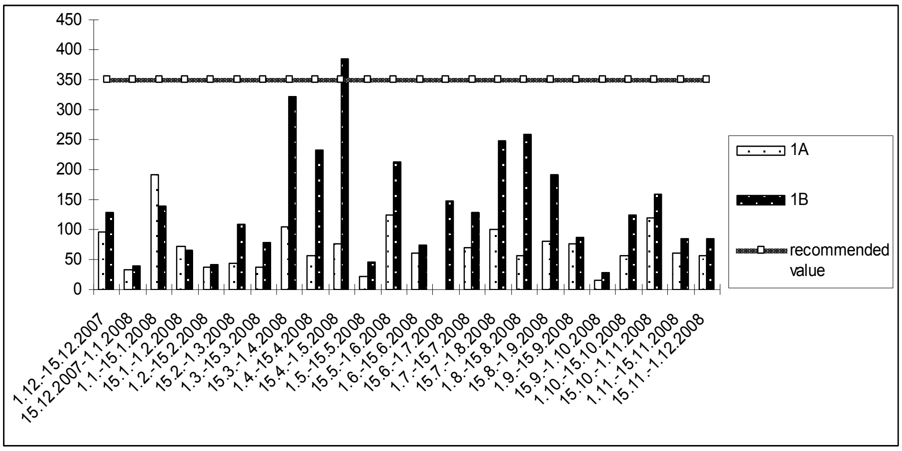


Figure 113: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 1)

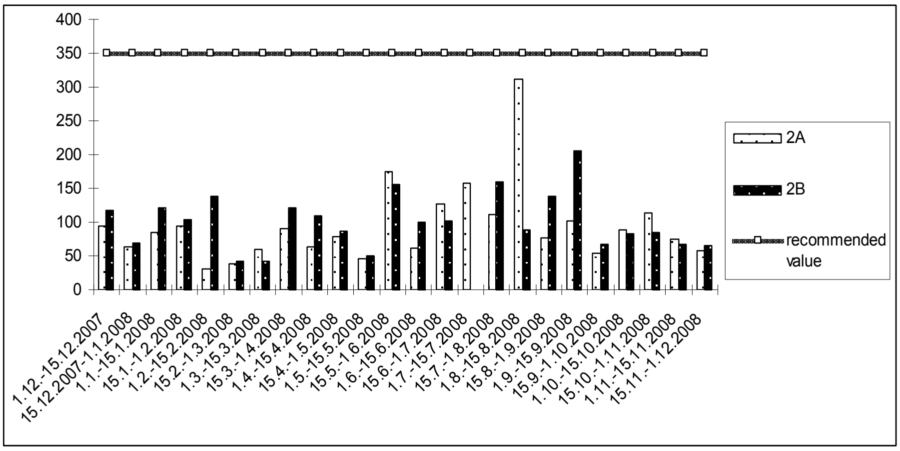


Figure 114: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 2)

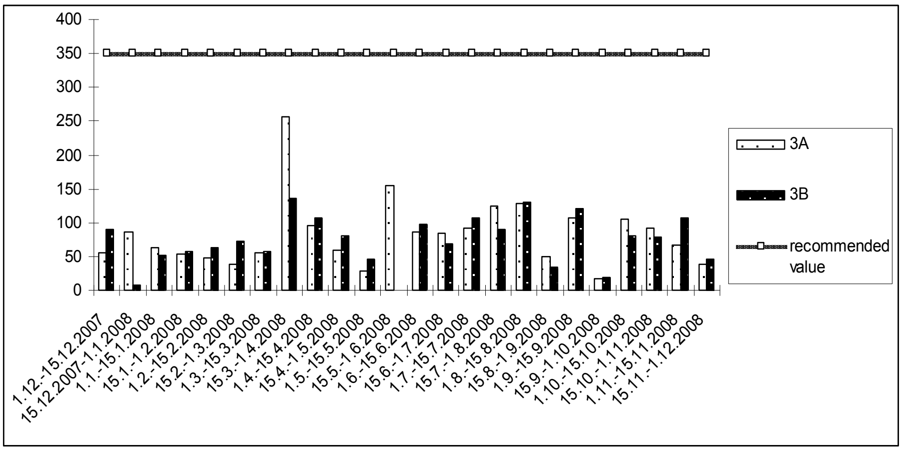


Figure 115: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 3)

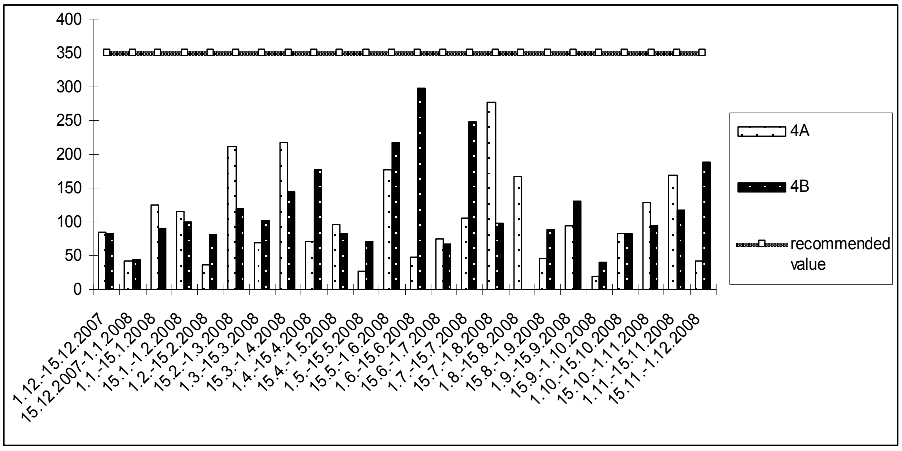


Figure 116: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 4)

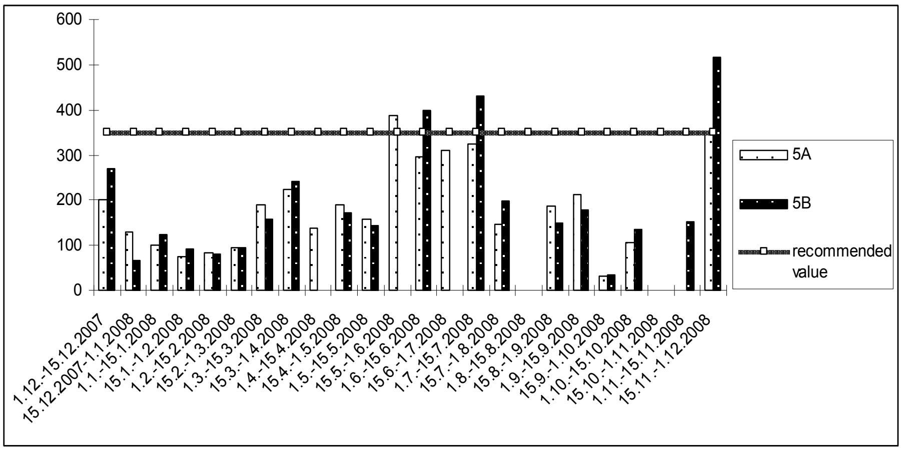


Figure 117: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 5)

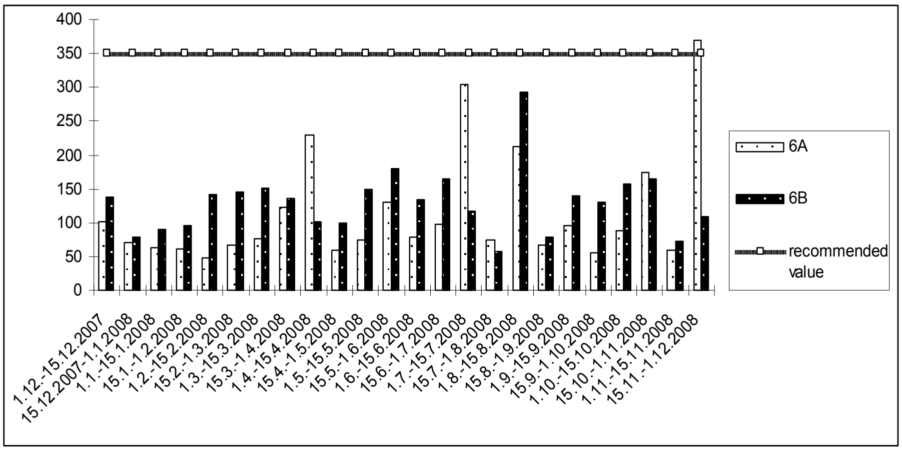


Figure 118: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 6)

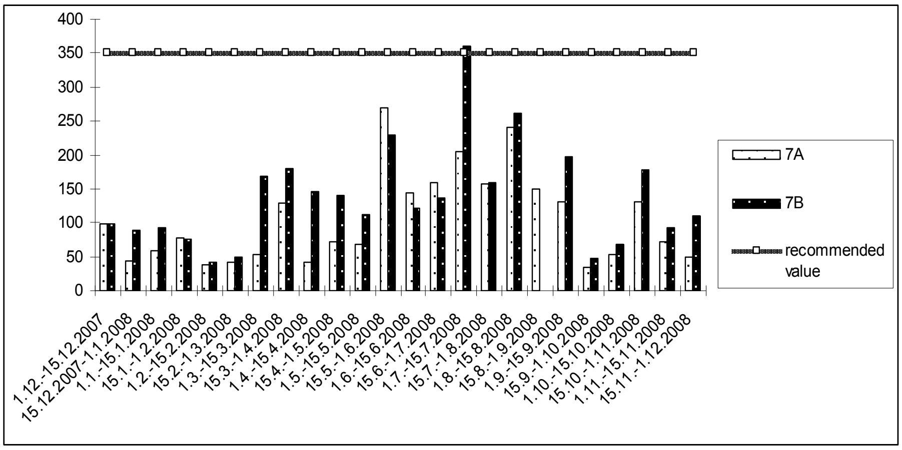


Figure 119: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 7)

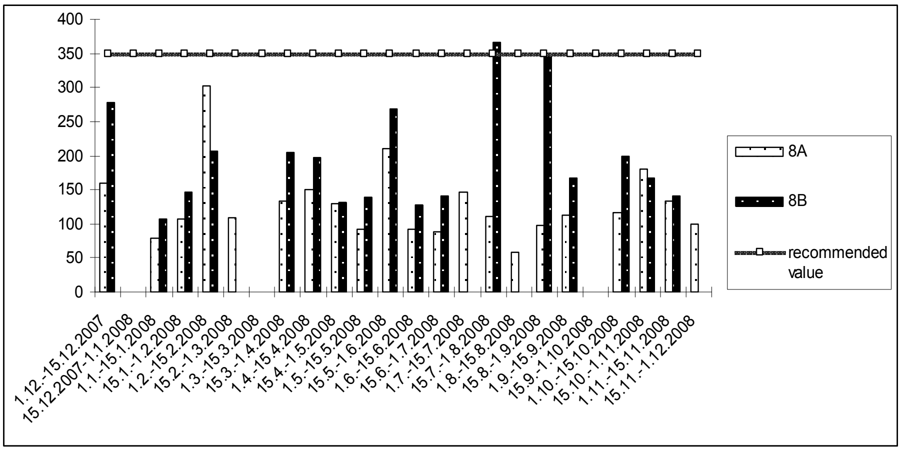


Figure 120: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 8)

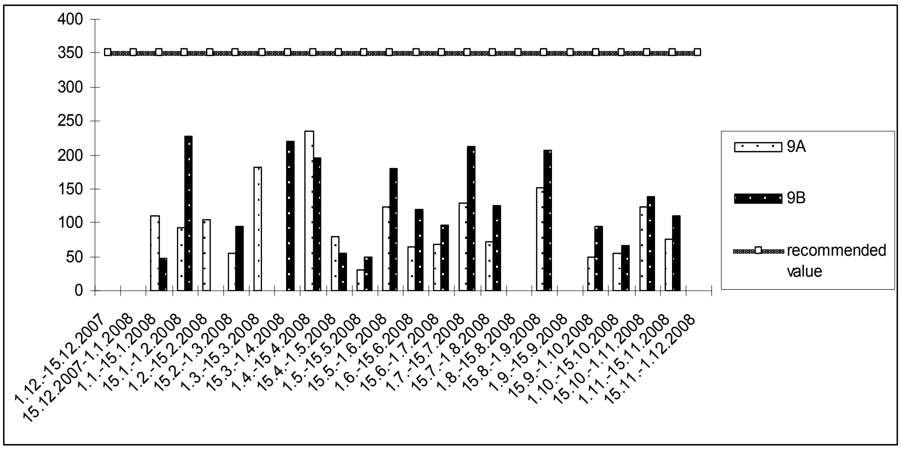


Figure 121: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 9)

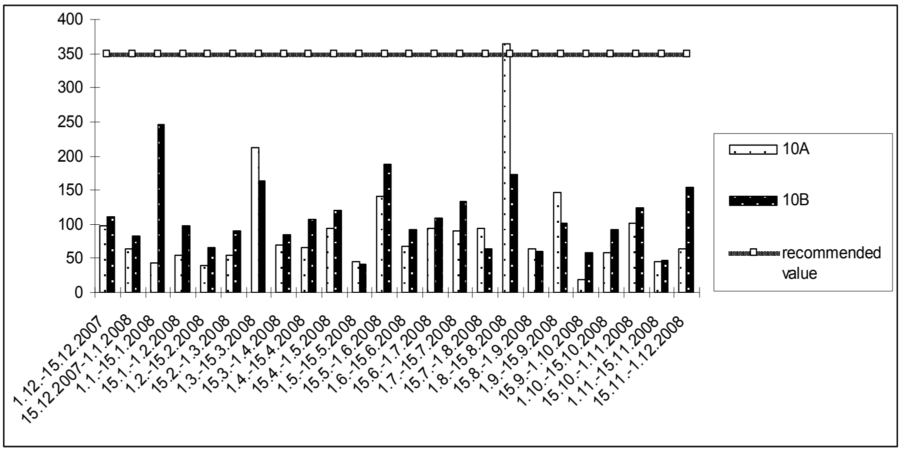


Figure 122: Comparison between the vertical deposition (A) and horizontal contribution (B) to particulate matter deposition (sampling site 10)

4.2.7 Correlation between particulate matter deposition and coal and iron ore manipulation at EET

Data of coal and iron ore manipulation at EET were obtained from the Department of Environmental and Occupational Health in Port of Koper. In Figure 123 and Figure 124 correlation among particulate matter deposition and ore manipulation at EET in Port of Koper is presented. According to the results of preliminary study the confirmation of the correlation was not expected since the method of particulate matter deposition monitoring is not sensitive enough and the sampling interval for searching such correlation were too long. On Figures 125 to 134 correlation between particulate matter deposition and coal and iron ore manipulation at EET on each sampling site is presented.

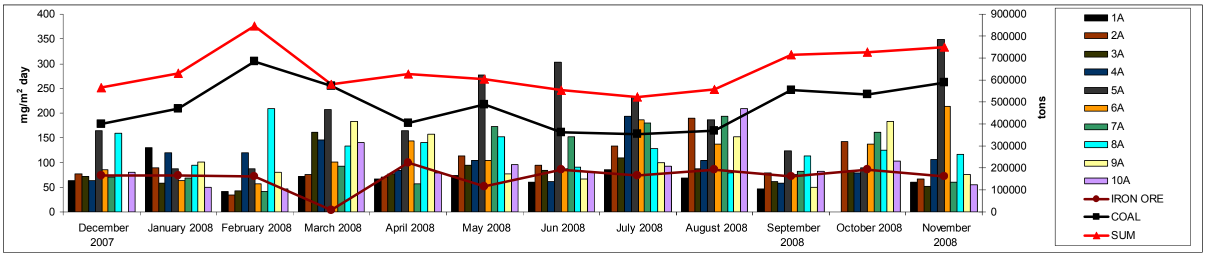


Figure 123: Correlation between particulate matter deposition and coal and iron ore manipulation at EET - sampling sites A

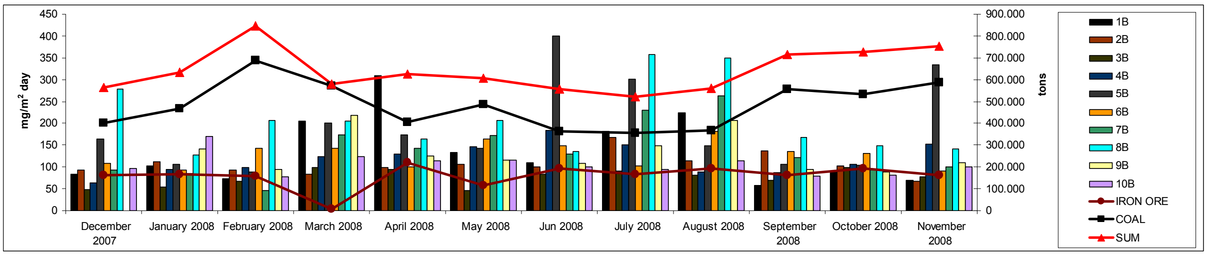


Figure 124: Correlation between particulate matter deposition and coal and iron ore manipulation at EET - sampling sites B

4.2.7.1 Correlation between particulate matter deposition and coal and iron ore manipulation at EET on each sampling site

As seen from Figures 125 to 134, the data show no correlations between coal and iron ore manipulation and amount of particulate matter deposition in Port's surroundings, so correlation could not be confirmed.

