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SAMANŲ TAIKYMAS ORO TARŠOS SUNKIAISIAIS METALAIS EKSPERIMENTINIUOSE TYRIMUOSE

USING MOSSES AS BIOINDICATOR OF AIR POLUTION WITH HEAVY METALS IN EXPERIMENTAL INVESTIGATION

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ANOTACIJA

Šiame baigiamajame magistro darbe analizuojama galimybė oro taršos sunkiaisiais metalais tyrimuose naudoti samanas kaip bioindikatorių. Buvo surinkti samanų Pylaisia polyantha ėminiai šalia Vingio parko skirtingu atstumu nuo Geležinio Vilko gatvės (5, 15, 25, 35, 45 bei 500 m).

Visi eksperimentiniai tyrimai buvo atlikti skirtingų sezonų metu (pavasarį, vasarą ir rudenį). Mėginiuose buvo analizuojami penki sunkieji metalai: Zn, Cu, Pb, Cr and Ni. Buvo nustatytas sunkiųjų metalų akumuliacijos samanose eiliškumas: Zn > Cu > Pb > Cr, Ni.

Eksperimentiniai rezultatai buvo palyginti su rezultatais gautais naudojant Gauso pasiskirstymo matematinį modelį.

Darbą sudaro septyni skyriai: literatūros apžvalga, naudojamos metodologijos aprašymas, eksperimentinių rezultatų analizė, oro taršos matematinis modeliavimas. Darbo pabaigoje yra pateiktos išvados, rekomendacijos bei naudotos literatūros sąrašas. Baigiamojo magistro darbo sudėtis: 103 p. teksto be priedų, 5 lentelių, 49 paveikslų, 131 literatūros šaltinių. Darbo gale pateikti priedai.

Raktiniai žodžiai: bioindikatorius, samanos, sunkieji metalai, akumuliacija, Gauso pasiskirstymas

ABSTRACT

This master thesis analyzes the ability of mosses Pylaisia polyantha to use as a biomonitoring tool for heavy metals determination directly from the atmosphere.

Studies were carried nearVingis park and Geležinis Vilkas street, samples of Pylaisia polyantha mosses were collected in three different seasons (spring, summer and autumn) at different distances from the street: 5, 15, 25, 35, 45 and 500 meters.

Samples of mosses were analyzed and the concentrations of five heavy metals were estimated: Zn, Cu, Pb, Cr and Ni.

Investigation results showed high concentrations of heavy metals, especially in samples of mosses near the street. Moreover, HM concentration had a tendency to decrease with the distance from intensive traffic street. Accumulation order in Pylaisia polyantha were determined in this order: Zn > Cu > Pb > Cr, Ni.

This work consists of seven main chapters: first chapter presents a literature review about environmental properties of most popular bioindicators (lichen, tree – bark and mosses), what makes them (especially mosses) to be suitable tool for biomonitoring; in second chapter – methodology of experimental part of this work (how to determine the specie of mosses, how to calculate the results and standard errors) is presented; third chapter presents all results and analysis from experimental investigation; mathematical modeling based on Gaussian plume is presented in fourth chapter.

At the end of the work, conclusions, recommendations, references are presented Thesis consists of 103 p. text without appendixes, 5 tables and 49 figures, 131 bibliographical entries. Appendixes are included as well.

Key words: Bioindicator, mosses, heavy metals, accumulation, Gaussian plume

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ABBREVIATIONS

AAS - *atomic absorption spectrometry;*

EMEP - *European Monitoring and Evaluation Program;*

EU - *European Union*

FAAS - *flame atomic absorption spectroscopy;*

GFAAS - *graphite furnace atomic absorption spectrometry;*

HM – *heavy metal;*

ICP – AES - *inductively coupled plasma atomic emission spectroscopy;*

ICP – MS - *inductively coupled plasma mass spectroscopy;*

ICP – OES – *inductively coupled plasma optical emission spectrometry;*

PAHs – *polycyclic aromatic hydrocarbons*;

UNECE - *United Nations Economic Commission for Europe;*

INTRODUCTION

In the world are about 23.000 species of bryophytes and highly approximately 15.000 species of mosses have been recognized (Chapter ...2009).

From the ancient times till nowadays mosses are very usefulness plant, for instance, in China, Europe and North America mosses have been applied as medical plants (Kang et *al.*, 2004). In the World War II some species were used as first-aid dressings on soldiers wounds. In Alaska mosses are used for chinking till nowadays. In some Europe countries peat mosses were used to make a bread during famines. Till today it is very popular material in florist trade and home decoration. Some species of mosses are the major component of peat.

Nowadays, mosses are well known as a good bioindicators of air pollution due to their bioaccumulative features.

Topicality of the problem

Clean air is vital to all living beings, each person inhales highly approximately 20.000 liters of air every day (The formidable...2009). Atmospheric HM deposition represents a major risk to the environment because of their toxicity (Lee, et *al.*, 1994).

Air pollution effects are dangerous and various to all environment. Due to increasing traffic, contamination of the environment by motor vehicles which emit a substantial amount of gaseous and solid pollutants that deposit on the surface of soil and plants is also increasing. People breed vegetables, crops and berries near road, which can be polluted by heavy metals from the traffic. Wayside grass usually is used to feed animals (Brannvall, 2006; Naszardi et *al.*, 2004).

Actuality of the work

The control of atmospheric air quality is one of the most important tasks of the environmental protecting program (Mankovsa, 2003). It is important to measure concentration of heavy metal in the atmosphere. One of the easy - to apply and cheap method would be to use mosses as bioindicators.

Mosses as bioindicitors are popular not only due to their environmental features, but economic advantages are important too. Without a doubt it is easy to collect samples, there is no need for any special modeling programs, extra employees or extra equipment.

Two Swedish scientists Åke Rühling and Germund Tyler made first research (they discovered that mosses can be good bioindicator of heavy metal pollution in the atmosphere) in early 1960 years in Sweden, after this research mosses became popular tool of biomonitoring in all over the world. Biomonitoring with mosses is based on the fact that terrestrial carpet - forming species obtain most of their nutrients directly from wet and dry deposition. Mosses are bio – organisms that are sensitive to air pollution, especially well suited to heavy metals, on a larger time scale (Čeburnis et *al*. 2002; Semi – empirical…2010).

In Lithuania were made only few surveys by using mosses as bioindicators, almost all investigations were performed by D. Čeburnis, K. Kvietkus and D. Valiulis. In Europe, as mentioned before - Åke Rühling and Germund Tyler.

Aim of the work: to use mosses as bioindicator as feasible methodology to assess air pollution with heavy metals.

***Tasks of the work*:**

- to find a most wide - spread species of mosses in investigative area;
- to evaluate the level of heavy metal pollution;
- to calculate air pollution by modeling programs;

Practical value

The result of this work will help to find out the relationship between traffic flow and heavy metal pollution in the atmosphere by using mosses as bioindicators. This work was concentrated on one high intensive traffic street between people living area and park.

The scope of the work

This master thesis consists of general environmental and economic characteristics of mosses being as a useful tool in biomonitoring for air pollution investigations, material and methods of this work experimet, analytical data, mathematical model constructing, conclusions and recommendations. At the end of this work a list of literature and appendixes are presented.

1. AIR QUALITY RESEARCHES BY USING BIOINDICATORS

1. 1. Bioindication of atmospheric pollution

Air pollution has been one of the major threats to human health and the environment since the Industrial Revolution in the early 19^{th} century. The degree and extent of environmental change over the last decades has given a new urgency and relevance to the detection and understanding of environmental change. Nowadays, human activities have altered global biogeochemical cycling of heavy metals and other pollutants, approximately 5 million chemicals are presently known and 80 000 in use; 500 – 1 000 are added per year resulting in a progressive increase in the flux of bioavailable chemical forms to the atmosphere (Hock and Seifert, 2003; Obbard *et* al., 2005; Batzias and Siontorou, 2006; Dmuchowski and Bytnerowicz, 2009).

The majority of the heavy metals, and sulphur and nitrogen compounds that are considered pollutants originate from anthropogenic sources. Natural sources of these compounds include volcanoes, forest fires, biological decomposition processes and the oceans. The degree and extent to which emissions are spread depends on e.g., the type of emission source, composition of the emissions and the weather conditions. The majority of the emissions remain close to the source, but some can travel for thousands of kilometres. HM can be accumulated on different materials like: soil, peat, sediments and biological materials. (Poikolainen 2004; Mocanu and Cucu - Man, 2002).

The main heavy metals emitted into the atmosphere by human activities are zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), chromium (Cr), selenium (Se) arsenic (As), mercury (Hg) and cadmium (Cd). These pollutants can be highly toxic and damage the soil, surface waters, forests and crops (Heavy metal toxicity…2010).

Between 1990 and 2007, emissions of heavy metals have declined sharply, particularly for lead (-97%) due to its suppression in gasoline, chromium (-90%), zinc (-86%) and mercury (-70%). Emissions of copper only slightly decreased during the same period (-4.5%) due to increased road and rail traffic at the source of most emissions (catenary wear and brake pads) (World today...2010).

Monitoring toxic air pollutants is needed for understanding their spatial and temporal distribution and ultimately to minimize their harmful effects. In addition to direct physical and chemical methods of air pollution monitoring, bioindication has also been used to evaluate air pollution risk (Dmuchowski and Bytnerowicz, 2009).

There are many traditional studies on atmospheric contamination but most of them have been limited by problems of high costs and the difficulty of carrying out extensive sampling, in terms of both time and space (Szczepaniak and Biziuk, 2003).

Air quality can be monitored by measuring the pollutants directly in the air or in deposition, by constructing models depicting the spread of pollutants, or by using biomonitors. Direct measurements provide objective information about the level of pollutants, but they are expensive and there is a risk of contamination when determining low concentrations (Poikolainen, 2004).

The models provide information about extensive areas and they can be used to produce predictions of future air quality. However, their accuracy is dependent on the quality of the data used in constructing the models. Although the methods are fast and inexpensive, they only provide a relatively approximate picture of air quality and the deposition of pollutants (Poikolainen, 2004).

Most analytical data on atmospheric pollution are obtained by conventional methods, requiring great efforts as to investments in infrastructure and manpower. Besides, it is not possible to install equipments in all locations needed due to the great extension of territory (Saiki et *al.* 2007).

Bioindication methods

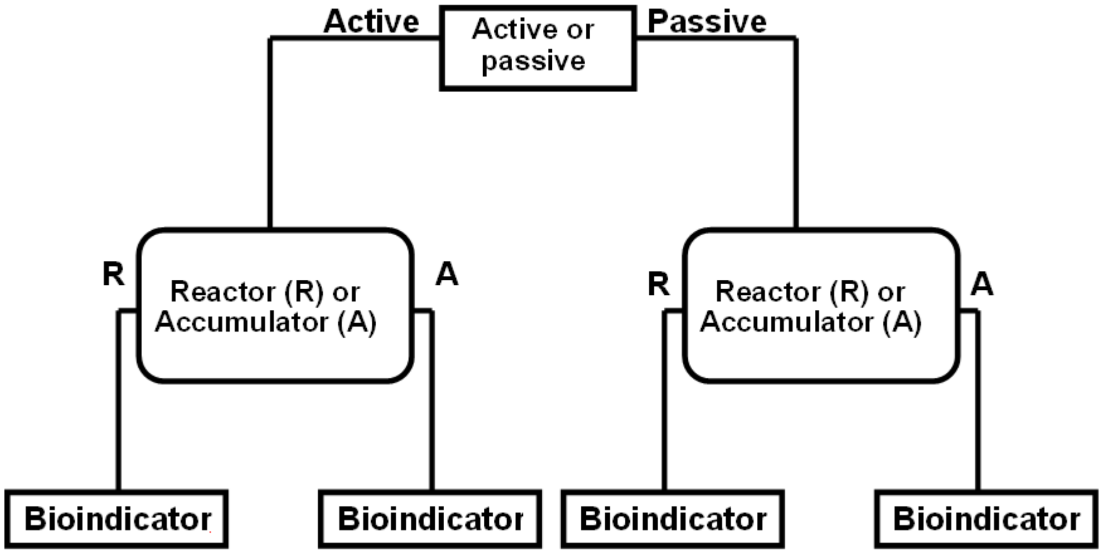
Environmental monitoring methods are based on expensive and sophisticated measuring systems. Since the element composition of vascular plants, bryophytes and lichens can change as a consequence of pollution, a complementary use of their parts as bioidicators may be an appropriate alternative (Aprile, *et* al., 2010).

Biological methods may be classified (Arndt et al., 1987; Guderian et al., 1985) as either passive or active (Fig. 1.1). Passive methods use plants growing naturally in the study area, where they are ecologically adapted (Biologic markers...2010).

However, with *in situ* vegetation it is difficult to partition the variation in response among individuals between that caused by different exposures and that caused by genotypic variation. Also, the specific responses of many species to specific pollutants have not been established, rendering a definitive diagnosis difficult. Despite these limitations, visible injury to vegetation has repeatedly provided the first indication of pollutant impacts. In contrast, active biological methods use standardized plants (known genotype and response) placed at specific locations to detect the presence of air pollutants (Biologic markers...2010).

The term bioindicator is used to refer to an organism, or a part of it, that depicts the occurrence of pollutants on the basis of specific symptoms, reactions, morphological changes or concentrations. Bioindicator generally refers to all organisms that provide information on the environment or the quality of environmental changes (Poikolainen, 2004). Bioindicators can be plants, animals or bacteria that regularly produce certain molecular signals in response to changes in their environmental conditions (What are...2010).

An organism may be classified as either a reactor to or an accumulator of the pollutant (Fig. 1.1). According to the fig. 1.1, mosses represent passive, accumulative biomonitoring.



1.1. Figure. A classification of biological methods used in air pollution biomonitoring (Biologic markers...2010)

A reactor displays a typical symptom or a measurable response to the pollutant. Any measurable response of an organism can be used; however, foliar injury is probably used most frequently. To be a suitable bioindicator, the response of an organism must be specific for a particular pollutant and not readily confused with other similar symptoms with different causes. In contrast to a reactor, an accumulator will not necessarily display an overt symptom but will accumulate the pollutant causing significant tissue enrichment.

Accumulators are only suitable for pollutants (e.g., fluorides or heavy metals) that have a long residence time in the tissue or for which the metabolic products are known (Biologic markers...2010).

Biological monitoring of airborne contaminants has made a great progress since the early observations of environmentally induced stress on plants and its applications have grown to an extent hardly envisaged just a few decades ago (Kuang, et *al*. 2007).

An obvious advantage of using bioindicators is that these show the results of the action of particular pollutants on living material – a relevant, if at times rather emotive, approach to determining human technological impact on the biosphere. It will never be possible to replace direct physical and chemical measurements of pollutant concentrations entirely by the use of bioindicators; nevertheless, both approaches are necessary for making a detailed or large scale survey of the distribution of pollutants, where the extensive use of technical equipment on-site is costly or impractical (Seaward, 1994). Using bioindicators as an early warning of pollution or degradation in an ecosystem can help assess critical resources (Biological indicators...2010).