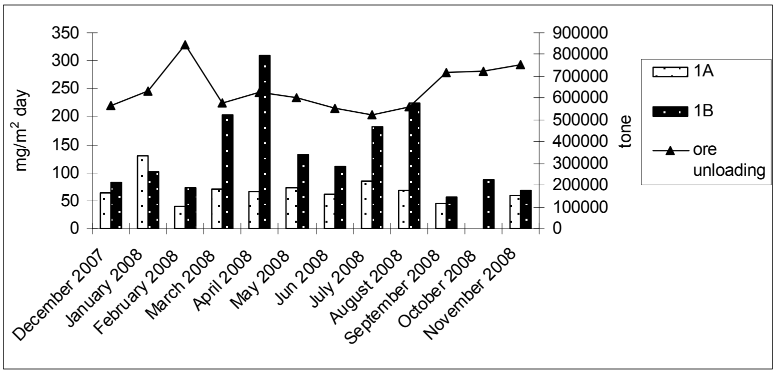


Figure 125: Correlation between particulate matter deposition and ore manipulation at terminal EET - sampling site 1A and 1B

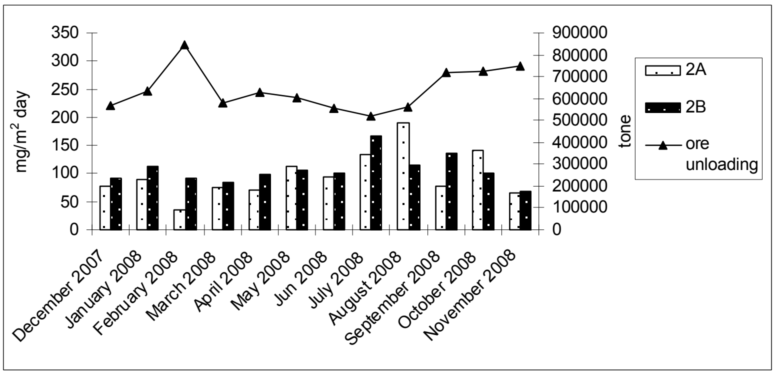


Figure 126: Correlation between particulate matter deposition and ore manipulation at terminal EET - sampling site 2A and 2B

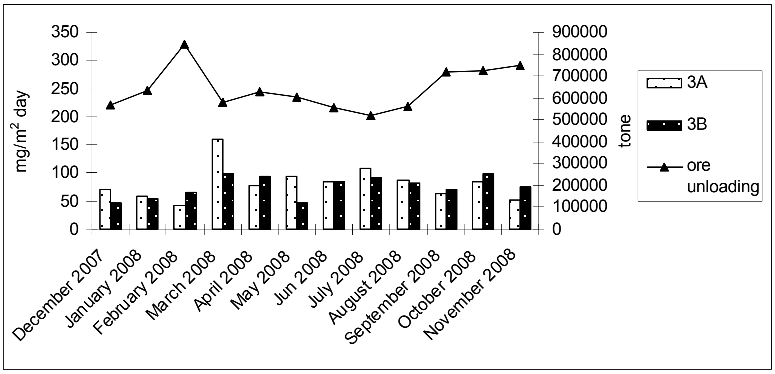


Figure 127: Correlation between particulate matter deposition and ore manipulation at terminal EET - sampling site 3A and 3B

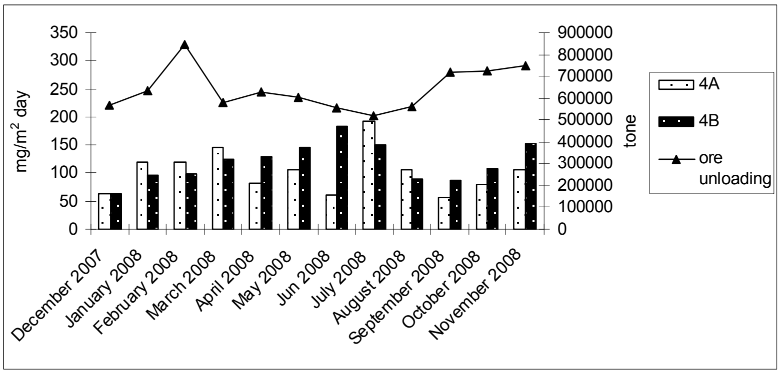


Figure 128: Correlation between particulate matter deposition and ore manipulation at terminal EET - sampling site 4A and 4B

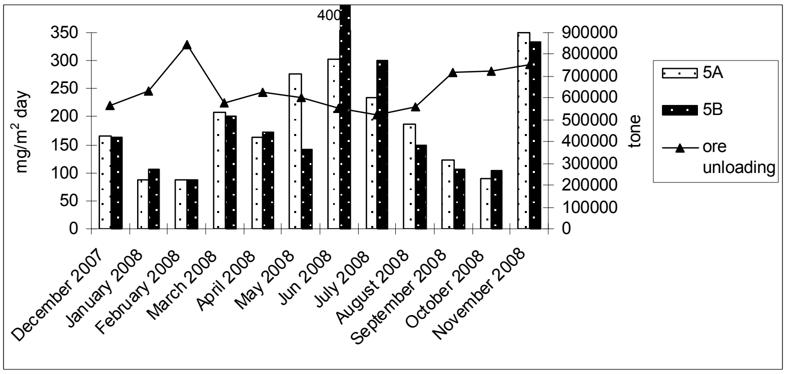


Figure 129: Correlation between particulate matter deposition and ore manipulation at terminal EET - sampling site 5A and 5B

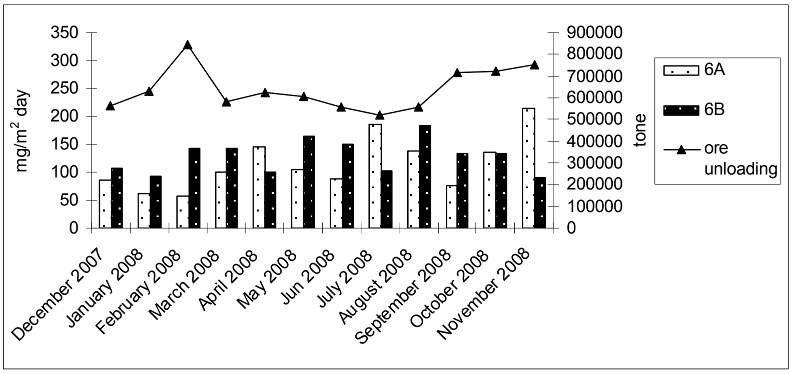


Figure 130: Correlation between particulate matter deposition and ore manipulation at terminal EET - sampling site 6A and 6B

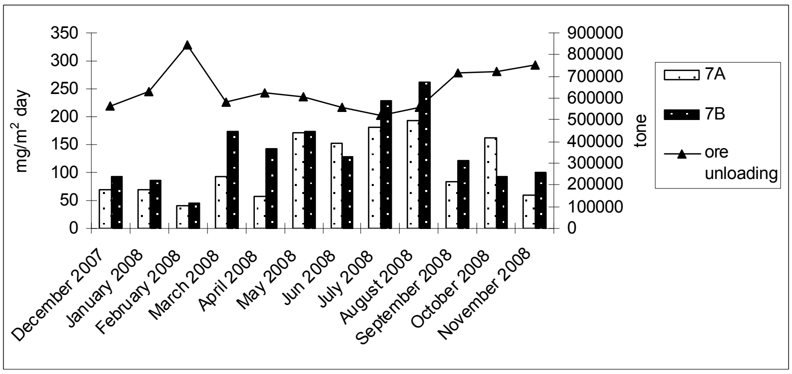


Figure 131: Correlation between particulate matter deposition and ore manipulation at terminal EET - sampling site 7A and 7B

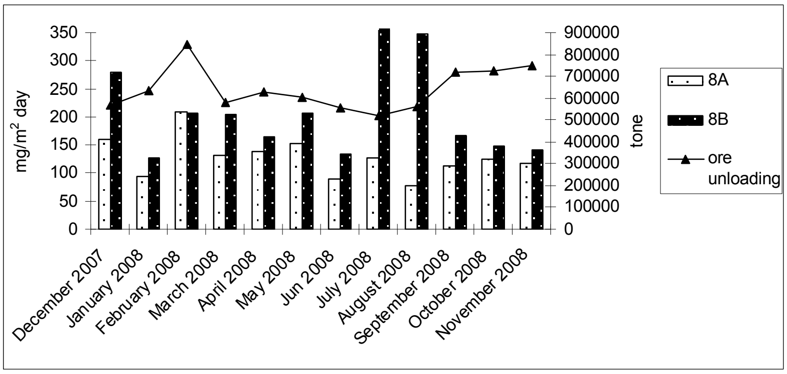


Figure 132: Correlation between particulate matter deposition and ore manipulation at terminal EET - sampling site 8A and 8B

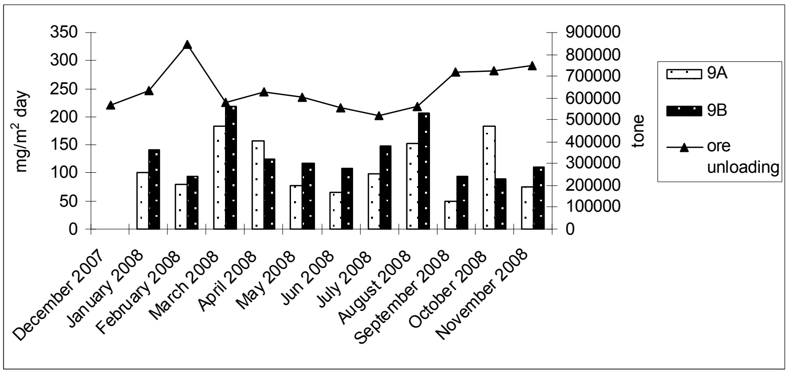


Figure 133: Correlation between particulate matter deposition and ore manipulation at terminal EET - sampling site 9A and 9B

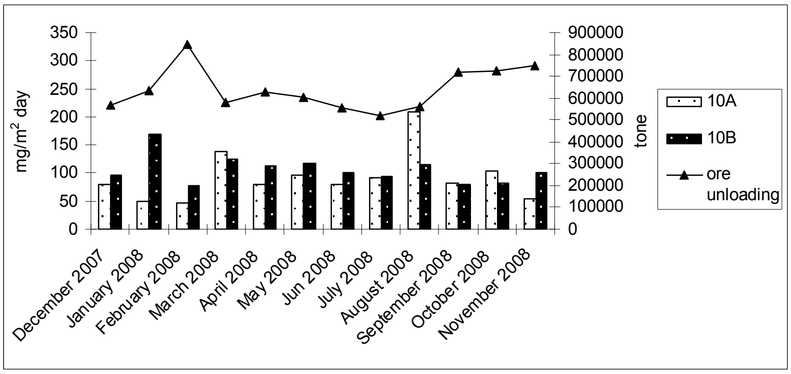


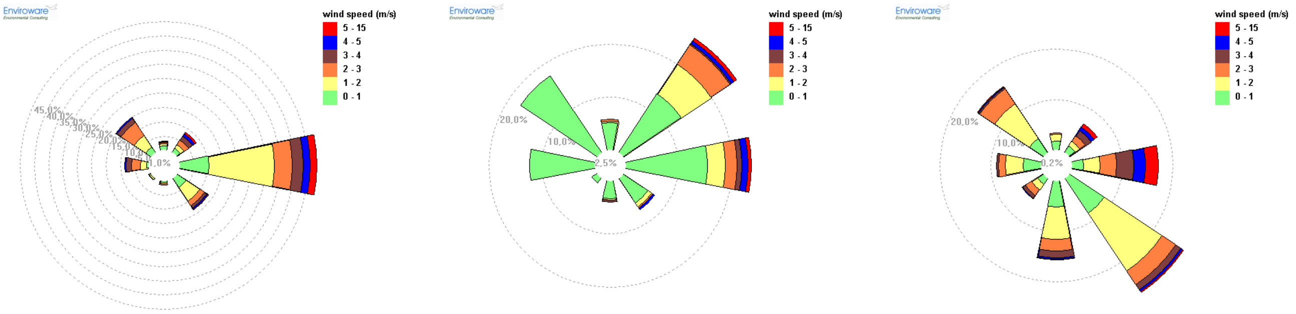
Figure 134: Correlation between particulate matter deposition and ore manipulation at terminal EET - sampling site 10A and 10B

The proportion of particulate matter deposition increased during dry summer months. The reason for this is most likely dryness of ground which contributed to the dustiness in surroundings. In addition, during the summer period wind blows predominant from sea towards land (across ore depot). This is reflected in increased quantities of measured particulate matter deposition. The amount of ore up-loading and unloading is rather constant during entire year with slightly increased values of coal unloading during winter. For this reason the hypothesis that the emission values of dust particles at the source significantly affects the process of up or un-loading of ore at EET can not be confirmed. However, results of carbon $C^{13/12}$ ratio show that during time period of maximum ore manipulation (February 2008) at all sampling sites % of coal as source of carbon in sample increased (in relation to the other months - see Figure 112).

4.2.8 Meteorological data for the period from 1.12.2007 to 30.11.2008

Since wind, humidity, and temperature could influence dust deposition, meteorological data are considered also. Meteorological data on temperature, amount of precipitation and wind direction and strength were obtained from the Environmental Agency of the Republic of Slovenia (ARSO) and Port of Koper (measured by Primorska Institute for Natural Sciences and Technology - PINT).

Data on wind direction and strength included in the study were acquired from the meteorological stations located within the Port of Koper (roof of the administrative building EET). Data on temperature and amount of precipitation (and also data of wind speed and direction) were acquired from the meteorological station Koper (located on the hill Markovec of Koper). Both meteorological stations are managed by ARSO. From the Department of Environmental and Occupational Health of Port of Koper, information on the speed and direction of wind, measured at the meteorological station in the Port of Koper were obtained (measurements performed by the PINT). Unfortunately, the data included a lot of blank entries, and only for daily values were provided. It is likely that there are discrepancies between the data for the wind direction and speed at the measuring station of the Port of Koper (PINT) and data obtained by measuring by ARSO (meteorological station Markovec and Port of Koper - EET) - see Figures 135 to 137. Although the distance between this two measuring locations is less then 4 km, significant differences can be observed, most probably due to the configuration of the terrain.



December 2007 - November 2008 (station EET - ARSO)

December 2007 - November 2008 (inside Pot of Koper - measured by PINT)

December 2007 - November 2008 (meteorological station Markovec, Koper)

Figures 135, 136 and 137: Wind Rose for the time period December 2007 - November 2008 (station EET - ARSO; inside of Port of Koper - PINT; meteorological station Markovec, Koper - ARSO)

Figures 135 to 137 show how the results of the measurements of meteorological data on different locations (Port of Koper and Markovec) differ. It is necessary to emphasize that the results of the automated monitoring station at Markovec (ARSO) gave a half-hour data, the measuring station on the building EET (ARSO) provided hourly data, but the measurement stations within the Port of Koper (PINT) provided only single-day value for the observed parameter. The data measured on the EET (ARSO) were used in this study. The interpretation of results require additional care, because the measured values from all three measuring sites differ and probably depend on the micro location and the morphology of the terrain on site. For example, during one period of time, the measuring station within EET recorded maximum wind speed 10.8 m/s (38.9 km/h), the measuring station at Markovec recorded a slightly higher maximum value (12.4 m/s or 44.64 km/h) during the same period of time, but measuring station inside Port of Koper in the management of the Institute PINT, the measured max values was 7.3 m/s (26.3 km/h).