Selection criteria

Referring to the determination of the biomonitor's elemental content, organisms may be further selected on basis of their accumulative and time-integrative behaviour (Wolterbeek, 2002). Biomonitoring consists of the use of responses of individual plants or plant associations at several biological organization levels in order to detect or predict changes in the environment and to follow their evolution as a function of time (Kuang, et *al*. 2007).

Some plant species are sensitive to single pollutants or to mixtures of pollutants. Those species or cultivars are likely to be used in order to monitor the effects of air pollutants as bioindicator plants. They have the great advantage to show clearly the effects of phytotoxic compounds present in ambient air. As such, they are ideal for demonstration purposes. However, they can also be used to monitor temporal and spatial distributions of pollution effects (Temmerman, et al., 2005).

1.2 Characteristics of the most popular indicators in atmospheric biomonitoring: lichen, tree bark and mosses

Biological indicators are applied as the cheapest and simplest indicators for monitoring the heavy metal concentrations in the atmosphere (Kord, et *al*. 2010).

But a unique species that can be a suitable biomonitor for the biomonitoring of toxic metal pollution all over the world has not been found yet. For this reason, different species are useful as biomonitors in different parts of the world (Coskun, 2006).

The use of cosmopolite organisms to assess pollution has achieved a notable development during the last decades. Such organisms assume environmental contaminants and may be used as indicators of the bioavailability of a given contaminant over time, allowing in certain cases the possibilities to establish comparison between contamination levels in geographically different areas (Alvarez, et *al*., 2006).

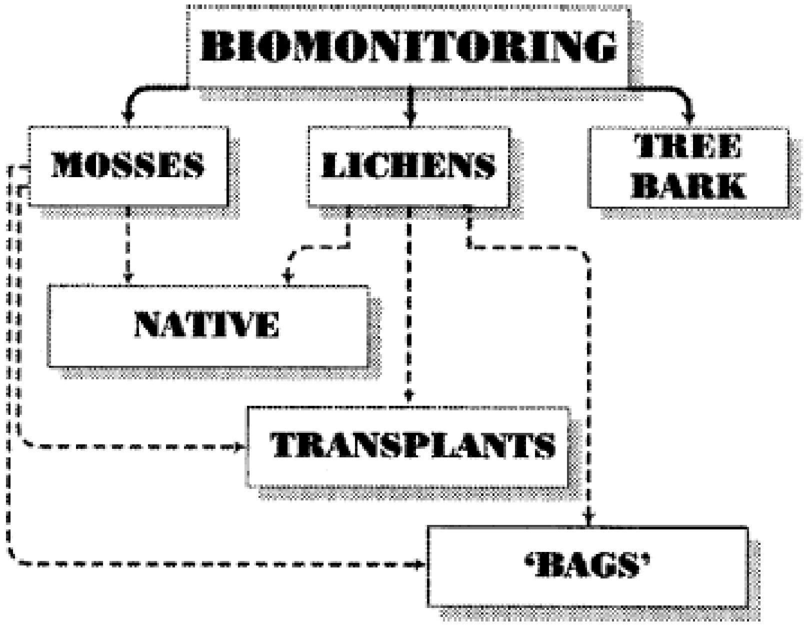
Due to plants and ecosystems function across a wide range of scales of time and space, a diverse array of responses ranging from cellular processes (i.e., photosynthesis) to ecosystem responses (i.e., community changes) can be used to assess the state of the system.

The selection of a bioindicator(s) should consider several factors:

- be easily measured and describe responses of concern within the ecosystem;
- have a distinct response which is capable of predicting how the species/ecosystem will respond to the stress;
- measure the response with acceptable accuracy and precision;

- be based on a knowledge of the pollutant and its characteristics; consider the final use of the data (Biologic markers...2010).

Biomonitoring based on mosses, lichens, and tree bark as HM pollution indicators has been widespread all over the world, especially in Europe, as an alternative to the traditional (instrumental) methods of studying regional deposition of natural and anthropogenic substances from the atmosphere to the terrestrial environment (Szczepaniak and Biziuk 2003; Pacheco et *al*., 2001).



1.2. Figure. General scheme of heavy metal biomonitoring using mosses, lichens and tree bark as bioindicators and sampling techniques (Szczepaniak and Biziuk 2003)

Fig. 1.2 represents a general scheme of various possibilities of HM biomonitoring using different materials and sampling techniques.

Lichens

Lichens are the dominant organisms of *ca*. 8 % terrestrial ecosystems and are typically found in environments subject to extremes of temperature, desiccation and nutrient status. Lichens are generally considered as useful organisms to monitor air quality, they are the most studied biomonitors of air quality, since 1866. (Bačkor and Loppi, 2009; Dobben et al., 2001; Blasco, et *al.* 2008).

Lichens represent a special vegetal group, they are slowly growing symbiotic associations of fungi (*Ascomycetes* fungus), green algae (*Chlorophyceae*) and/or blue-green algae (*Cyanobacteriae*), which depend mainly on atmospheric input of mineral nutrientsichens are perennial cryptogams. In this association, the alga is occupied with the formation of nutrients, since it contains chlorophyll, while the fungus supplies the alga with water and minerals. These organisms are perennial and maintain uniform morphology over time (Falla, et *al.,* 2000; Marques, et *al.*, 2004; Poikolainen, 2004; Blasco, et *al.*, 2008).

Lichens may grow horizontally, vertically or in any other direction. Regardless of this variability, or to rule out any specific influences, in many surveys lichen sampling is from all around the tree and/or from all positions. This fact makes them one of the best bioindicators of air pollution (Marques, et *al.,* 2004). The lichen species best suited as biomonitors are foliose and fruticose epiphytic lichens (Poikolainen, 2004).

They live on different types of substrate, usually on dry or nutrient - poor sites in boreal and sub - arctic regions (Poikolainen, 2004).

The high sensitivity of lichens is related to their biology. They have been defined as “permanent control systems” for air pollution assessment. Due to their high sensitivity toward specific pollutants and ability to store contaminants in their biological tissues without significant adverse effects on survival or growth, lichens are defined as bioindicators and/or bioaccumulators, respectively (Policnik et *al.*, 2004; Blasco, et *al.*, 2008; Obbard, et *al.*, 2005).

Lichens exhibit a number of attributes that make them a suitable bioindicators for air pollutants. Most lichen species obtain their nutrients from wet and dry deposition. They possess many of the same properties as mosses that make them suitable for monitoring purposes: the cuticle and vascular bundles are weakly developed, they do not have any real roots, they are slow-growing and long-lived, and they have an extremely broad distribution (Ikingura and Akagi, 2002).

1.3. Figure. Different species of lichen (Wildlife and...2009; Enchanted rock...2010)

Lichens (Fig. 1.3 above) possess the same physiological-chemical mechanisms that affect the accumulation of air pollutants in mosses. The physiological processes affecting accumulation in lichens have been studied much more than for many other plants. Clear differences in the accumulation of elements have been found between different lichen species and even different populations as a result of these morphological and physiological differences (Poikolainen, 2004).

Lichens as air quality bioindicators allow the measurement of a broad range of pollutants. Indeed, due to their specific structure, both gaseous and particulate forms can be studied. Different species of lichen have been used by researchers to monitor certain airborne pollutants, such as heavy metals, nitrogen oxides, SO_2, fluoride compounds, ozone, and polycyclic aromatic hydrocarbons (PAHs) (Falla, et *al.*, 2000; Guidotti, et al., 2009; Poikolainen 2004).