4.2.8.1 Daily temperatures and amount of precipitation

Maximum temperature over the entire time period was 34.6 °C measured 26th of Jun 2008 at 15:30 hour. Maximum rainfall was recorded on 18th of July when 35.5 L / m^2 of precipitation was received. Daily fluctuations in temperature and amounts of precipitation are presented in Figure 138. These data show 910 mm of precipitation fell during entire time of the study (December 1, 2007 to 30 November 2008). Most of the recorded rainfall on the coastal area was observed in the summer. Almost 60% (526 mm) of the precipitation fell during five summer months from April to August. Consequently wet ground probably attributed to the lower value of dust deposition during the summer months.

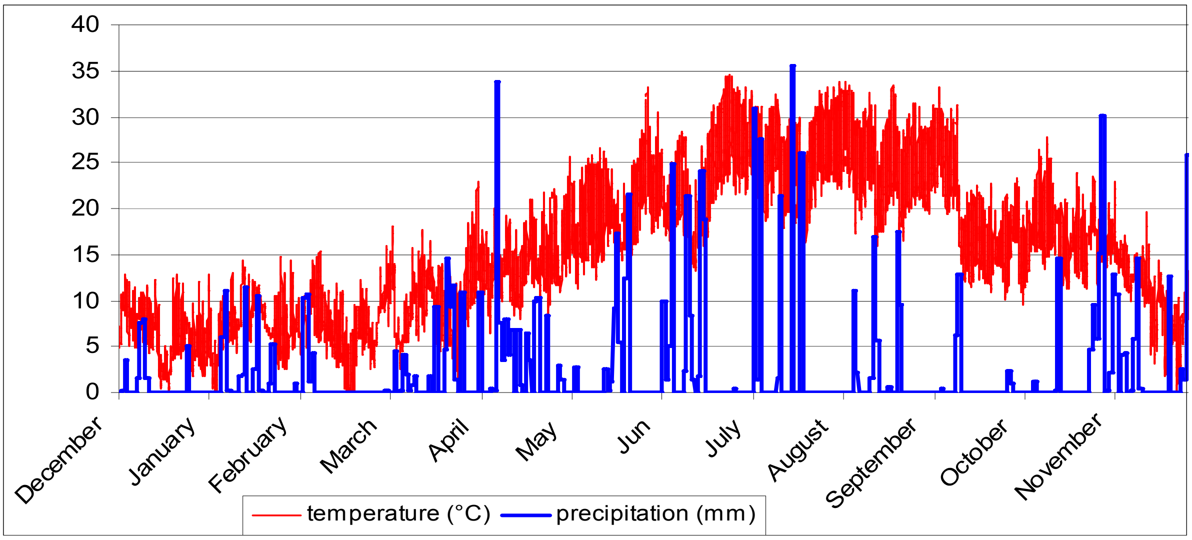


Figure 138: Daily temperature and amount of precipitation for time period 1.12.2007 to 30.11.2008 - automatic measuring station Markovec - ARSO

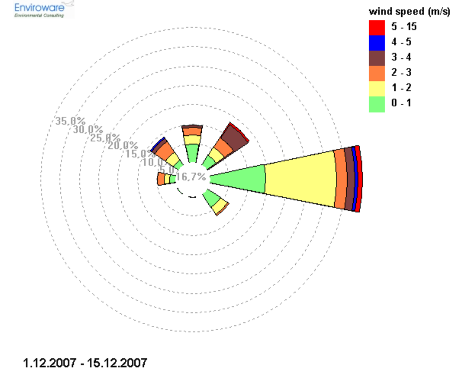
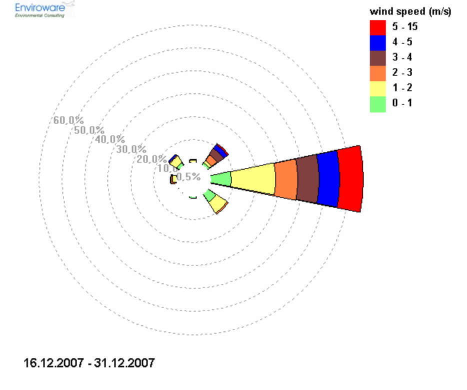
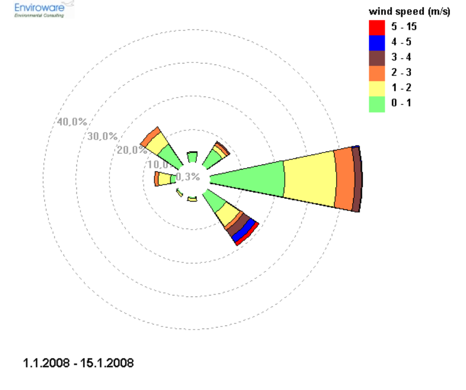
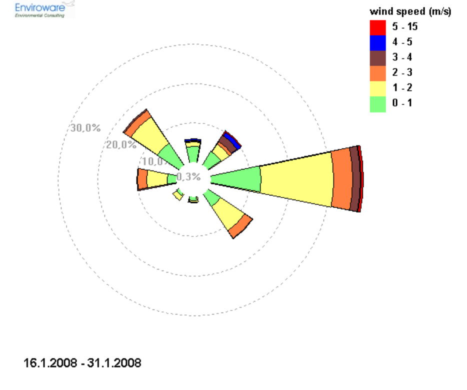
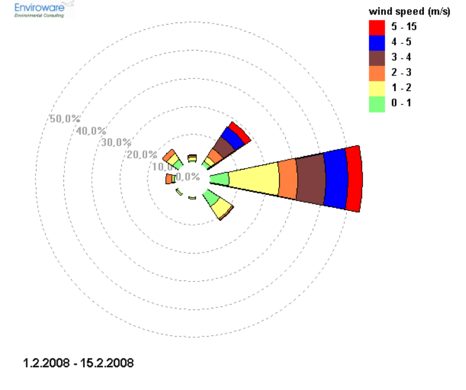
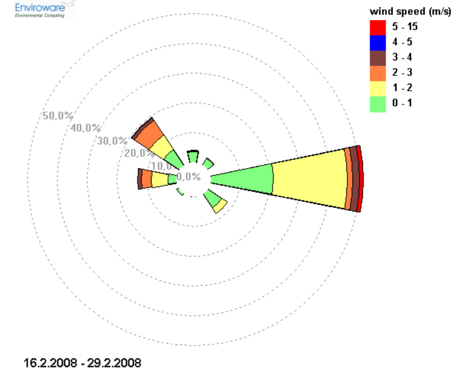
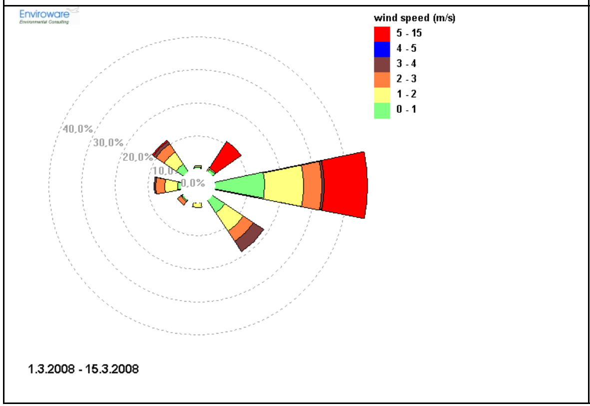
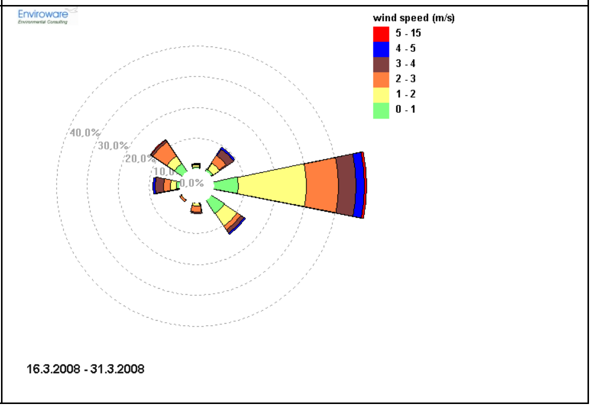
4.2.8.2 Speed and direction of winds

In Table 29 wind roses for individual sampling interval (monitoring of particulate matter deposition) are presented (from 1st to 15th in and from 16th to the last day of the month) from 1.12.2007 to 30.11.2008.

Data on wind direction are divided into eight points of the compass (N, NE, E, SE, S, SW, W, NW), and the data for wind speed are divided into six categories or intervals: from 0 to 1 m/s; from 1 to 2 m/s; from 2 to 3 m/s, from 3 to 4 m/s, from 4 to 5 m/s and greater than 5 m/s. In each chart, information of the calms is presented too. Data were obtained from measurements made at the administrative building of EET in Port of Koper managed by ARSO (Environmental Agency of the Republic of Slovenia).

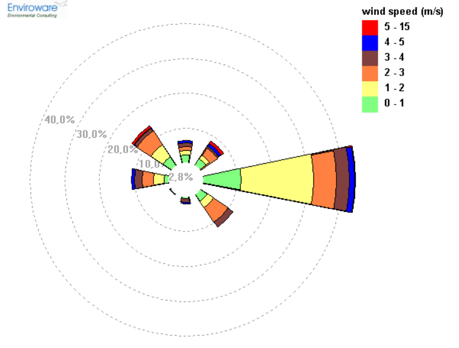
Recorded maximum wind speed was during observed time period 10.8 m / s (38.9 km / h).

Table 29: Wind roses for individual sampling interval (wind speed and direction)

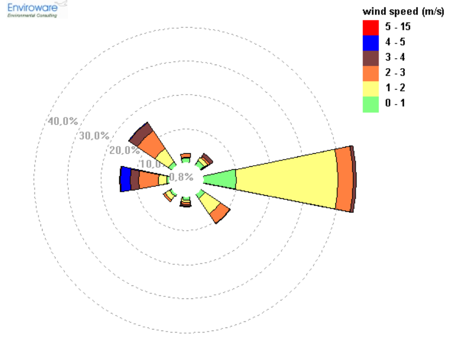
 1.12.2007 - 15.12.2007	 16.12.2007 - 31.12.2007
 1.1.2008 - 15.1.2008	 16.1.2008 - 31.1.2008
 1.2.2008 - 15.2.2008	 16.2.2008 - 29.2.2008
 1.3.2008 - 15.3.2008	 16.3.2008 - 31.3.2008

- Table continue -

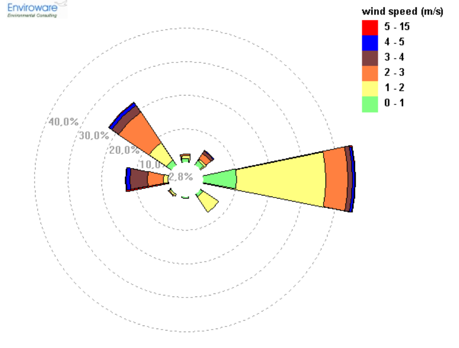
- Continuation of the Table 29 -



1.4.2008 - 15.4.2008



16.4.2008 - 30.4.2008



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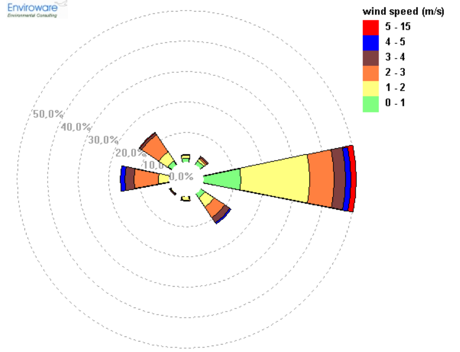

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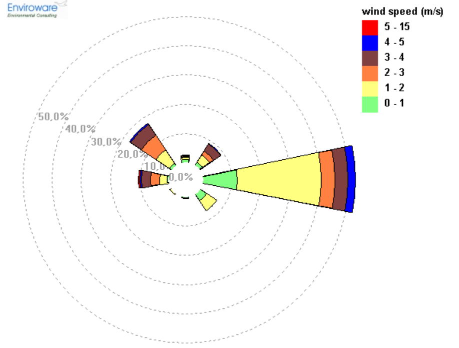

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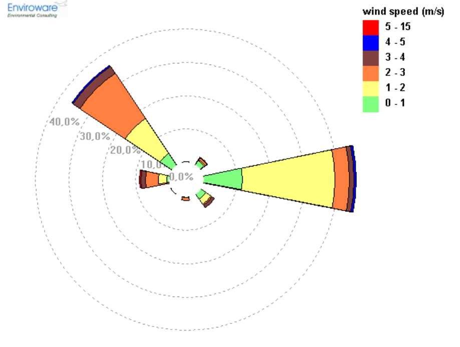

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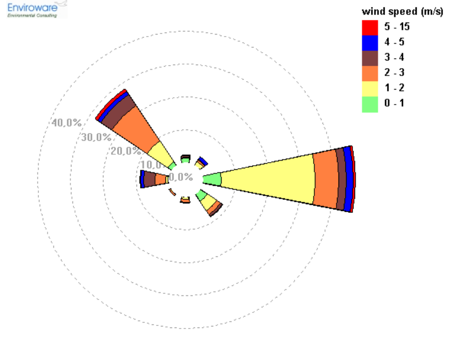

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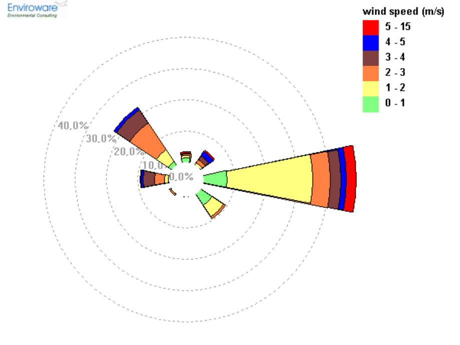
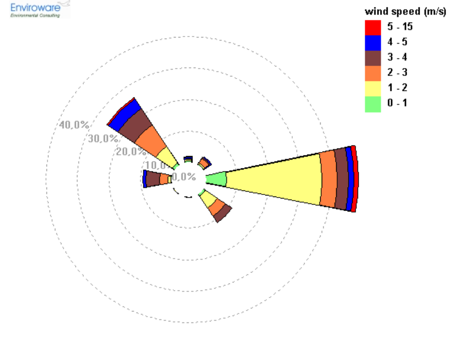


16.7.2008 - 31.7.2008

- Table continue -

- Continuation of the Table 29 -



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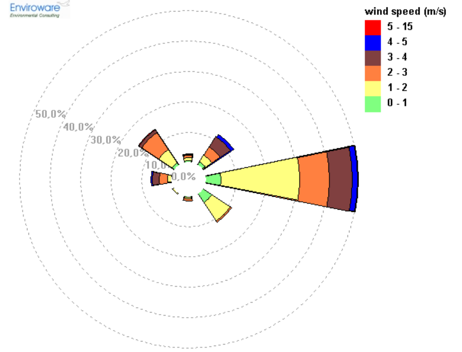

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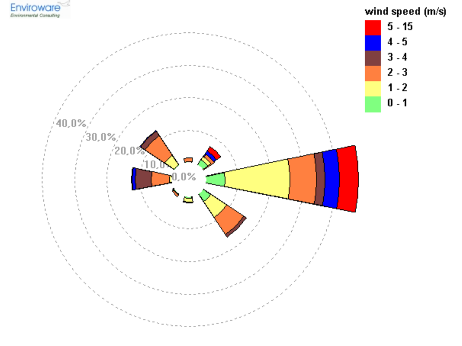

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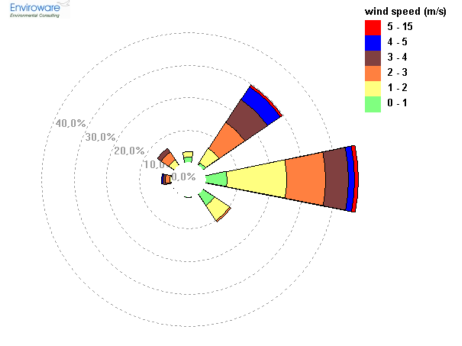

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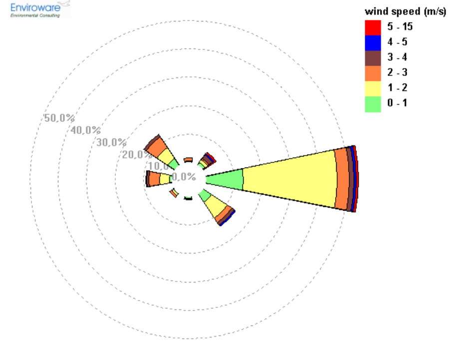
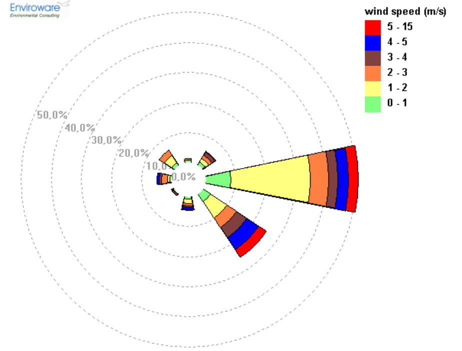
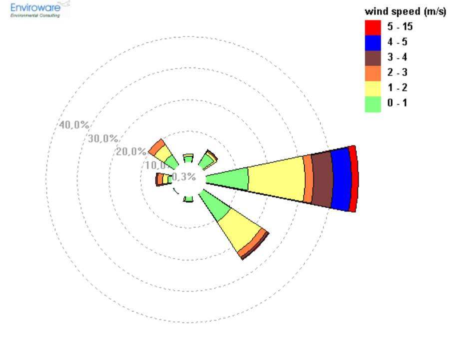


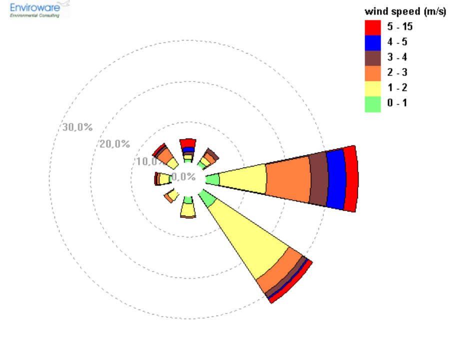
1.10.2008 - 15.10.2008



16.10.2008 - 31.10.2008



1.11.2008 - 15.11.2008



16.11.2008 - 30.11.2008

Data which were available represent wind directions and wind speed expressed as % of frequency.