However, the detrimental effects of HMs on e.g., the occurrence of lichens usually only become apparent at high heavy metal concentrations. HMs have also been reported to increase a lack of water in the thallus. Air pollutants have a different effect on the fungal and on the algal partner. The algal partner has been reported to react more sensitively e.g., to acidic deposition and heavy metals, and to show varying accumulation of metals depending on the acidity of precipitation. Sporadic desiccation of lichens may also have an effect on the accumulation and absorption of elements. After a dry period, rainfall may result in appreciable washing off of particles and the exchange of cations bound on negatively charged exchange sites on the cell walls and plasma membranes of the cells (Poikolainen, 2004).

HM accumulation by lichens is a dynamic process. Short-term investigations on the effects of excess metals showed that lichens soaked into metal solutions accumulated metals quickly, in most cases within a few hours. In the case of Cu, maximum accumulation was observed after 3 - 6 hours (Bačkor and Loppi, 2009).

There are a considerable number of factors, associated with the site where lichens are growing, which may change the concentrations of pollutants in lichens. These factors are, in most cases, the same as those affecting mosses: quality of the deposition (form of occurrence, composition, pH), climate (composition of precipitation, temperature, wind, drought, length of the growing period) and local environmental factors (vegetation, quality of the substrate, stand throughfall and stemflow, dust derived from soil, altitude of area).

On the other hand, throughfall and stemflow, which vary according to the type of canopy cover, have a greater effect on epiphytic lichens than on terricolous mosses. Nutrients and other elements may pass from the substrate into lichens (Poikolainen, 2004).

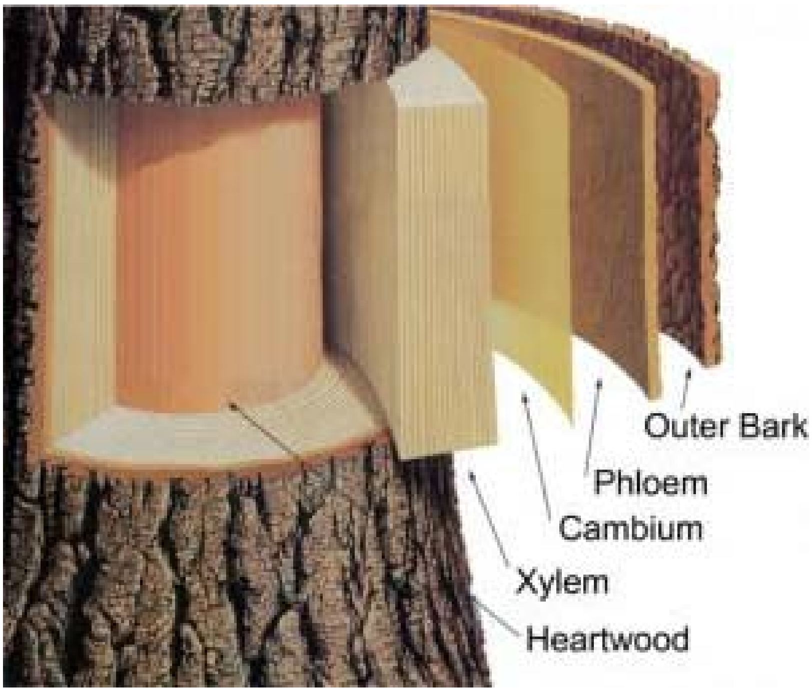
Tree bark

The use of trees is often related to the need for following the air quality evolution and the extent of its impact. The species used are then native to be liberated from the plants growth conditions (acclimatisation and maintenance problems). The coniferous trees (fir tree, spruce, woodland pine) have been used since 1980 to highlight the diffuse pollution impact, from SO_2 or ozone, in mountainous areas (Falla, et *al.,* 2000).

Tree bark as an indicator has been used far less than lichens, bryophytes and non-lichenised fungi. Even in the context of vascular plants, bark stands far behind leaves. Studies of tree bark are much scarcer and mostly related to environmental acidification (Pacheco, 2001).

Bark protects trees from mechanical injury, damaging agents and excessive evaporation. Bark quality varies considerably in different tree species and at different stages in the lifetime of a tree species (Poikolainen, 1997).

The porous structure of bark makes it good collector for airborne pollutants and the tree bark biomonitoring method is low cost compared to other monitoring methods. Tree bark is continually exposed to the environment over a period of several years (Santamaria, J. M. and Martin, A. 1997; Coskun, 2006).



1.4. Figure. The composition of tree trunk (How trees...2010)

Tree bark (Fig. 1.4) can be subdivided into the living inner bark (phloem), the cork-forming layer (*phellogen*) and non-living outer bark (*rhytidome* or *phellem*) composed of dead cork cells. This dead cork layer has usually been employed in biomonitor studies. Although the tree bark is known to absorb and accumulate airborne contaminants due to their hard, rough and thick structure. As a tree grows, new periderms are formed that seal off older phloem and thereby add tissue to the outer bark (Kuang, et al., 2007; Leung and Eberhardt, 2006; Poikolainen 2004).

The bark is exposed to air pollutants either directly from the atmosphere or from steam flow (Mandiwana, et al., 2006).

The advantages of biomonitoring with bark are enormous: the availability of biological material throughout the year, easy identification, and sampling. Additionally, highly trained specialist is not required to identify or differentiate between close looking species (Olowoyo et al., 2009).

Therefore, it can give precise information about changes that occur in the air conditions of ecosystem. This and other characteristics make tree bark a suitable material for the evaluation of air pollution. It is frequently used in the analysis of heavy metal deposition, sulphur (SO_2) and acid pollutants (Santamaria and Martin, 1997).

Depending upon the level of detail needed, or suggested applications, researchers characterize the inner and outer barks separately. Several studies on the cell wall and extractives chemistry of the inner and outer barks have shown significant differences. For example, the amount of aqueous ethanol-soluble materials in benzene ethanol extracts were 4-fold greater for the inner bark; the amounts of specific components (e.g., fatty acids, fatty alcohols, sterols) also showed significant differences. Given that there are caveats for the absolute characterization of the cell wall components, data indicate that the outer bark is lower in polysaccharides and more lignified (Leung So and Eberhardt, 2006).

The quality of bark varies according to the composition of the walls of the phellem and the thickness of the outer and inner bark layers. There are considerable differences in the chemical composition of the bark of different tree species. Bark is formed in layers, each new layer being formed below the old layer within a certain period of time, e.g., in Scots pine during a period of about two years (Poikolainen, 2004).

The old surface layer is dead and no changes occur after it has been formed. The accumulation of atmospheric pollutants in bark is purely a physiological-chemical process. The pollutants either accumulate passively on the surface of the bark surface or become absorbed through ion exchange processes in the outer parts of the dead cork layer. For example, sulphur accumulates in bark as sulphuric acid (H_2SO_4), most of which subsequently reacts with calcium to form gypsum ($CaSO_4$).

The accumulation of HM depends on the particle size and on the form in which the metals occur. They form compounds with other elements or occur in particles together with compounds of similar particle size.

It was reported already at the beginning of the 1970’s that particles containing lead derived from traffic emissions in the US were mainly located on the surface or in the surface tissues of bark, and that their size ranged from 3 - 13 μm. Bark acidity has an effect on the concentrations of some heavy metals. For instance, it was found a clear negative correlation between bark pH and the Fe concentration in a study on the occurrence of epiphytic lichens on oak and ash. They concluded that this is due to the increased mobility of Fe with decreasing bark pH. Here is no significant migration of elements from the bark surface through the cork tissue into the underlying wood, or vice versa (Poikolainen, 2004).

Nevertheless some authors found an appreciable correlation between the acidity of pine bark and the concentration of SO_2 in the atmosphere. Several researchers have used the measurement of the conductivity of bark extracts as bioindicator of environmental pollution, especially of the concentration of SO_2 in the air. It was found that conductivity is a more sensitive bioindicator of pollution than the pH of the bark. This is due to the fact that even low emissions of SO_2 produce changes in the conductivity, whereas the pH remains unchanged (Santamaria and Martin, 1997).

Also the migration of heavy metals from the soil via the roots into the bark as it is being formed is also usually insignificant. On the other hand, heavy metals and other compounds may be carried by the wind from the soil to the bark surface (Poikolainen, 2004).

The surface structure of the bark has a considerable influence on passive accumulation on the surface of the bark. A coarse, rough surface more readily accumulates atmospheric pollutants than a smooth surface. The study carried out by Szopa and co-authors on lead concentrations along highways in the US indicated that the lead concentration in bark reacts rapidly to marked changes in lead concentrations in the atmosphere (Poikolainen, 2004).

Factors, in addition to atmospheric pollutants, that affect the chemical composition of tree bark are mainly the same as those for mosses and lichen, although the chemical reactions that occur in bark are somewhat different because bark is a non-living plant material. The concentrations in bark are mainly affected by bark quality, stand throughfall and stemflow. In general, the element concentrations in the bark of deciduous trees are much higher then those in coniferous bark. Even so, there can be considerable differences in concentrations between conifers. For example, the zinc and manganese concentrations in Norway spruce bark are usually higher than those in Scots pine.

The concentrations are highest in the surface layers of the outer bark, and decrease rapidly on moving towards the inner layers. Variation in bark concentrations along the stem has also been reported. Clear seasonal variation has been observed in the conductivity and sulphur concentrations of bark due, for instance, to weather factors and emission levels. In a study carried out in Graz, Austria, the microclimate was found to have a significant effect on the amount of pollutant deposition and, through this, on bark concentrations (Poikolainen, 2004).

There are no standard methods are available for sampling and analysing bark samples. The following points have to be taken into account when sampling bark: the location and number of sample trees, tree age and health, height of the sampling point on the tree stem, bark quality and sampling time (Poikolainen, 2004).

Mosses

The broad and, in some cases, cosmopolitan distribution of many moss species suggests that these gametophyte - dominant plants are among Earth's most adaptable taxa. Mosses can be found on every continent and in every terrestrial ecosystem, from tropical rain forests to arid deserts and in polar tundra as well. Moreover, mosses play a crucial role in preventing soil erosion and conserving large amounts of water thereby regulating the water budget of local ecosystems (Poikolainen 2004; Fernandez et *al.*, 2006; Wang, et *al*., 2008; Cui, et *al*. 2009).

Ectohydric bryophytes, which take up water and elements through their entire surface, are regularly used as bioindicators for deposited airborne pollutants (Wolterbeek, 2002).

Mosses have been used for monitoring atmospheric heavy metal levels in various forms. These include indigenous naturally-occurring epiphytic forms, moss transplants, moss-bags, and *Sphagnum* mosses or peat profiles (Onianwa, 2000).

Mosses as bioindicators reflect elevated sulphur dioxide (SO_2) concentration, accumulation of heavy metals and other contaminants emitted to the atmosphere from natural and anthropogenic sources. It has been reported in a large number of studies including local investigations as well as regional surveys in different parts of the world (Giordano et al., 2004; Čeburnis *et* al. 1997a).

1.5. Figure. Most commonly reported mosses as bioindicators (from left to right): *Hypnum cupressiforme*, *Hylocomium splendens*, and *Pleurozium schreberi* (Mountain mosses...2009)

In the literature the most commonly reported mosses (1.5 fig.) as bioindicators are: *Hypnum cupressiforme*, *Hylocomium splendens*, and *Pleurozium schreberi*, particularly in parts of Europe where they are largely abundant (Onianwa 2000).

Mosses possess many properties that make them suitable for monitoring air pollutants. These species obtain nutrients needed for vital processes from wet and dry deposition and they do not have real roots. Nutrient uptake from the atmosphere is promoted by their weakly developed cuticle (the relationship with the substrate beneath is negligible), large surface to weight ratio, and their habit of growing in groups (Poikolainen, 2004; Čeburnis, et *al.* 2002).

Other suitable property is a slow growth rate. Growth rates of mosses have been rarely studied worldwide because the methods are time consuming and often inaccurate. Other suitable properties of mosses include undeveloped vascular bundles, minimal morphological changes during the mosses' lifetime, perenniality, wide distribution, ease sampling, and the possibility to determine concentrations in the annual growth segments (Poikolainen 2004; Wang, et *al*., 2008).

Moreover, bryophytes are resistant against many substances which are highly toxic for other plants – they are able to survive in hihgly polluted environments, to survive in such diverse and often extreme environments, these sedentary organisms must possess an equally diverse set of physiological adaptations. Mosses have been shown to be capable of surviving complete desiccation and temperatures as extreme as 110°C (Cenci et *al*., 2003; Fernandez, et *al.* 2006; Dragovič, Mihailovič, 2009).

Ion accumulation and cation exchange in mosses

Air pollutants are deposited on mosses in aqueous solution, in gaseous form or attached to particles. The accumulation of pollutants in mosses occurs through a number of different mechanisms: as layers of particles or entrapment on the surface of the cells, incorporation into the outer walls of the cells through ion exchange processes, and metabolically controlled passage into the cells (Poikolainen, 2004).

The cell wall has a high polyuronic acid content which makes moss a very good natural ion exchanger. The cell walls of bryophytes possess many negatively charged anionic sites to which cations are bound in exchangeable form. In addition, the highly reduced presence or absence of cuticle in the moss means the ions have direct access to the cell wall, mosses surfaces and rhizoids do not perform any active HM ion discrimination (Lee, C. K., 1994; Shakya *et al.*, 2008; Reimann *et al.*, 2006).

Electron microscope studies have showed that the sorbed metal may be held either in the extracellular region outside of the cytoplasm, bound to the cell wall, or actually held within the nucleus of the leaf cells (Onianwa, 2000).

The attachment of particles is affected e.g., by the size of the particles and the surface structure of the mosses. Ion exchange is a fast physiological-chemical process that is affected e.g., by the number and type of free cation exchange sites, the age of the cells and their reaction to desiccation, growing conditions, temperature, precipitation pH, composition of the pollutants and leaching. In the ion exchange process, cations and anions become attached to functional organic groups in the cell walls among other things through chelation. Mosses cannot prevent ions penetrating into their tissues because they have high counter-gradient mechanisms by which they accumulate significant concentrations of metals in their bodies (Shakya *et al.,* 2008).

As a consequence of their nutrient cycling and uptake mechanisms they tend to accumulate pollutants (Dragovič and Mihailovič, 2009).

The degree of metal uptake efficiency retention proved to decrease in the order Cu > Pb > Ni > Co > Cd > Zn, Mn (Čeburnis *et al.,* 1997). Lead is very strongly fixed in the moss, and for which the correlation between concentration in moss and bulk deposition is particularly high (Rosman, et *al*., 1998).