These data show the dominant wind direction is from the east, and these easterly winds are the strongest. The dominant wind direction changes with the season. From April to June, the wind comes from northwest. From September to November wind from the southeast is frequent. As already mentioned in the interpretation of preliminary study results, occasionally strong Mistral (west - northwest) winds blow for very short periods of time in the study area. Residents of Rožnik detect high pollution of their living environment with black particles after such events. Usually particulate matter deposition from these strong winds of short duration are not detected because of the long time scale (14 days or even 1 month) between sample collections.

Moreover, during the time period December 2007 - November 2008 there were no records of extreme weather events, such as the sudden emergence of a strong wind, blowing from the landfill EET toward the selected sampling sites. Also the surrounding residents during that time have not pointed out such events. However, the results of the previous studies show that such events are possible (March and October 2006).

4.2.9 Results of electron microscopy

SEM/EDXS was employed to differentiate particles from the coal and iron ore depot at EET in Port of Koper from other particles collected in the sampling device. Particles of coal, iron ore and bauxite were distinguished from other particles in dust deposition on the basis of morphology and chemical composition. Since only surface of sample can be analyzed samples were diluted prior analysis.

4.2.9.1 Identification of particles regarding morphology and chemical composition

In the annual samples (time period from 1.12.2007 to 1.12.2008), the presence of particles of coal, alumina, compounds with Al, Si and K (silicates, alumosilicates, etc.), titanium dioxide and iron oxides (FeO, Fe_2O_3, Fe_3O_4) were detected. Particles were identified according to their chemical composition and morphological structure. Results are shown in Figures 139 to 145.

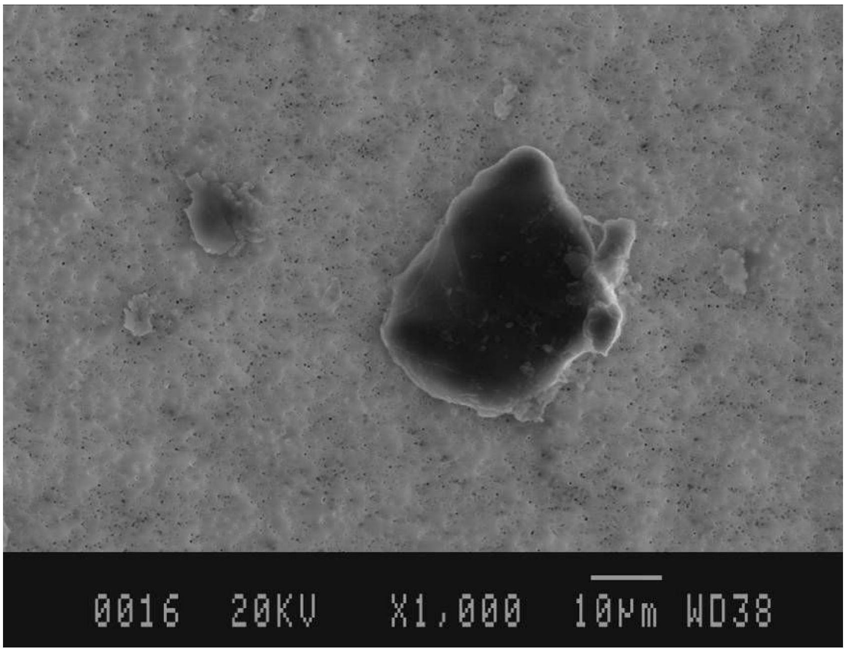


Figure 139: SEM micrograph of typical coal particle (particle diameter of ~ 25 µm)

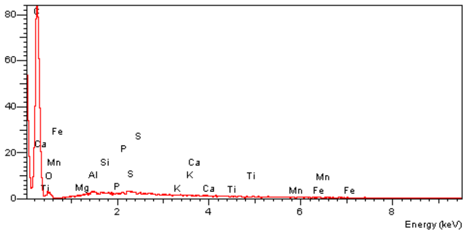


Figure 140: Typical EDXS spectrum of coal

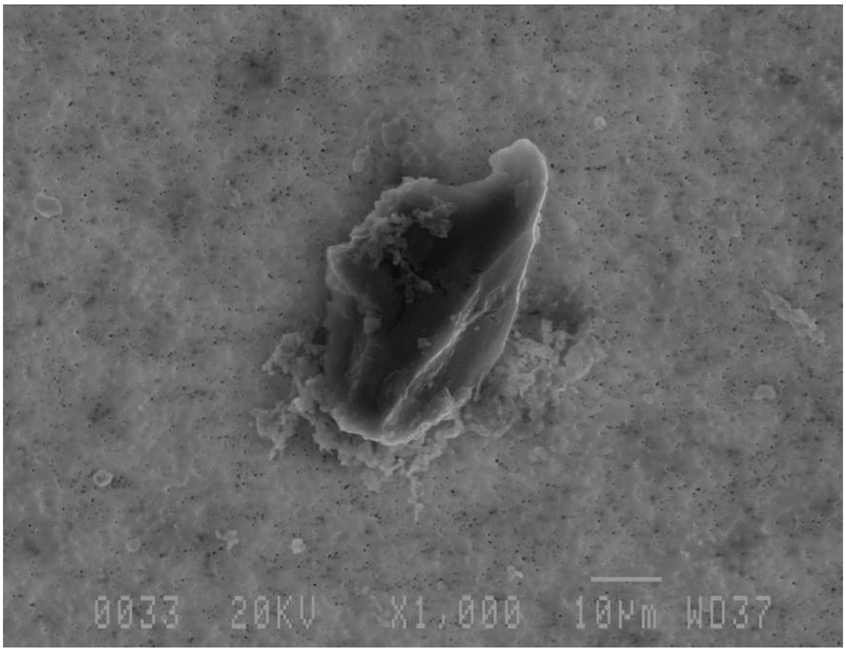


Figure 141: Coal particle with impurities (particle diameter of ~ 35 µm)

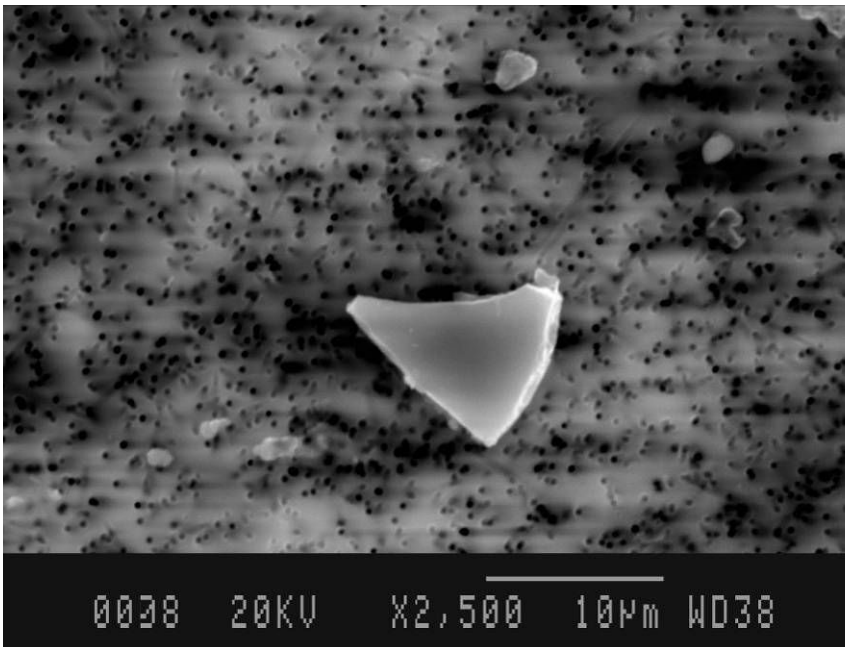


Figure 142: Bauxite (alumina) (particle diameter of ~ 10 µm)

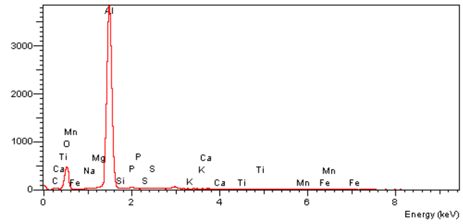


Figure 143: Typical EDXS spectrum of bauxite (alumina)

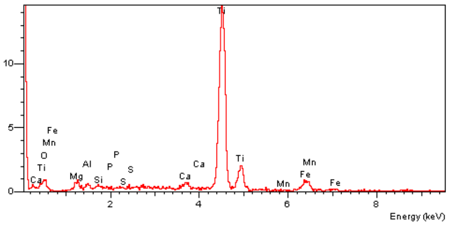


Figure 144: Typical EDXS spectrum of TiO_2

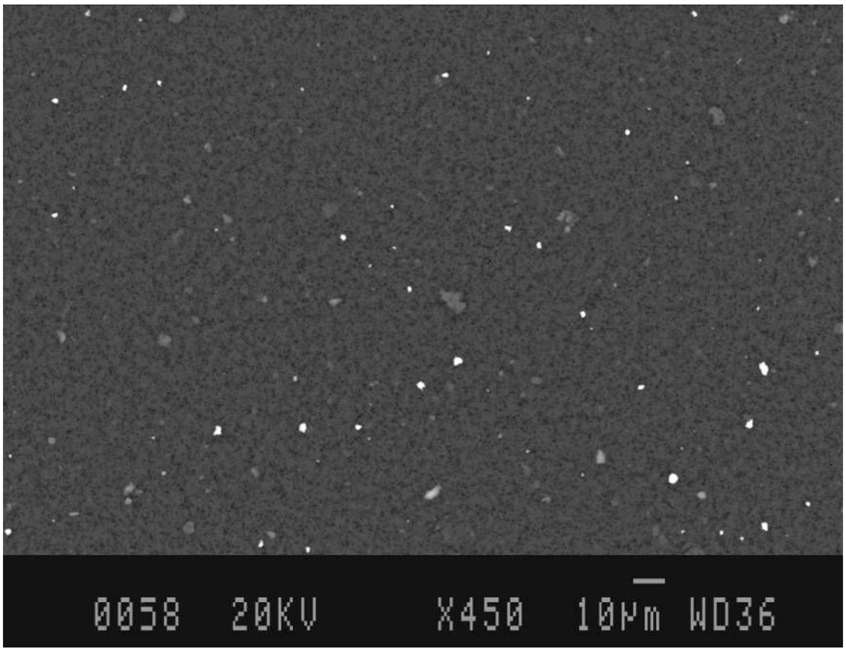


Figure 145: SEM micrograph (back scattered electrons (BSE) image) of particles of titanium dioxide (TiO_2) - (particle diameter of ~ from 1 up to 5 µm)

Based on these results, the contribution of activities within the Port of Koper (coal and iron ore depot and ore manipulation, alumina manipulation as well as transshipment of other bulk cargoes) on particulate matter depositions in the surrounding area can be confirmed. In order to estimate impact on dust deposition from Port of Koper to surroundings, the samples of airborne particulate matter were analyzed quantitatively using SEM. Particles on individual sampling sites were counted.

4.2.9.2 Quantification of particles collected in the annual sample

With analysis of samples from the preliminary study (2005/06) using SEM, the presence of coal in particulate matter deposition was demonstrated. It is for this reason, samples from only one time interval (15.2. - 15.3.2006) were analyzed. During study of 2007/08, samples from the entire study were analyzed after combining samples from individual sampling period into one yearly sample for each sampling site. For analysis a part of filter was selected for further processing. Since particles were not analyzed only qualitatively (size, chemical deposition and morphology of individual particles) but also quantitatively (number of particles from individual sampling sites), dilution of samples was required. Since particulate matter deposition was rather low during entire sampling period (compared to preliminary results), lower numbers of particles were expected. Correspondingly, lower numbers of coal and iron ore particles were expected too. This prediction was demonstrated by SEM since more particles of alumosilicates originated from surrounding soil were detected than were particles of coal and iron ore. Even residents of nearby residential areas Rožnik did not detect disturbing emissions of black dust over the time period of the study.

The number of particles per cm^2 of the filter is calculated from the number of particles on the filter after dilution. For the conversion of this number to the entire dust deposition, the results should be multiplied by a factor 3079.5. Because all the samples were processed using the same procedure, the values are given as the number of particles per cm^2 of treated filter for all samples. Results given according to the size and chemical composition of a particles grouped by individual size classes are shown in Table 30.

Table 30: The average number of particles per square centimeter of filter surface area

size (µm) / sample	compounds with Al, Si, K (silicates, alumosilicates, …)				titanium dioxide				iron oxides (FeO, Fe2O3, Fe3O4)				particles, containing carbon (coal)				SUM
	< 1	1 - 5	5 - 10	> 10	< 1	1 - 5	5 - 10	> 10	< 1	1 - 5	5 - 10	> 10	< 1	1 - 5	5 - 10	> 10	
1A	0	20918	4082	1020	2041	4082	0	0	0	1531	0	0	0	510	0	0	34,184
1B	0	7289	1822	364	1093	3644	0	0	1093	2551	364	364	0	1822	364	364	21,137
2A	0	5102	1701	850	9354	14456	0	0	0	850	0	0	0	0	0	0	32,313
2B	0	5952	6803	0	11054	9354	850	0	0	850	0	0	0	0	7653	2551	45,068
3A	0	0	0	0	638	0	0	0	0	0	0	0	0	1913	638	0	3,189
3B	1020	1276	255	0	765	1020	0	0	255	0	0	0	0	510	0	255	5,357
4A	283	1134	0	0	850	567	0	0	0	283	0	0	0	283	283	0	3,685
4B	1786	2041	0	0	255	255	0	0	255	0	0	0	0	255	255	255	5,357
5A	0	425	0	0	0	0	0	0	0	0	0	0	0	0	0	0	425
5B	0	1160	696	0	4638	0	0	0	0	232	0	0	0	696	928	232	8,581

- Table continue -

- Continuation of the Table 30 -

size (µm) / sample	compounds with Al, Si, K (silicates, alumosilicates, …)				titanium dioxide				iron oxides (FeO, Fe2O3, Fe3O4)				particles, containing carbon (coal)				SUM
	< 1	1 - 5	5 - 10	> 10	< 1	1 - 5	5 - 10	> 10	< 1	1 - 5	5 - 10	> 10	< 1	1 - 5	5 - 10	> 10	
6A	0	2551	5102	0	1701	17857	0	0	0	0	0	0	0	2551	4252	0	34,014
6B	0	5102	638	1913	7015	6378	638	0	0	0	0	0	0	0	3189	2551	27,423
7A	0	1701	0	0	5952	0	0	0	0	0	0	0	0	3401	850	0	11,905
7B	6633	14286	510	0	7143	4592	0	0	0	0	0	0	0	0	2551	1020	36,735
8A	3189	9566	0	0	4464	5102	0	0	0	0	0	0	0	638	1276	0	24,235
8B	1913	5740	0	638	5102	0	0	0	638	1276	0	0	0	0	0	0	15,306
9A	1913	7653	638	638	3827	4464	0	0	0	0	0	0	0	0	1276	0	20,408
9B	3189	16582	5102	0	1913	8929	0	0	0	0	0	0	0	1276	5102	0	42,092
10A	18707	52721	2551	850	3401	20408	0	0	0	0	0	0	0	0	0	2551	101,190
10B	12755	38265	51020	2551	58673	114796	0	0	0	0	0	0	0	0	0	7653	285,714

Only the surface of the particles is measured by SEM. Therefore, dilution of samples prior analyzes were necessary. In Table 30 the number of particles per cm^2 of the filter (sample after preparation) on each sampling site is presented. Results show size and chemical composition of various fractions of particles on the individual sampling site.

According to results the highest number of particles in samples were alumosilicates (compounds of Al, Si, K and O), mostly in the size range from 1 to 10 µm. The majority of these particles have natural origin. An extremely large number of particles of titanium dioxide (TiO_2), all of which are present mainly in the smaller size fractions (less than 1 µm up to 5 µm). Coal particles, majority of them larger than 5 µm, were also detected. None of coal particles were smaller then 1 µm. Coal particles were also found at the control sampling sites 6 and 7. Possibly their origin is the coal transported by boat daily from port of Koper to Trieste for the needs of local industry.

Only few particles of iron oxide were detected, majority of them were rather small (from 1 µm to 5 µm). Most of the iron particles were detected at the sampling site 1, which is the nearest sampling site to EET depot. A difference in the number of particles between sampling sites A (vertical deposition) and B (vertical deposition + horizontal contribution) could be observed. In three sampling sites higher number was observed at sampling site A (sampling site 1, 6 and 8). In all others higher number were observed in sampling site B. Highest total number of particles were observed at sampling site 10, locating in center of Ankaran.

Figure 146 represent % of the various fractions of particles at individual sampling sites. The larger fractions are alumosilicates, most probably of natural origin. However, some bauxite (alumina) particles were found too. These could come from the bauxite transshipped in Port of Koper. The presence of these particles is another indication of the influence of port activities on dustiness of the surroundings. TiO_2 is also a fraction, which occurs very often. Fewer coal particles were observed, but the least of all particles present were those of FeO.

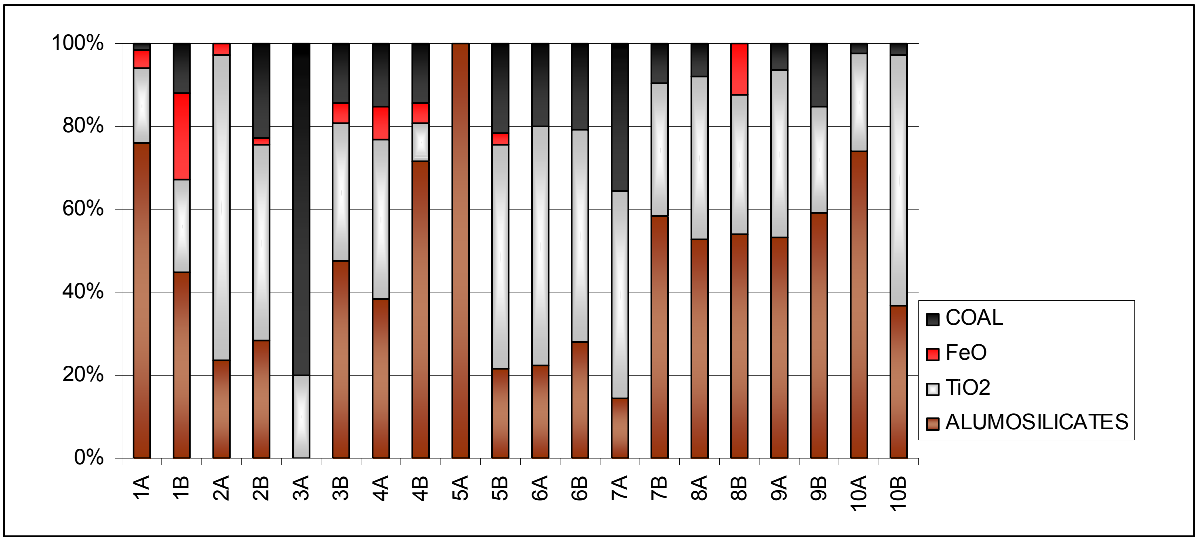


Figure 146: % of different particles at individual sampling site

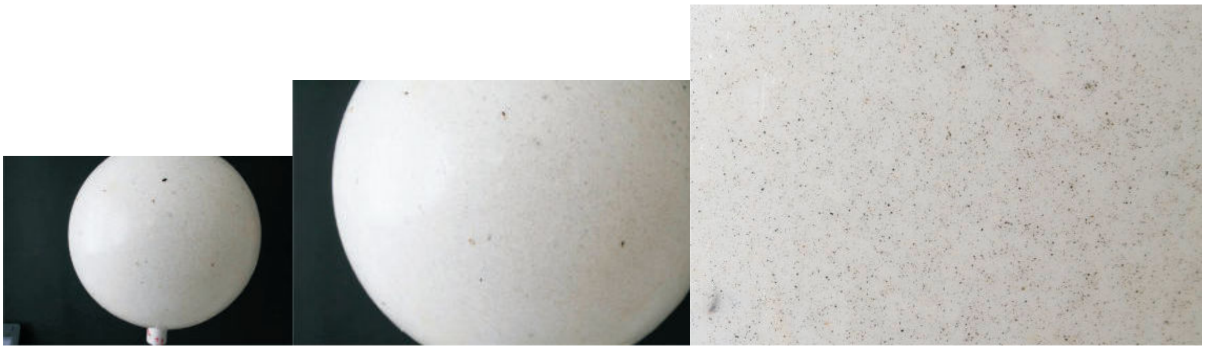
However, it should be noted that only particles trapped on the filters were analyzed using electron microscopy. Theoretically, only particles larger than 3 µm should be present. Particles, trapped in the filtrate (particles smaller than 3 µm), were determined only gravimetrically.

4.2.10 The results of alternative method for the particles monitoring - sampling device type 1 (the ball) - particle counting

4.2.10.1 Visual perception

For quick estimation of the direction and quantity of particulate matter and therefore the determination of the main sources of emissions of dust particles in the area under investigation, a simple alternative measurement device, based on deposition and adhesion was developed. The basic idea was to collect particulate matter from air on adhesive material (medical Vaseline). This simple measuring device enabled collection of particles in both, the horizontal and vertical directions. Sampling devices were placed in the residential zones around the coal and iron ore depot of Port of Koper.

After visual assessment of sampling devices (Figure 79 to 82) indicated that they were quite effective. Uneven depositions of particles were observed on the surface of the ball. These could be associated with the direction from which the dust particles came. To quantify the results, the number of particles per unit area were counted.



Figures 147, 148 and 149: Collected particles on the surface of a sampler oriented toward Port of Koper and EET depot

Figures 150, 151 and 152: Collected particles on the surface of a sampler oriented away from Port of Koper and EET depot

As shown on Figures 147 to 152 and also results of particles counting (Table 31) this simple sampling device appeared to be useful and efficient for assessing the impact of the EET depot on the surroundings (contribution to the increased number of dust particles in the surrounding area).

4.2.10.2 Manual counting

Results show that particles on the alternative sampler are not evenly distributed. Differences of up to ten times or more have been observed in the number of particles at different locations on the sampler (the main point of the compass) for each ball. The maximum number of particles was detected on the side of the sampler oriented toward Port of Koper and EET depot (Table 31). The side of the sampling device oriented toward Port of Koper and EET depot in Table 31 and Figure 153 is labeled with an asterisks, *.

Time intervals from 1st April to 1st May, 1st May to 1st Jun, 1st August to 1st September, 15th September to 15th October and 15th October to 15th November were selected randomly. For analyses sampling sites 1, 2, 3, 4, 5, and 10 were selected due to their location. Samples from all sampling sites and time intervals were analyzed by manual counting while counting particles using computer software were performed only on samples from time interval 15th October to 15th November.

Table 31: Number of particles on 1 cm^2 - sampling device 1 (the ball)

	location	**sampling site 1**					**sampling site 2**					**sampling site 3**					**sampling site 4**					**sampling site 5**					**sampling site 10**				
	direction	N	S	E	W	SW*	N	S	E	W	SW*	N	S	E	W	SW*	N	S	E	W	S.SW*	N	S	E	W	S*	N	S	E	W	S*
1.4. do 1.5.2008		15	57	32	146	134	21	12	17	130	108	3	71	12	32	134	41	11	13	101	85	11	200	15	39	200	20	85	41	25	85
		21	64	24	149	184	25	15	26	124	78	0	98	18	34	184	33	12	8	154	103	21	151	8	51	151	26	84	44	16	84
		7	94	31	178	148	20	16	10	149	42	2	98	26	26	148	28	21	13	95	128	19	209	15	17	209	21	88	40	20	88
																						17	204	8	31	204	25	63	23	20	63
	No. of particles/ cm²																					23	187	17	67	187	13	79	36	16	79
	average No. of particles / cm²	14.3	71.7	29	157.7	155.3	22	14.3	17.7	134.3	76	1.7	89	18.7	30.7	155.3	34	14.7	11.3	116.7	105.3	18	190	13	41	190	21	80	37	19	80
1.5. do 1.6.2008		41	84	11	186	309																2	17	3	16	17					
		28	53	19	232	301																14	25	2	17	25					
		34	63	25	211	292																7	17	4	19	17					
		39	86	36	141	248																4	10	3	6	10					
	No. of particles / cm²	28	45	35	238	224																8	20	1	10	20					
	average No. of particles / cm²	34	66.2	25.2	201.6	274.8																7	17.8	2.6	14	17.8					
1.8.do 1.9.2008		28	99	46	85	153	16	47	18	50	102	13	5	17	60	16	68	25	29	69	52	29	52	26	27	52	19	26	36	26	26
		31	53	50	117	152	15	39	21	56	93	15	19	33	39	19	60	14	41	91	62	31	36	40	23	36	13	28	38	29	28
		31	79	36	95	136	17	30	16	53	96	20	16	15	42	14	59	22	25	87	47	32	24	26	7	24	8	34	24	20	34
		30	78	36	64	150	7	34	19	39	69	8	6	16	41	14	59	26	21	61	27	9	29	9	11	29	5	37	39	18	37
	No. of particles / cm²	32	45	44	116	148	14	31	8	47	66	19	10	12	48	7	35	17	22	58	45	13	20	12	14	20	12	33	42	21	33
	average No. of particles / cm²	30.4	70.8	42.4	95.4	147.8	14	36.2	16.4	49	85	15	11	18.6	46	14	56	20.8	27.6	73.2	46.6	23	32.2	23	16	32.2	11	32	36	23	32

* direction towards EET depot

- Table continues -

- Continuation of the Table 31 -

	location	**sampling site 1**					**sampling site 2**					**sampling site 3**					**sampling site 4**					**sampling site 5**					**sampling site 10**				
	direction	N	S	E	W	SW*	N	S	E	W	SW*	N	S	E	W	SW*	N	S	E	W	S,SW*	N	S	E	W	S*	N	S	E	W	S*
15.9. do 15.10.2008	No. of particles / cm²	41	35	74	171	/											53	57	36	28	/										
		49	29	109	184	/											29	60	63	36	/										
		27	37	89	153	/											53	49	49	17	/										
		14	33	62	131	/											48	39	31	16	/										
		11	34	89	159	/											32	40	28	13	/										
	average No. of particles / cm²	28.4	33.6	84.6	159.6	/											43	49	41.4	22	/										
15.10.do 15.11.2008	No. of particles / cm²	40	173	55	68	332	12	65	39	82	177	48	29	23	101	153	32	68	33	67	87	48	146	15	23	146	34	109	49	14	109
		26	111	82	117	324	12	42	49	103	174	53	35	32	128	92	32	39	39	77	81	47	159	18	41	159	35	129	48	20	129
		22	181	83	108	283	10	60	33	99	158	51	37	21	120	101	31	54	27	52	85	29	124	17	21	124	27	105	39	21	105
		26	186	71	42	228	11	77	38	80	194	14	31	18	108	115	36	30	21	57	86	13	91	24	25	91	31	122	40	12	122
		24	111	84	101	256	6	57	42	113	131	25	45	22	123	73	15	32	49	64	77	27	105	18	16	105	37	116	49	13	116
	average No. of particles / cm²	27.6	152	75	87.2	284.6	10	60.2	40.2	95.4	167	38	35	23.2	116	106.8	29	44.6	33.8	63.4	83.2	33	125	18	25	125	33	116	45	16	116

* direction towards EET depot

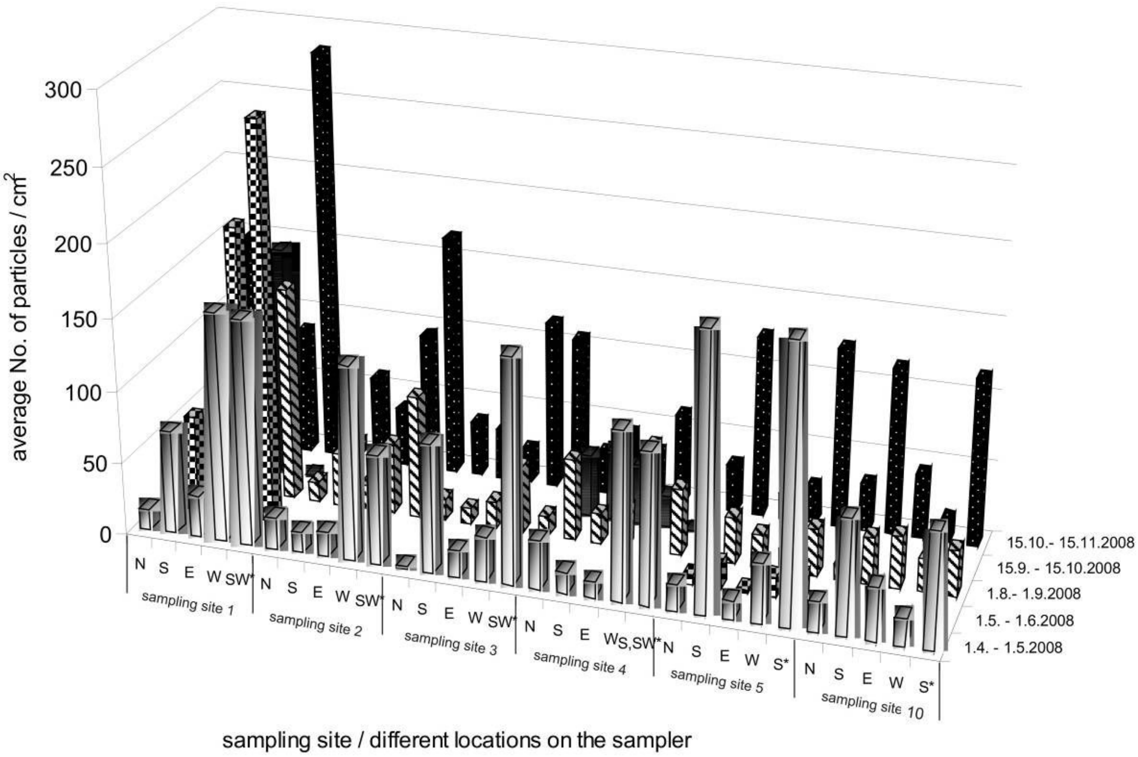


Figure 153: The number of particles on a sampling device according to the main point of direction of the compass in different time periods ***(* in chart indicates the direction towards EET depot)***

In Figure 154, the number of particles at the sampling site 1, 2 and 3 are presented. With the exception of time interval from 1.4. to 1.5.2008 in all other cases, the results show decrease in the number of particles with the distance from the landfill. The minimum number of particles is observed on sampling site 3 and maximum number of particles were measured on sampling site 1. At all three sampling sites only numbers of particulates on sampler, oriented toward EET coal and ore depot were compared.