A high proportion of the pollutant load accumulates in mosses through wet deposition. The amount, duration and intensity of precipitation affect accumulation and leaching. The contribution of dry deposition increases on moving from humid to arid climates (Poikolainen 2004).

There are considerable differences in the leaching of elements depending e.g., on whether they are bound to the cell walls or have accumulated on the surface of the mosses. Uptake efficiency is also affected by competition for free cation exchange sites; for instance, the presence of sea salts and acidic deposition has been found to have an effect on the absorbtion of metals by mosses. The type of vegetation and soil dust have also been reported to cause regional differences in uptake efficiency. In general, the best correlation between the concentrations in mosses and in wet deposition have been found for elements (e.g., Pb, Cd, Co, Cu) that have a high uptake efficiency from wet deposition (Poikolainen, 2004).

In addition to air pollutants that originate from anthropologic sources, the concentrations in mosses are also affected by many "natural" factors associated with the morphological and physiological properties of the mosses, the site where the mosses are growing, and their immediate environment. There are natural differences in chemical composition between individual species and even between populations of the same species, between individuals with different growth and condition, and between the separate parts of individual mosses. Small amounts of nutrients may pass into the mosses from the substrate, and nutrients can also be translocated from one part of the moss to another. Mineral particles originating from soil and bedrock also increase e.g., the Fe, Cr, Al and Ti concentrations in areas which have a sparse vegetation, an arid climate or exposed mineral soil (Poikolainen, 2004).

Other factors affecting the concentrations include stand throughfall and leaching from vegetation layers located above the mosses, the nutrient status of the site and snowmelt water. The concentrations may also vary from one vegetation zone to another. The altitude may also have an effect, due e.g., to changes in the amount of precipitation, dust or biomass production. The sampling and measuring methods employed can also have a considerable influence on the analytical results in biomonitoring studies. For example, the concentrations obtained in chemical analyses performed by e.g., AAS, ICP-AES or ICP-MS only depict the proportion of elements that dissolve in acid, while methods based on radiation techniques give the total concentration of each element in the material under study (Poikolainen, 2004).

Biological properties of mosses

Mosses share numerous features with the two other classes of bryophytes. They are more complex than algae yet simpler than the higher vascular plants. Like higher plants, bryophytes use chlorophyll-a, chlorophyll-b, and carotenoids as photosynthetic pigments (Bryophyte characteristics...2009).

Their food reserves are stored as starch. Cellulose is found in their cell walls (cell-produced rigid structures that are external to the plasma membrane) and they form cell plates (structures made of membranes representing the site of newly created cells) during cell division (Bryophyte characteristics...2009).

Their spores, units capable of maturation, develop as a tetrad (a group of four cells) by meiosis, divisions of the cell nucleus that halve the number of chromosomes (Bryophyte characteristics...2009).

Two features of bryophytes tend to restrict them to moist environments, such as bogs and and all kinds of woodlands (Fig.1.6).

1.6. Figure. Mosses habitat - moist environments (The natural...2009)

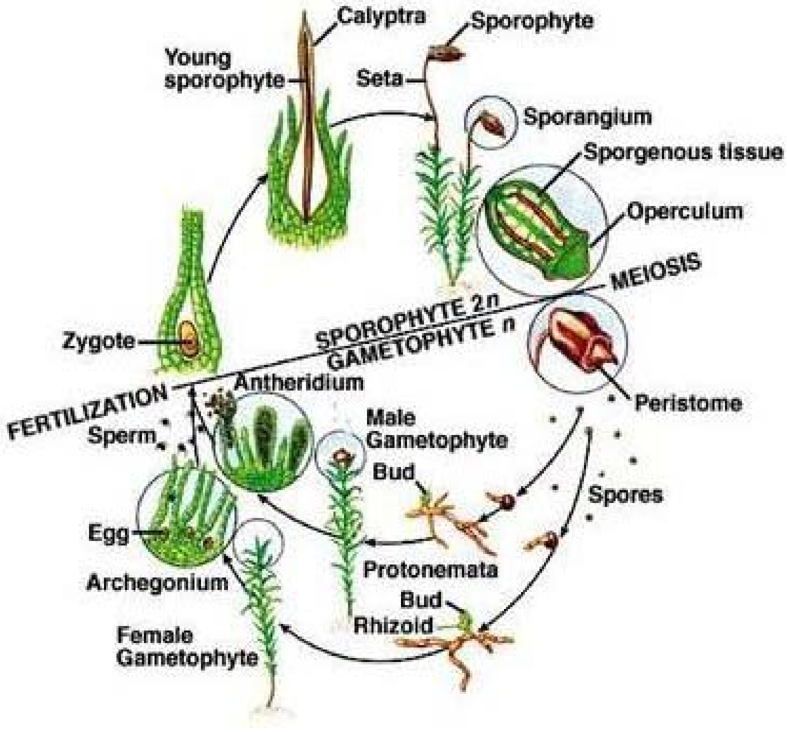
First, unlike vascular plants, bryophytes lack a system with xylem and phloem for efficient transport of water and food. Second, the male sperm cells of bryophytes must swim through water to reach the female egg cells. Bryophytes also differ from higher plants in that the sporophyte, the spore-producing diploid tissue, is nutritionally dependent on the dominant haploid gametophyte. In higher plants the gametophyte is dependent on the dominant sporophyte (Bryophyte characteristics...2009).

A typical Life Cycle of briophyte

As with every plant, the life cycle of a moss can be subdivided into several generations. Another characteristic of mosses which makes them stand apart from most other plants is the fact that they are mostly haploid, which means that their cells only have one set of chromosomes, in opposition to diploid cells, which possess a pair of identical chromosomes and which make up the great majority of higher plants excluding algae (The life-cycle...2010).

As do all plants, bryophytes (Fig. 1.7) alternate a gametophytic generation with a sporophytic one. Each of the haploid (1 *n*) spores is capable of developing into a multicellular, haploid individual, the gametophyte. The first structure formed from spores in most mosses is a filamentous, algal-like, green protonema (plural, protonemata). In some mosses the protonemata are long lived with rhizoids and aerial filaments and they often form dense green mats in suitable sites (The life-cycle...2010).

Cells in the protonema, probably stimulated by red light and kinetin, give rise to shoots, which enlarge and become the mature gametophytes. In the bryophytes, these are the dominant, independent (photosynthetic) plants (General life...2009).



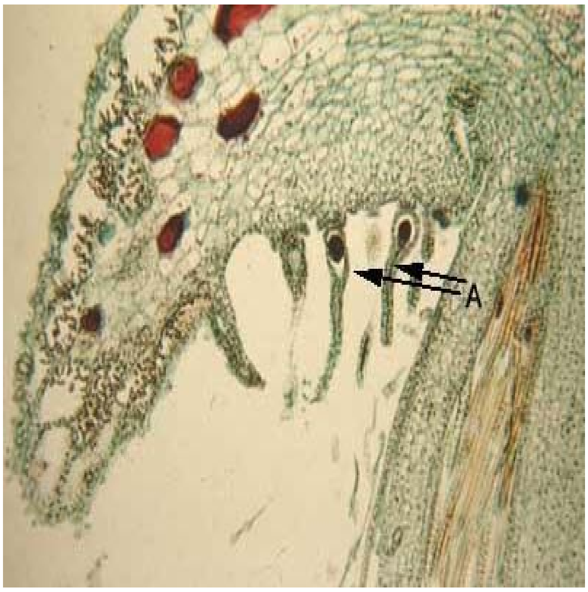
1.7. Figure. A life - cycle of bryophytes (General life...2009)

The gametophytes initiate gametangia on special branches or at the tip of the main shoot. In these structures the gametes - eggs and sperms - are produced during the sexual portion of the cycle. The female gametangium - called an archegonium - and the male antheridium may be produced on the same plant or on different plants. In both kinds of gametangia, a protective layer of non - reproductive tissue - a sterile layer - surrounds the inner reproductive cells (General life...2009).

Mature sperm, released from the tip of the antheridia when dew or rainwater is present on the surface of the plants, swim to the archegonia and down the necks to reach the eggs. One fuses with the single egg in each archegonium - the process of fertilization - thus combining the sperm and egg nuclear and cytoplasmic material (General life...2009).

The resulting cell, a zygote, has a diploid (2 *n*) chromosome number and is the beginning of the sporophytic generation. This reproduction is termed oogamy - a large, nonmotile egg is fertilized in the archegonium by a small, motile sperm that swims to the egg (General life...2009).

After fertilization, the zygote remains in the archegonium and divides by mitosis repeatedly to form a multicellular, diploid embryo, the young sporophyte (Fig. 1.8; 1.9).



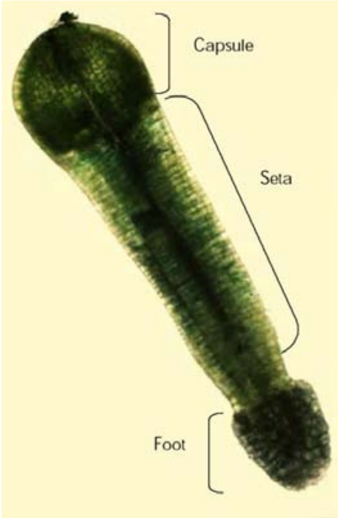
1.8. Figure. The zygote develops into a sporophyte." A „ is a young sporophyte (Biology...2010)

1.9. Figure. Young sporophyte (Young sporophyte...2010)

Sugars and other materials are translocated from gametophyte to the developing sporophyte through placental tissue, a type of nutrition called matrotrophy. The sterile jacket cells also divide and in mosses form a tight cap, the calyptra, over the tip of the developing sporophyte (A typical... 2009).

The mature sporophyte in both liverworts and mosses consists of a foot, seta, and capsule (Fig. 1.10). The moss capsule has modifications to assist in spore release: a cap, the operculum, covers the opening, and peristome teeth form a ring around the mouth of the capsule (A typical... 2009).

Sterile cells, elaters, within the capsule are hygroscopic and as they alternately absorb water and dry out, they twist and turn pushing the spores upward and outward (A typical... 2009).



1.10. Figure. Main parts of young sporophyte (Life - cycle...2010)

The hornwort sporophyte that develops from the zygote is an erect, long, green cylinder with an absorbing foot embedded in the gametophyte thallus (A typical... 2009).

The sporophyte is photosynthetic and has stomata so it does not depend entirely upon the gametophyte for sustenance (A typical... 2009).

Spores are produced in the cylinder around a central columella of sterile tissue and are released as the mature tip of the sporophyte dries out and twists in the air. At the base of the foot, a zone of meristematic tissue continues to divide and the sporophyte is thus continuously renewed from the base (A typical... 2009).

Reproduction through fertilization

The actual fertilization and thus sexual reproduction of a moss can only take place in the presence of water, as the male sperm swims to the archegonia and there enters a venter to swim all the way down to the egg cell, where they fuse and produce a diploid sporophyte: This generation possesses the sum of the two single chromosome sets of both the sexual cells and thus has a complete pair of them, which makes it diploid (Life cycle…2010).

The sporophyte eventually grows by cell division and pushes it's way out of the venter where it starts maturing, which takes from 3 to 6 months until it is fully developed: It now is a capsule closed by a cap and sheathed by the remaining bit of the venter, the calyptra. In this capsule, special cells produce haploid spores through meiosis, the process by which a cell generates two new cells each one having half the number of chromosomes of its diploid parent (Life cycle…2010).

As soon as the spores are mature, the calyptra dries up and falls off and the spores fall out and get carried away by the wind or animals. The whole process repeats from here on (Life cycle…2010).

Moss or lichen?

Mosses, lichens and present an extraordinary ability to accumulate certain kinds of elements. The results obtained from the differences between mosses and lichens as accumulator indicators depend on: 1) the species used in the studies, and 2) the type of emissions and environment in the studied area (Poikolainen, 2004; Buchmann, et *al.*, 2006).

Lichens are different from mosses, they are symbiotic organisms composed of fungi and green algae or cyanobacteria, but both organisms (mosses and lichen) tend to prefer the same habitats, and frequently occur together either in epiphytic (on trees) or epigeic (on the ground) form (Coskun, et *al*., 2009).

Throughfall can have an especially strong effect on element concentration in epiphytic lichens. The effect of throughfall on ground mosses varies and depends on whether the moss is growing under or between the crowns (Poikolainen, 2004).

In biomonitoring studies, moss samples are collected in open areas between the crown canopies in order to minimize the effect of throughfall. The amount of throughfall and stemflow varies according to the type of tree crown. The crown canopy retains a part of the elements transported in free precipitation, but precipitation also leaches and washes off; e.g., nutrients (Ca, K, Mg, Mn) from the canopy, which subsequently are absorbed by stemflow by epiphytic lichens (Chakrabortty, Sh. *et al*., 2006).

There is also variation in the element concentrations in mosses and lichens, especially in arid areas where precipitation is concentrated in the winter period. The differences between the concentrations in mosses and epiphytic lichens in areas in northern Europe may be due to the fact that the epiphytic lichens are exposed to air pollutants throughout the year, while mosses are protected by snow cover for almost half a year (Poikolainen, 2004).

The different morphological and physiological properties of mosses and lichens account partly for the differences in metal-uptake efficiency. Since the surface structure of mosses is different than that of lichens, they have a larger surface-area-to-weight ratio. The surface of lichens in most cases is rougher and more porous than that of mosses (Chakrabortty, Sh. *et al*., 2006).

Many studies, such as Finnish surveys, show that epiphytic lichens accumulate more heavy metals per dry weight than in mosses. The reason for the difference may be because of the variation in uptake efficiency in different deposition conditions, or due to the effect of throughfall on epiphytic lichens. Lichens also accumulate volatile heavy metals (Hg, Pb), which are continuously re-circulated back into the atmosphere more readily than in mosses (Poikolainen, 2004).

Many studies have shown that moss accumulates dust more easily than lichens. In Finland, the metal concentration in mosses were usually higher close to the emission sources, and lower in background areas, than the corresponding values in epiphytic lichens. It is also reported that the relative contribution of particulate material to the total concentration in mosses increases in places near emission sources, in arid areas and in agricultural areas. Especially in arid regions and those with sparse vegetation cover, metals that originate from the soil (Al, Cr, Fe, Ti) accumulate more readily in mosses than in lichens (Poikolainen, 2004).

Mosses and lichens seem to depict wet deposition in different ways. Laboratory tests have shown that cation exchange is a very fast process in *Hylocomium splendens*, and that led to the conclusion that the concentration measured in this species of moss reflects the effects of the composition of rainwater prior to the sampling, rather than the effects of long-term accumulation (Chakrabortty, Sh. et al. 2006).

Reimann *et al*. (1999) reported in their studies carried out in the Kola Peninsula in northwest Russia that the concentrations of many of the elements in mosses were more closely related to the chemical composition of rainwater than to the annual deposition levels as reflected by terricolous lichens.