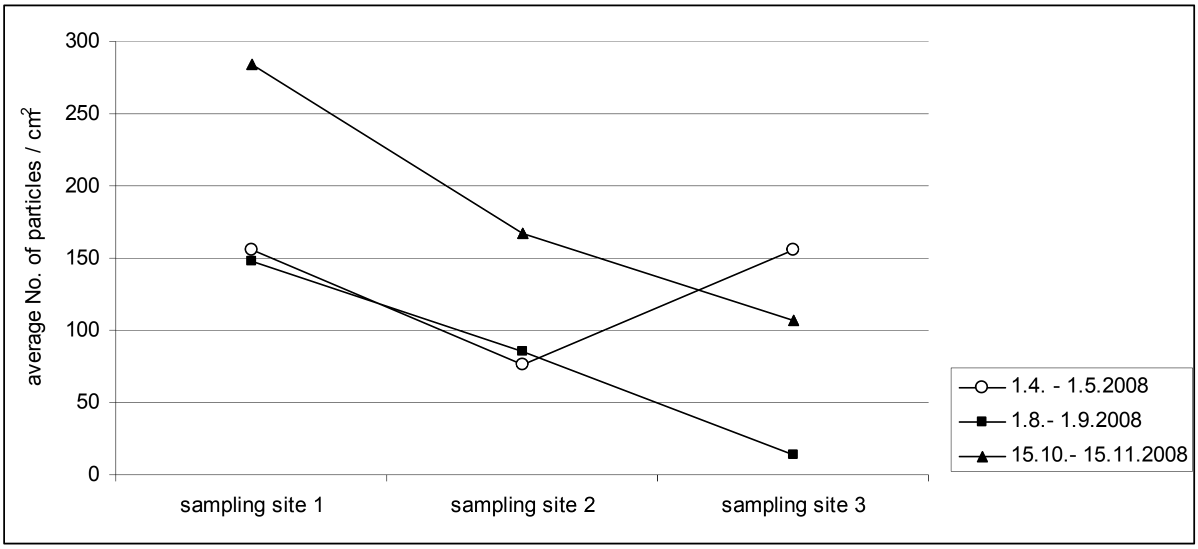


Figure 154: Comparison of sampling site 1, 2 and 3 - number of particles per 1 cm^2

4.2.10.3 Computer software (IT 3,0) counting

Table 32 and Figure 155 represent the number of particles per cm^2 using computer software (IT 3,0) counting on alternative sampling device (ball). Number of particles were counting only for time period from 15th of October to 15th of November 2008. Maximum number of particles observed on each sampling device was on part, oriented towards EET depot. Individual deviations can be explained by mistakes in determining the exact direction for main point of direction of the compass at each sampling device.

Table 32: Number of particles on 1 cm^2 - counting with software IT 3,0

	location	sampling site 1					sampling site 2					sampling site 3					sampling site 4					sampling site 5					sampling site 10				
	direction	N	S	E	W	SW*	N	S	E	W	SW*	N	S	E	W	SW*	N	S	E	W	S.SW*	N	S	E	W	S*	N	S	E	W	S*
15.10.do 15.11.2008	No. of particles/ cm²	30	185	64	46	450	14	257	30	45	122	79	52	35	119	125	53	55	45	50	104	8	141	15	40	141	13	128	55	6	128
		96	95	58	107	475	9	269	31	33	142	111	48	35	123	120	55	52	87	63	92	12	140	18	38	140	20	150	52	18	150
		43	154	62	61	429	14	209	58	57	194	69	40	48	134	108	17	34	27	47	80	14	163	14	39	163	26	161	30	19	161
		26	89	57	84	408	7	103	51	70	179	94	60	55	158	143	25	36	61	78	82	25	124	41	16	124	24	178	28	7	178
		33	103	65	43	445	16	88	14	78	173	73	74	48	142	90	44	33	38	66	85	37	112	42	28	112	27	179	45	15	179
	average No. of particles / cm²	45	125	61	68	441	12	185	37	57	162	85	55	44	135	117	39	42	52	61	89	19	136	26	32	136	22	159	42	13	159

* direction towards EET depot

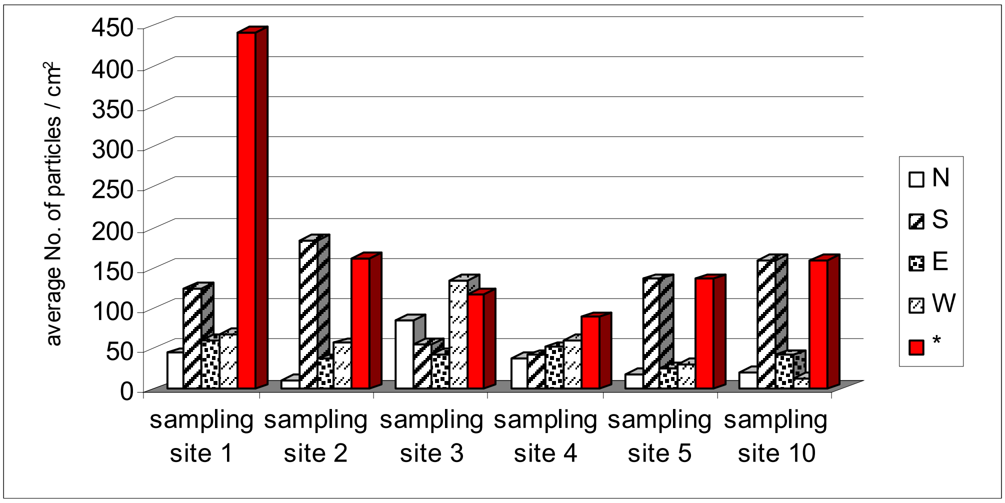


Figure 155: Number of particles on 1 cm^2 - alternative sampling device (the ball) - computer software counting (15.10. - 15.11.2008)

4.2.10.4 Comparison of both counting methods

Trend in the number of particles, counted using computer software, is consistent with the number of particles observed by manual counting (Figure 156). Trend can be observed also for the average number of particles (Figure 157). Results shows very good correlation between both methods (manual and computer counting). Spearman's (rho) correlation coefficient for computer counting vs. manual counting is relatively high, correlation is 0,874 (p=0,000). However in spots where enormous number of particles on 1 cm^2 were observed, computer counting gives us higher number of particles. Probably in such cases results are more accurate using computer software, especially if a large number of particles appear in small area and therefore mistakes using manual counting are more likely. It is hard to focus on each individual particle in case of high saturation. Such example are results for sampling site 1, where 35% more particles were counted using IT 3,0 compare to manual counting. Although, the trend stays the same, the data obtained by manual counting provide is adequate for assessing the direction from which the particulate matter came.

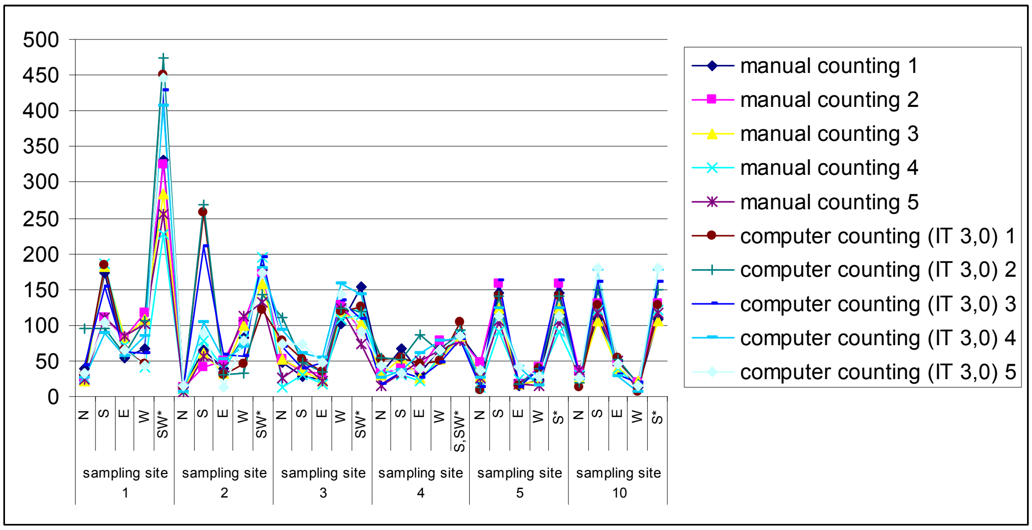


Figure 156: Comparison between manual and computer counting

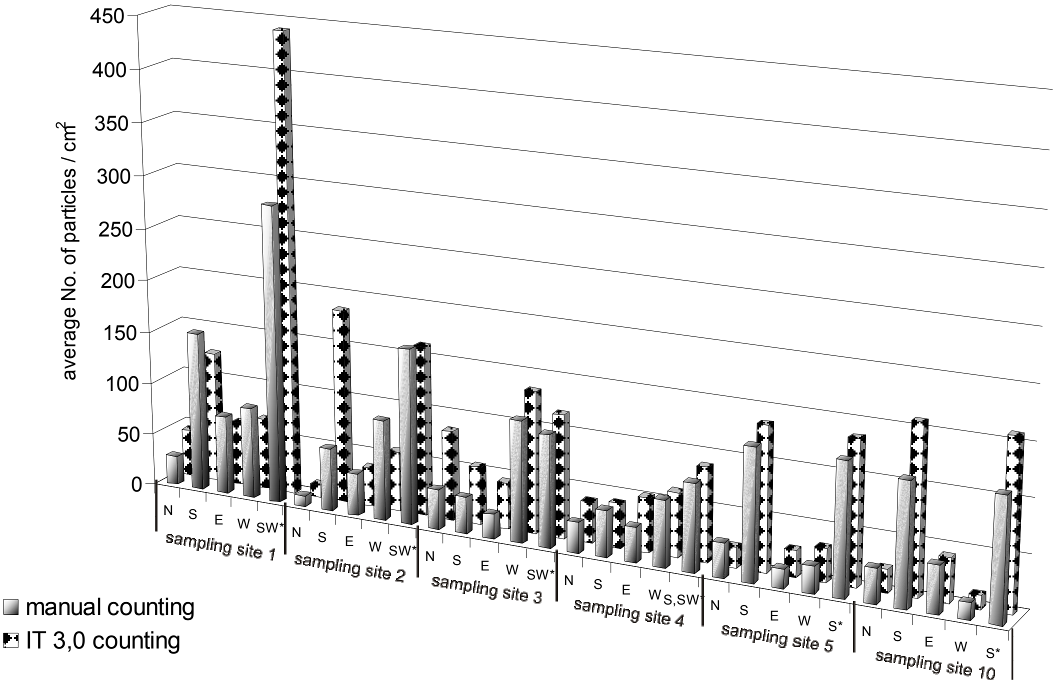


Figure 157: Comparison between manual and computer counting - average results

4.2.10.5 Identification of particles regarding morphology and chemical composition using SEM/EDXS

Dust particles collected using the alternative collector (ball - sampling device type 1) were analyzed using electron microscopy with aim to confirm presence of particles from EET depot in Port of Koper.

The SEM/EDXS analysis of the material collected using the simple measuring device detected particles of coal, iron oxide, titanium oxide, as well as particles of organic origin from the natural environment (Figure 158). Especially particle of coal as well particles of iron oxides could originate from depot of coal and iron ore at EET in Port of Koper. The particles recovered from the alternative collector were morphologically similar to the particles collected in the conventional sampling devices (Section 4.2.9).

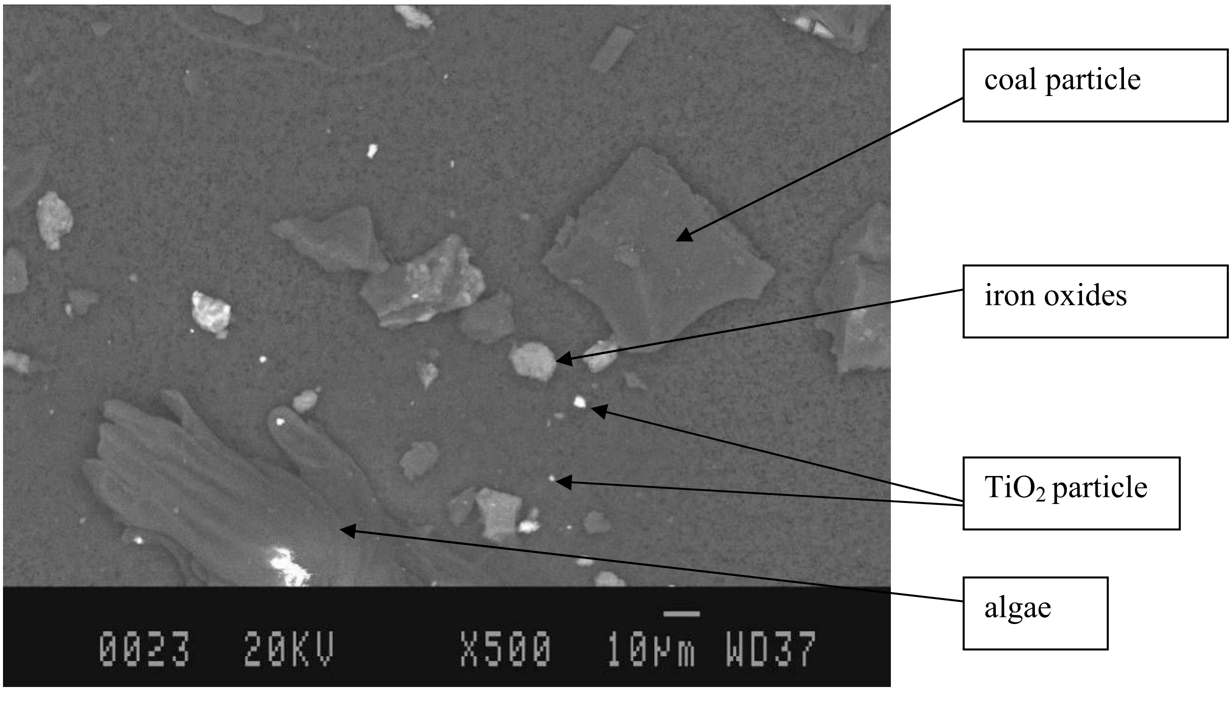


Figure 158: Sample from simple measuring device (ball) analyzed using electron microscopy

5 DISCUSSION

Atmospheric dust (large or coarse particles) has traditionally been considered mainly as a nuisance rather than a health hazard. Therefore particulate matter deposition represent a major concern due to nuisance for people, but can also be a cause of health and other problems, either from direct inhalation or ingestion or trough secondary pathways after particles have deposited (on vegetables, fruits, or in drinking water).

For many years the inhabitants of Ankaran (distance from the iron ore and coal storage sites at EET is approximately 1800 m) and its surroundings (the closest residential area is 1000 m from the storage sites) have been pointing out the problem of the pollution of their residential area with emissions from the terminal EET in the Port of Koper. They believe the mayor contributor of dust is activities at the Port of Koper, especially activities on coal and iron ore depot at EET. Inhabitants visibly perceived particulate matter deposition on their yards, places of residence, linen and vegetables. These perceptions of the inhabitants were one of the reasons for starting the study aimed to reveal the impact of Port of Koper on dust pollution of the surrounding area.

The purpose of the study was to collect, analyze and characterize the air borne particulate matter deposited in the residential areas around the port of Koper with aim to correlate these particles with port activities, especially with activities on EET terminal (coal and iron ore manipulation). The aim of the study was therefore not to make the risk assessment regarding the impact of dust deposition on the health of the people. Although such study would be reasonable to made in the future. Such risk assessment should be focused on respiratory disease incidence. According to the results of epidemiological study (Eržen et al., 2003) additional epidemiologic research on respiratory problems in the impact area would also be reasonable to make.

5.1 Legislation

The basis of the Slovene legislation in the field of outdoor air quality is the Environmental Protection Act (2002) and its subsequent Decrees. The particulate matter deposition and its limit values were regulated by the Decree on limiting values, alert thresholds and critical emission values for substances into the atmosphere (1994). This decree has provided maximum value for the monthly and annual deposition as well as the content of selected metals in deposition. The Decree on sulphur dioxide, nitrogen oxides, particulate matter and lead in ambient air (2002) was adopted. This Decree annulled its prior Decree on limit values, alert thresholds and critical emission values for substances into the atmosphere (1994). However limiting values regarding particulate matter deposition from annulled decree were still in use (according to interpretation of ARSO) until July 2007. On July 27th 2007 (Decree, 2007) those limiting values were finally annulled.

Particulate matter in ambient air is regulated in the Decree on sulphur dioxide, nitrogen oxides, particulate matter and lead in ambient air (2002), which applies to the regulation only fine particles (PM_{10} and $PM_{2.5}$). It does not regulate particulate matter deposition anymore. Therefore today the dust deposition limiting values are used by the annulled decree (1994) as recommended values.

The Ministry of Environment and Spatial Planning of Republic of Slovenia (MOP) has provided no informastion about the reasons for the removal of dust deposition (and thus coarse particles) from the legislation. The fact is that fine particles represent greater risk for health then coarse particles. Larger particles may also represent a risk to health (mainly depending on their chemical and morphological structure) and represent a disturbance for the environment. Slovenia has a 40-year history of monitoring of dust deposition by different institutions (for instance EIMV), particularly in the vicinity of the coal power plants. By annulling the limiting values, monitoring dust deposition is likely to be gradually abolished, although monitoring of particulate matter deposition is mentioned in European directive. European Directive 2004/107/EC of the European Parliament and of the Council from 15th of December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air (2004) assume monitoring of these elements in fine particles (PM_{10}) as well as in particulate matter deposition. One of the objective of Directive is also to ensure that adequate information on concentrations of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air as well as on the deposition of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons is obtained and to ensure that it is made available to the public. For the analyses of particles deposition specific standard (Air Quality - Ambient Air - Determination of lead, nickel, arsenic and cadmium in atmospheric depositions; oSIST prEN 15841:2008) was enforced. Limiting or target values for metals in deposition is still (no longer) regulated.

Coarse particles are usually perceived as a nuisance, but they can also affect health and well-being. The WHO definition: "Health is a state of complete physical, mental and social well-being and not merely the absence of disease or infirmity" should not be forgotten (WHO, 1948). After all, even if coarse particles only offend inhabitants when they visually detect pollution in their homes, that too can affect an individual's welfare and health.

5.2 Collection of samples

For collection of particulate matter deposition standard and modified methods were used. Some modifications were made in order to optimize method, and other to maximize the number of sampling sites and to minimize costs. Therefore six sampling sites were used during preliminary study and ten sampling sites during study in 2007/08.

The method for collection of particulate matter deposition is not perfect, because it does not entirely include the wind contribution. In addition already trapped particles could be lost due to wind blowing across the measuring device. To improve that distilled water was added to prevent the wind from blowing away the particulate matter deposition from the containers. On the other hand, the addition of water in the summer time give raise of algae growth. To resolve this problem small peaces of copper wire were added to the water. Additionally, when wind blows through the sampling gauge, majority of particles are not deposited on the ground or in the sampling gauge. They are blown away with the wind and precipitate when wind stop blowing or when hits the obstacle. That's why metal screen (oriented toward ore depot at EET) was added as an obstacle. By adding a metal screen (20 cm x 30 cm - sampling sites marked with letter B) the horizontal dispersion of particulate matter was intercepted. The main purpose of the modification was to establish and quantify the particulate matter brought also by the wind from the direction of its source.

On almost all sampling sites with the exception of a few measurements during individual time periods higher values of particulate matter deposition were observed in sampling sites B (modified device with metal screen) compared to the sampling sites A (standardized measuring device). In nature (and living environment) there are always flat countryside as well as barriers, where dust particles spread with wind can deposited. Therefore additional wind contribution should also be considered while monitoring dust deposition.

Additionally, a new instrument (the plastic ball coated with petrolatum) for quick estimation of direction and quantity of airborne particulate matter and therefore determination of the main emission sources of dust particles in the observed area was developed.

5.3 Results - preliminary study

Deposition was determined gravimetrically. In addition, further analysis of metals content in the samples, analysis by SEM/EDXS and analysis of stable carbon isotopes were employed, all with aim to detect and characterize particles in deposition samples and correlate these particles with activities at EET. Budgetary constraints necessitated limiting analysis for metals, measurement of carbon isotope ratios and electron microscopic determination of chemical composition and morphology to only the annual composite samples.

Dust deposition were collected using standardized method of sampling with Bergerhoff sedimentators. The mass of dust deposition collected in this way were compared with the limiting (2006) and recommended (2008) levels. During preliminary study carried out from October 2005 to October 2006, the total amount of particulate matter deposition at all sampling sites in the area of the municipality of Ankaran and surroundings exceeded the emission limit value of 350 mg/m^2 a day eleven times, corresponding to 15 % of all measurements. The results presented in Section 4.1 (Results of preliminary study) indicate periodically extremely elevated values of particulate matter deposition around the Port of Koper. According to the results of the gravimetric analysis, the highest measured amounts of particles were observed during time period from 15.9 to 15.10.2006 at sampling site 4. With standardize method of collection (sampling site A), 4283 mg/m^2 a day was measured; this value exceeded the limiting value (350 mg/m^2 a day) by a factor of 12. Furthermore, on sampling site B, 5743 mg/m^2 a day was measured, the limiting value was exceeded by more than 16 times, most probably due to wind contribution. During this time period also in all other sampling sites elevated values were observed. During entire time period of the study also two other elevations of particulate matter deposition were observed (15.2.-15.3. and 15.6.-15.7.); however, measured values were lower and limiting value was not exceeded in all sampling sites. The results show significant differences between sampling sites and monthly and seasonal levels. Increased values are noticed in the hot dry periods, mainly in summer and autumn months due to the dryness of the terrain and strengthening of the wind, which blew from the sea across the storage piles of ore toward the sampling sites (and residential areas). During winter, a north wind, which blows across the storage piles towards the sea, prevails in the study area. However, correlations between the amount of dust deposition and frequency of wind from the direction of EET could not be confirmed due to insufficient data of the wind speed (only information about the wind speed above and under 1 m/s) and too long measurement interval (1 month) (highest Spearman's rho correlation is 0,48). Increased emission concentrations could be expected during strong winds blowing through the EET. Therefore, using selected method of data acquisition, it is not possible to detect the impact of the extremely strong wind that blows for only a very short period of time. For the time period 15.9. - 15.10.2006, therefore, there is no correlation between the increased particulate matter deposition and the wind although the residents from Rožnik residential area detected increased depositions of dust in their living environment after the strong Mistral. During same time period also increased amount of deposition were measured, however increased levels of wind were not detected. For example if the wind blows 5 hours with high wind speed it represent only 0.5 % of wind frequency on monthly average data, although many dust particles can be transported from the landfill to surrounding environment during this short time event.

The main source of dust deposition in living environment around EET most likely comes from the coal and iron ore depot rather than from manipulation of the ore. On the basis of the data collected, correlation between amount of particulate matter deposition and ore manipulation at EET can not be confirmed (highest Spearman's rho correlation is 0.44).

Sampling sites 1, 2, 3 were placed in a linear direction in line with predominant wind direction (NE - SW) to evaluate the impact of distance from the EET depot for coal and iron ore on the amount of particulate matter deposition.

In the case of modified sampling device (added metal screen), maximum dust depositions were measured at site 1 (closest to the EET depot). Using the Bergerhoff sedimentators, higher amounts of particulate matter deposition were measured in sampling site 2. This could be attributed to the morphology of the surrounding terrain. The median values of particulate matter deposition at sampling sites 1, 2 and 3 show decrease in mass of particulate matter deposition with distance from EET ore depot in case of sampling device B and increase in case of standardize sampling device A.

In order to identify the source of the particulate matter, it as well as the surrounding soil, coal and iron ore were analyzed. The elemental composition of the samples of soil, coal or iron ore does not contain a specific ratio of elements, which would helps us to correlate suspended dust with the source. Hence, no conclusions could be drawn from the elemental analysis. Only high amount of iron were found in soil sample, probably due to fact that surrounding soil "terra rosa" is rich in iron.

The results of chemical analysis of annual deposited matter show that the limiting value for Zn, Cd and Pb (Decree, 1994) were not exceeded. The only exception was the concentration of zinc at the sampling site 5A. The regulations do not specify limits for amounts of Al, Cr, Cu, Fe and Ni. Results also show increased values of Fe, Al, Cu, Zn and Pb at the sampling site 4.

It was not possible to distinguish the coal and iron ore originating from the Port of Koper from other organic sources of carbon (burning of fossil fuel, traffic, pollen, etc.) and iron compounds in the soil on the basis of the results from the metal determinations.

Since in nature there are many natural radioactive isotopes, which could be present as impurities also in coal and iron ore (Van Hook, 1979; Dowdall et al., 2004; Ward and Suárez-Ruiz, 2008) representative sample of coal and iron ore from EET depot in Port of Koper was measured for gamma-ray emitters' activity. Because the activity of the gamma-ray emitters from sample of coal and iron ore was not significantly increased compare to soil sample additional analyses of samples of particulate matter deposition were not performed.

Chemically coal particles contain predominantly carbon and some other elements. The situation is similar with other particles in the environment such as pollen, smaller parts of plants and animals. In order to differentiate the particles of coal and iron ore from other organic dust particles in the sample, a new approach was employed. For this differentiation, the electron microscope was used to determine the chemical composition of the particles as well as to define their morphological structure. The presence of both coal and iron ore particles linked the dust deposition with the activity on the coal and iron ore depot. For purpose of preliminary study only samples from time period from 15th of February to 15th of March 2006 were analyzed. During that time presence of coal (black particles) was detected with visual inspection of the filtered samples and also higher particulate matter deposition was detected in all sampling sites. Presence of coal was confirmed with morphological and chemical analysis using SEM/EDXS. Additionally particles of iron ore (probably Fe_2O_3), bauxite (Al_2O_3) and also titanium dioxide (TiO_2) were found, all of which can be linked with activity at Port of Koper.

Several conclusions can be drawn from preliminary study. (1) Monthly monitoring intervals may be too long to correlate the influence of cargo manipulation on the quantity of the particulate matter deposition in the environment. (2) The off-loading, on-loading and storage of the iron ore has a small influence on the dustiness of the environment. (3) The main influence is the sudden strong wind, which blows from the sea crosses the storage piles and continues towards the residential area (Poljšak et. al., 2006). (4) The quantity of particulate matter depositions depends mostly on weather conditions, especially the strength and direction of the wind and also the quantity of rainfall, which determined the dryness of the terrain and also dryness of coal and iron ore. (5) Building the 11 m high anti-dust emission wall and the spraying of the landfill with water probably lowers the emissions of dust particles in the environment. Unfortunately no data on emission from the period before the anti-dust emission wall was build are available. (6) Based on the analysis of samples using electron microscopy dust deposition can be with certainty attributed to activity in the Port of Koper.

5.4 Results - study 2007/08

As was done in the preliminary study, particulate matter deposition was determined by gravimetric analysis during the study 2007/08. The duration of the sample collection, however, was shortened from monthly to twice per month. Later on additional analyses were made.

On the basis of the annulled Decree on limit values, alert thresholds and critical emission values for substances into the atmosphere (1994), a recommended value of 350 mg/m^2 day for particulate matter deposition was established. This value is still in use. During the entire monitoring period from December 2007 to November 2008 out of 240 samples only values of 4 samples approached or exceeded the recommended value. These excessive values were observed in the samples collected from 15th May to 1st June at the sampling site 5A, from 1st

August to 15th August on the sampling site 10A, and from 15th November to 1st December at sampling sites 5A and 6A. During these periods, the wind was blowing with increased intensity (longer period of time as well as higher speed) in the direction of S and SW - from the EET depot towards the sampling site 5 and 10 (and residential areas Rožnik and Ankaran). In order to compare dust sediments with the recommended values from the annulled Decree (1994), 14-days results were calculated to monthly values. It is important to emphasize that the mass of monthly particulate matter deposition was considerably lower and did not exceed the recommended values in any case. Also yearly particulate matter deposition never exceeded recommended yearly values of 200 mg/m^2 day.

To determine the possible impact of the horizontal contribution of dust particles, the results from sampling sites B (modified sampling device) were also analyzed. This analysis revealed higher content of particulate matter collected on sampling sites B compared to the corresponding sampling sites A. Increased amount of collected dust was due to horizontal contribution, which confirms the hypothesis that standard method of sampling underestimates the importance of horizontal (wind) dust transport.

By comparing two different wind measurement locations, the importance of topography of the terrain on the impact of wind distribution was revealed. The interpretation of results in correlation with wind requires additional effort (on the basis of the acquired data from all three measuring sites). The measured values of wind distribution differ and probably depend on the micro location and the morphology of the terrain at the sampling site. During the period of observation, the measuring station within EET recorded maximum wind speed of 10.8 m/s (38.9 km/h). At this time, the measuring station Markovec recorded a higher maximum value (12.4 m/s or 44.64 km/h), while at the measuring station inside the Port of Koper (managed by PINT) a maximum value 7.3 m/s (26.3 km/h) was obtained. Even so, it is difficult to correlate particulate matter deposition with the wind. Method of collecting dust deposition is relatively rough, the measurement time intervals relatively long and the wind velocity appears to depend on the micro-location and terrain topography.

The East wind was predominate both by frequency and strength in the study area during time period 2007/08. During different seasons of the year other wind characteristics were observed. From April to June, the wind frequently came from the north west. During autumn period, from September to November, South East winds were frequent. As already mentioned in interpretation of preliminary study results, occasionally strong Mistral (West - Nord West) blows very short period of time in the study area. However, inhabitants of Rožnik usually detect high pollution of their living environment with black particles after periods of strong winds from the sea side. During the study time period (December 2007 - November 2008), there were no record of extreme weather events, such as the sudden emergence of a strong wind, which blowing from the landfill EET toward the selected sampling sites. Also the surrounding residents during that time have not pointed out such events. However, the results of preliminary study show that such events can occur (March and October 2006).

The concentrations of selected metals in the average yearly sample of dust were determined by chemical analysis. The impact of the iron ore depot on the amount of iron at different sampling sites and the share of other sources (e.g.soil) on total metal concentration was estimated from these analyses. According to the potential impact on health particulate matter deposition were assessed on presence of individual elements (also Pb, Cd and Zn) and compared with the limited values. Based on the results of metal content in the annual samples, it can be noticed that in any of the 10 sampling sites (A and B) levels of metals (Pb, Cd and Zn) in the samples did not exceed the recommended value. In addition to these metals, Cr, As, Ni, Cu, Fe and Al were determined. The levels of iron (between 250 and 2800 $\mu g/m^2$day) and aluminum (between 140 and 750 $\mu g/m^2$ day) were relatively high, while the values for other metals were relatively low (up to 10 for chromium, for lead up to 7, cadmium in most cases below the detection limit (<0.1), up to 0.2 for arsenic, for nickel up to 6, and for zinc up to 81 $\mu g/m^2$ day). Before the collection of dust deposition started, copper wire was added as an inhibitor of algal growth. Therefore, increased levels of copper may result from leaching of copper in the sample from a copper wire, added into the collecting tank for algae growth prevention and not reflect the copper levels from the suspended dust.

When sampling sites A and B were compared regarding mass of particulate matter deposition, results showed that the horizontal contribution of the wind (metal screen - sampling site B) significantly contributed to increased quantities of dust at the sampling site 1, which is the nearest to the landfill. In 22 out of 24 samples, the mass of particulate matter deposition on sampling sites B were higher than the corresponding masses from sampling site A. A similar observation was made on other sampling sites (only not so frequently). At sampling sites 1, 2, 6, 7, 8 and 10, 15 out of 24 samples shoved the mass of particulate matter deposition on sampling sites B is higher than mass on sampling site A. However, one of the reasons why in some cases amount of particulate matter deposition is higher in sampling sites A compared to sampling sites B could be relatively low amount of particulate matter deposition during entire period of monitoring; another reason could be good weather condition (low wind velocity in observed directions). Also modified sampling device were oriented in direction toward EET and Port of Koper. If predominant wind blows from any other direction, sampling gauge was practically protected from such influence (while sampling site A was not).

As seen from the data collected, correlation among coal and iron ore manipulation and amount of particulate matter deposition in Port's surroundings could not be confirmed. However, according to the results of preliminary study, a confirmation of such correlation was not expected since the method of particulate matter deposition monitoring is not sensitive enough and the sampling interval for finding such correlation may have been too long.

The proportion of particulate matter deposition increased during dry summer months. The reason for this is most likely dryness of ground which contributed to the dustiness in surroundings. In addition, during the summer period, wind blows predominant from sea towards land (across ore depot) what reflects in increased quantities of measured particulate matter deposition. The amount of ore up-loading and unloading is rather constant during entire year with slightly increased values of coal unloading during winter.

Among all metals analyzed, the highest values were observed for iron and aluminum. A possible source or reason for high values could be natural composition of the surrounding soil. However, the high values of iron could be linked also to the impact of iron ore in the ore depot at EET in Port of Koper. Also high values of aluminum could be linked to Port activities (unloading of bauxite (alumina).

The stable carbon isotopes $^{13}C/^{12}C$ ratio of the samples of particulate matter deposition were analyzed. By using the ratio of carbon isotopes $^{13}C/^{12}C$ measurements determination of the presence of coal in samples of particulate matter deposition was attempted. Coal from one source has more or less constant isotopic ratio of carbon isotopes and therefore the same $\delta^{13}C$ values. Using results of carbon isotopes $^{13}C/^{12}C$ ratio in individual monthly sample and ratio of carbon isotopes $^{13}C/^{12}C$ from the coal and control, the content of the carbon in samples which may originate from coal was estimated. From these results it appears that the largest amount of carbon in samples which could be associated with coal appears in the period of

February and April 2008, especially in February almost in all sites. But it is necessary to stress that the chosen method represents new approach for the source of carbon assessment. The possibility of an error must be highlighted because the investigated sample by its composition and structure is not homogeneous but consists of different particles from environment. Among others sources carbon could originated from particles of coal, scrap of insects (parts of legs or skeleton), pollen, plant parts (decomposed fragments of leaves in the sample), algae, soot (heating of buildings, cars, transport etc.) and others. The isotopic value ($\delta^{13}C$) is specific for each of these sources and in case of non-homogeneous sample measured $\delta^{13}C$ values could represent the average value of the various sources, which may lead to a false conclusion about the origin. In addition, an assessment with which the estimation of the proportion of carbon origin from coal was given in % of carbon in the sample. With the methodology employed, the amount of carbon in sample were not determined. Therefore, the correlation between the carbon in the sample, which probably originated from the coal, at each sampling sites and the amount of particulate matter deposition (gravimetric analysis) can not be established from data collected to date. For further investigation, therefore, quantification of carbon in samples as well as improving the method would be necessitated.

According to good experience and good results from preliminary study also during study 2007/08, electron microscopy was used not only to established the chemical composition and morphology of individual particles but also to determine the amount of dust particles originating from coal and iron ore depot from EET in Port of Koper. From morphological structure of particles and their chemical composition particles of coal, iron ore and bauxite were distinguished from other particles in dust deposition. Since only surface of sample can be analyzed and due to our purpose to count particles, dilution of samples were taken prior analyses.

In annual samples (time period from 1.12.2007 to 1.12.2008), the presence of particles of coal, alumina, compounds with Al, Si and K (silicates, alumosilicates, etc.), titanium dioxide and iron oxides (FeO, Fe_2O_3, Fe_3O_4) were detected. Particles were identified according to their chemical composition and morphological structure. Based on these results, the impact of activities within the Port of Koper (coal and iron ore depot and ore manipulation, alumina manipulation as well as transshipment of other bulk cargoes such as Titanium sludge) can be confirmed.

In order to estimate impact on dust deposition from Port of Koper to surroundings collected samples were analyzed quantitatively using SEM/EDXS, and particles on individual sampling sites were counted.

According to results the highest number of particles in samples represents alumosilicates (compounds of Al, Si, K and O), mainly in the size range from 1 to 10 µm. The majority of these particles have natural origin. An extremely large number of particles of titanium dioxide (TiO_2) were detected, all of them were present mainly in the smaller size fractions (less than 1 µm up to 5 µm). Reason for presence of TiO_2 and their source is rather unknown. As mentioned, one of the possible sources could be transshipment of titanium slag inside the Port of Koper. According to the data from the Department of Environmental and Occupational Health of Port of Koper, titanium sludge is transshipment only few times in year, and manipulation takes place at pier II. TiO_2 particles were detected at all sampling sites regardless of the distance from the Port of Koper. Since titanium is the most used element nowadays specially in nanotechnology (use in pigments and dyes, by the food industry, in production of printer cartridges and much more) there are great chances that titanium particles originate from activities other than those at the Port of Koper. Where to look for the source of these particles, therefore, remains a unanswered question for research in the future. However, these particles are of great interest for research due to their size. Most were detected in size classes smaller than 1 µm up to 5 µm. This size of airborne particulates is in terms of impact on the health of the most dangerous due to their ability to penetrate deep into the respiratory system.

Coal particles, majority of them larger than 5 µm, were also detected. None of coal particles were smaller then 1 µm. Coal particles were also found at the control sampling sites 6 and 7. Possible explanation could be the fact that the coal is transport by boat daily from port of Koper to Trieste for the needs of local industry.

Only few particles of iron oxide were detected, majority of them were rather small (from 1 µm to 5 µm). Most of the iron particles were detected at the sampling site 1, which is the nearest sampling site to EET depot.

As it is the case in mass of particulate matter deposition also in the case of particles number results showed that the horizontal contribution of the wind (metal screen - sampling site B) contributed to increased number of dust particles in almost all cases. In 7 out of 10 sampling sites higher number of particles were found in sampling sites B (vertical deposition + horizontal contribution), only in 3 sampling sites (sampling site 1,6 and 8) higher number was observed at sampling site A. The highest total number of particles was observed at sampling site 10 B, locating in center of Ankaran.

The larger fractions of particles at individual sampling sites are alumosilicates, most probably due to natural origin. However, some amount of bauxite (alumina) particles were found, which are transshipped in Port of Koper. Therefore, such particles also indicate influence of Ports activities on dustiness of the surroundings. TiO_2 is also a frequently found component of the particulate matter. Fewer coal particles were observed, but the least of all FeO particles were present.

As it was mentioned in results section, it should be noted that only particles trapped on the filters were analyzed using electron microscopy. Theoretically, only particles larger than 3 μm should be present. Particles, trapped in the filtrate (particles smaller than 3 μm), were determined only gravimetrically. After that filtrate was discarded. There could be at least two reasons for the appearance of particles smaller than 3 μm in electron microscopy analysis. The larger particles captured on the filter caused saturation of the filters and therefore particles smaller than 3 μm, which otherwise would have passed the filter pores, could be trapped on filters. Individual particles can also form agglomerates, or the fine particles clump together on larger ones. During sample preparation samples (part of filters) were exposed to ultrasonic bath. That could lead to the dismantling of such bonded fine particles. And under SEM such particles were detected as individual ones. It is interesting to note that only small particles of TiO_2 and alumosilicates were found. On the other hand, mostly large particles of coal were detected. Therefore, special precaution is needed when interpreting the results, and the method must undergo additional development and evaluation in future.

For the quick estimation of direction and quantity of particulate matter and therefore determination of the main sources of emissions of dust particles in the study area, a simple alternative measurement device, based on deposition and/or adhesion was developed. The basic idea is collection of particulate matter from air on adhesive material (medical Vaseline). This measurement device allowed the collection of particles in both the horizontal and vertical directions. A plastic ball of 20 cm diameter, covered with medical Vaseline was used for this alternative sampling device. By visual inspection of the alternative sampling device, a rapid assessment of the main direction of particles and therefore their origin as well as the intensity of occurrence of individual particles could be made. For more detailed evaluation and comparison, the trapped particles can be additionally assessed by digital photographic counting and SEM/EDXS. A more simple method for that is manual particle counting using magnifying glass.

Using the simple sampling device, the contribution of the EET depot to the increased number of dust particles in the surrounding area was confirmed. The maximum number of particles were detected on the side of the sampling device oriented in the direction of the EET depot. After counting the particles this findings were confirmed. Additionally results from electron microscopy also suggest a link between the dust particles collected and activities at EET in the Port of Koper.

Using simple sampling device mainly larger particles (coarse particles) were captured due to their rapid deposition or elimination from the atmosphere after emission from the source. Therefore not surprisingly the number of particles was found to decrease with increasing distance from EET. On sampling sites 1, 2 and 3, which were placed in a linear direction at different distances from the landfill EET correlation between number of particles and distance from EET were observed. The highest number of particles was detected on sampling site 1 (closest to the landfill) and the lowest number (on average only one half of particles compare to sampling site 1) on the sampling site 3, which is furthest from the landfill.

With intention to evaluate the manual counting for time period from 15th of October to 15th of November 2008 samples were counted additionally using a computer program IT3. Comparing the number of particles counted manually and the number of particles counted using computer software, essential differences between these methods was not observed. Results from both methods indicate same trend of particle number at each of the sampling sites. However, in spots where enormous number of particles on 1 cm^2 were observed, computer counting gave more accurate results. This is especially true when a large number of particles appear in small area. Under these conditions, mistakes using manual counting become more possible.

Since the basic use of simple sampling devices is determination of the most appropriate location for installation of costly and sophisticated sampling devices the determination of source of particles and screening the location is the most important outcome of such monitoring. Therefore, both manual and computer counting are sufficient methods for samples analyses.

Using visual perception we can estimate direction and location of maximum dust emission. This, however does not allow further detailed analysis. Using particle counting (manual or using computer software), the results can be evaluated and compared with each other during an extended period of time. So the data collected can give the rough estimation of the burden on the environment with dust particles (mostly with course particles) as well as determination of the most appropriate location for the installation of more complex and expensive measuring devices for more detailed monitoring of the environment.

5.5 Hypothesis

This research allows confirmation of the first hypothesis; Coal and iron ore depot at EET terminal in Port of Koper represent one of the sources for particulate matter deposition in surrounding area. Several methods were employed to connect the particulate matter deposition to dust from the activity at the coal and iron ore depot. The results of the analysis using electron microscopy can confirm with certainty the presence of coal particles in the particulate matter deposition. Regarding the location of sampling sites coal particles can only be associated with activity on coal and iron ore depot at EET in Port of Koper. The same applies to particles of iron oxide and alumina.

Second hypothesis, Ankaran and its surroundings is heavily burdened with dust deposition, can be confirmed partially. During the preliminary study enormous values of particulate matter deposition were detected. These significantly exceeded limiting values by as much as factor of 12. However, such extreme values were detected in two time intervals. In the remaining period of observations, such high values were not recorded. That events were also detectable by visual perception of the population (Figure 1 and figure 2). Similarly, the annual values were exceeded at individual sampling sites (sampling site 3, 4 and 5) due to this short extreme event. However, during study of 2007/08, the mass of particulate matter deposition at the sampling sites A, calculated on a monthly time period during entire monitoring interval from December 2007 to November 2008, has never exceeded the recommended value of 350 mg/m^2 day. Therefore, based on two one-year measurement campaigns, it can not be concluded that the surroundings of Port of Koper, especially Rožnik residential area, is heavily burden with dust deposition. However, as is noted by residents as well as the results of preliminary studies, heavy dust deposition does indeed occur in case of the extreme weather conditions.

Also third hypothesis, Dust preventive measures undertaken by the Port of Koper lead to reduction of particulate matter deposition in surrounding areas, can be confirmed only partially. Unfortunately there are no available data on the emission of particulate matter deposition in the surroundings of Port of Koper before the introduction of preventive measures. Port of Koper in 2005 started the construction of 11 m high metal fence surrounding the whole body of coal and iron ore depot. During the preliminary study fence was only partially built, while during study 2007/08 fence was completed and entirely surrounded ore depot at EET. Sprinkling system in the EET terminal was improving during years. For wetting the body of ore depot nowadays consume annually around 30.000 m^3 of water. The spraying is carried out on machines during ore handling in a ore depot, on lifts and also on the special belt conveyors transport systems. Several times a day access roads around the landfill are washed using so called special purpose vehicles. Unloading / reloading at the landfill is conducted in a closed conveyor line. For the future, complete covering of the landfill is being prepared (Source: Department of Environmental and Occupational Health of Port of Koper). Unfortunately, no data about dust emissions in living environment around port of Koper are available. Consequently, the extent these measures have an impact on the reduction of dustiness in the surroundings area can only be assumed. But if results from preliminary study (when all mentioned preventive measures were still in preparation) are compared with results of study 2007/08, when all of mentioned preventive measures were already implemented, results indicate that all of the measures were good and gave some results. However, during study 2007/08, there were no stronger winds, which blew through the ore depot towards the populated areas, and that could also be one of the reason for low values of particulate matter deposition during entire time of the study.

5.6 To conclude

The results of this investigation can be used for assessment of dust deposition in the area surrounding the Port of Koper. Additionally, on the basis of the results obtained during this investigation, the effectiveness of preventive measures undertaken by the Port of Koper for prevention of dusting in surroundings can be assessed (results of preliminary study versus results of the study 2007/08).

It can be concluded that there are various point and dispersed sources of emissions of various air pollutants in the area of the municipality of Koper. In this area there are located a large storage depot of petroleum products (emissions of benzene, toluene), chemical industry (emissions of formaldehyde, acetaldehyde), waste incinerator and the ironworks in Trieste (dioxins, furans, dust particles). Additionally heavy traffic pollution, ground-level ozone in summer months, transport of polluted air with the western winds from the Po river basin, etc. are present. For these reasons, it is necessary to take measures to reduce the environmental burden of these various pollutants from diverse sources. By no means should additional emissions into the environment, which would burden the air, be allowed.

6 CONCLUSION

During the preliminary study, which was carried out during 2005/06, extreme values of particulate matter deposition in Port's surroundings were detected. Values exceeded the monthly limiting value by a factor of 12. Also yearly limiting value were exceeded.

In time period from 1. 12. 2007 to 1. 12. 2008, elevated levels of suspended particles were not detected at the sampling sites. The reason for the low values of dust pollution might be in weather conditions (low wind in the observed directions). Beside the weather conditions, the additional precautionary measures taken by the Port of Koper to reduce the dustiness from the operations at the coal and iron ore depot at EET may be a significant factor. These precautionary measures are an effective approach to reducing or limiting emissions of dust particles to the neighborhood.

Using a new approach, correlation between the activities at EET ore depot in Port of Koper and particulate matter deposition in surroundings residential areas was confirmed. Using SEM/EDXS, particles of coal, iron oxides, alumina and TiO_2 were detected, the majority of them can be linked with port activities.

It would be reasonable to recomend continuation of the study because only on long-term observations it is possible to made a thorough assessment of the impact of EET on dust emissions on the surrounding area. In order to exclude the impact of annual fluctuations and weather conditions, further monitoring of dust deposition in the region are recommended.

Additionally, it would be reasonable to make risk assessment, focused specially on the respiratory disease incidence. According to the results of epidemiological study (Eržen et al., 2003) additional epidemiologic research on respiratory problems in the influential area would be reasonable to carry out.

From results, the new sampling device is suitable for quick estimation of direction of major airborne particles sources. Since the cost of sampling device is relatively low many such devices could be used for quick screening in order to find the most representative locations for later placement of more sophisticated, accurate and expensive devices for air monitoring.

Clean air is one of the necessities for healthy life now and in the future. Achieving this goal requires the active participation of legislators, experts from various fields and all those who burden the air with their activities.

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ANNEX 1

Table A: Discard samples

DISCARD SAMPLES		1A	1B	2A	2B	3A	3B	4A	4B	5A	5B	6A	6B	7A	7B	8A	8B	9A	9B	10A	10B
December 2007	1.12.-15.12.2007																	*	*		
	15.12.2007-1.1.2008															*	*	*	*		
January 2008	1.1.-15.1.2008																				
	15.1.-1.2.2008																				
February 2008	1.2.-15.2.2008																		**		
	15.2.-1.3.2008																*				
March 2008	1.3.-15.3.2008															*	*		**		
	15.3.-1.4.2008																	*			
April 2008	1.4.-15.4.2008										***										
	15.4.-1.5.2008																				
May 2008	1.5.-15.5.2008																				
	15.5.-1.6.2008						*				***										
Jun 2008	1.6.-15.6.2008																				
	15.6.-1.7.2008	***									***										
July 2008	1.7.-15.7.2008				*												*				
	15.7.-1.8.2008																				
August 2008	1.8.-15.8.2008								*	***	***						**	**	**		
	15.8.-1.9.2008														*						
September 2008	1.9.-15.9.2008																	*	*		
	15.9.-1.10.2008															*	*				
October 2008	1.10.-15.10.2008																				
	15.10.-1.11.2008									***	***										
November 2008	1.11.-15.11.2008									***											
	15.11.-1.12.2008																*	**	**		

* - sample was not analyzed (sample was destroyed)

** - high values due to presence of NaCl or Cu compounds

*** - high values due to presence of organic pollution of sample (decay parts of plants or insects, algae)