No clear-cut evidence exists showing which could be a better heavy-metal biomonitor for regional surveys, because the results appear to vary from one place to another. However, the mechanisms through which mosses and lichens accumulate heavy metal are so different that they can not be used to replace each another in national surveys. In Finnish conditions, mosses appear to be more suitable for regional surveys than epiphytic lichens. The differences between different parts of the country and the location of emission sources were expressed more clearly on the mosses than on lichens (Poikolainen, 2004).

Wolterbeek *et al*. (1996) recommended the use of mosses because they more readily reflect local changes in heavy-metal deposition.

However, lichens may be better accumulation indicators than mosses in arid conditions (Chakrabortty, Sh. et al. 2006).

It has been shown that mosses and lichens, in spite of all disadvantages, are good tools for air pollution monitoring, but best results could be achieved while using both of them together, because of differences in their metal uptake and retention. The researcher dealing with biomonitoring faces many difficulties; for example, in the use of lichens, those of similar composition are not easy to find, because of the differences caused by the tree on which the lichens are growing. Also, terrestrial moss is not always a good choice because of variations in its composition caused by the area it is growing on (Szczepaniak and Biziuk 2003).

1.3 Water movement and accumulation of heavy metals in mosses

Due to mosses ability to absorb pollution directly from wet deposition it is important to understand water movement mechanism in mosses.

Early experiments with dyes demonstrated that in mosses water is able to move in conducting tissue of the central cylinder, leaf traces, and the costa, depending on capillary spaces, as it does in tracheophytes. There are confirmed not only these internal pathways, but also movement from cell to cell in the cortex of the lower part of the stem as well as on the outer surfaces of leaves and stems. But it is more likely that most of the movement across the cortex and internal leaf is through the free space of the cell walls where it does not have to cross cell membranes until it reaches its destination. Such apoplastic (outside the cell or in free space) movement across the cortex is known even in *Polytrichum juniperinum,* where a central strand and leaf traces are available to facilitate movement of water (Water relations…2010).

As in tracheophytes, water movement in both endohydric and ectohydric mosses is facilitated by tension forces, but unlike the case in tracheophytes, water moves in both directions in a source-sink fashion dependent upon availability. This bi-directional movement applies not only to external movement, but to the hydrome as well (Water relations…2010).

For bryophytes, the first water availability most commonly does not start with the soil, but with the tips of stems and leaves by way of rain, fog, or dew. Early observations showed that in general external conduction is much more rapid than internal conduction. This most likely relates to frictional resistance in the small internal routes (Water relations…2010).

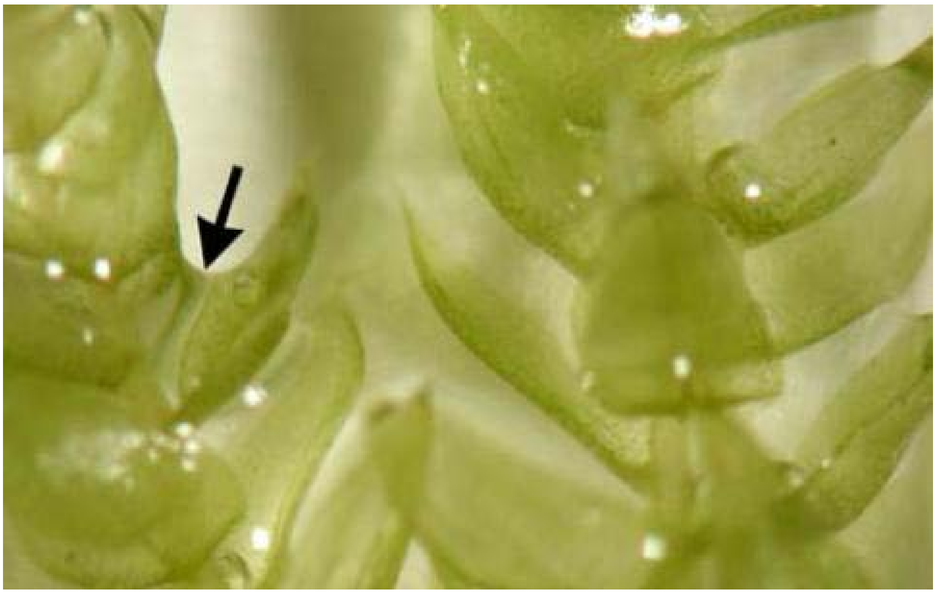
Ectohydric mosses

Ectohydric mosses (almost all mosses) rely primarily on external transport of water and can absorb water over the entire plant surface (Fig. 1.11) (Water relations…2010).

These taxa generally have no water repellent layers, or these are restricted to such locations as the apices of papillae, and they are easily wetted (Water relations…2010).

Movement is due to capillarity and the relationships are complex. As the moss becomes hydrated, its capillarity changes due to expansion of leaves, untwisting, and other forms of movement and gyration. They benefit from a large surface area relative to their volume due to numerous leaves and often such structures as paraphyllia (reduced leaflike structures on the stem or branches of some pleurocarpous mosses) and tomentum (felt-like covering of abundant rhizoids on stem) (Water relations…2010).

When water repellent layers are lacking, plants generally reach full hydration within minutes. Thus, virtually all pleurocarpous mosses, many of acrocarpous mosses, and most of leafy liverworts are readily wet by the first few minutes of rain. Only dousing in boiling water seems to coax the water inside the plant to restore its normal hydrated shape (Water relations…2010).



1.11. Figure. Capillary water (arrow) held among the leaves of Bryum (Water relations…2010)

The ectohydric habit depends on entry of water through the moss surface and permits a moss to respond to dew and fog by absorbing water directly, even though rooted plants may never receive a drop of it. Such bryophytes can live in high elevations and on deserts that receive less than 25 cm rainfall per year, obtaining water that cannot be measured by conventional precipitation methods (Water relations…2010).

Most tuft-forming (acrocarpous) mosses are (partially) endohydric, whereas most mat and carpet formers (pleurocarpous mosses) are ectohydric. In addition, some upright mosses such as *Sphagnum* (Fig. 1.12) and *Andreaea* (Fig. 1.13) are ectohydric. It is clearly showed this by clipping the capitula from the stem; these clipped capitula were unable to recover from desiccation, whereas unclipped capitula became rehydrated. But even *Sphagnum* has highly specialized cells in the stem that have all the traits of a bryophyte type of conducting cell (Water relations…2010).

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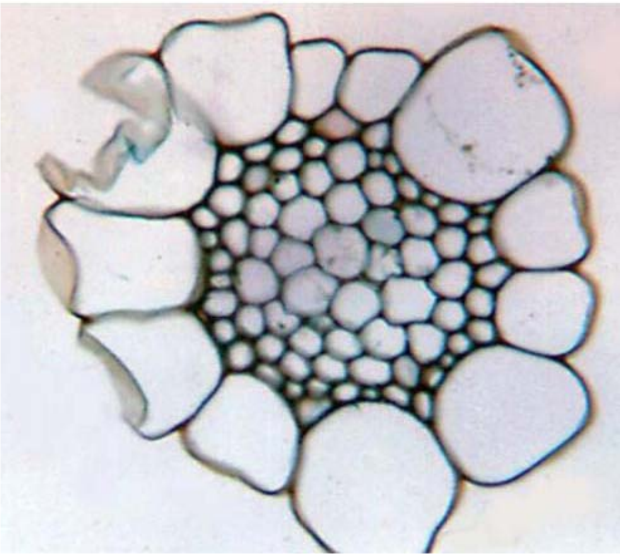
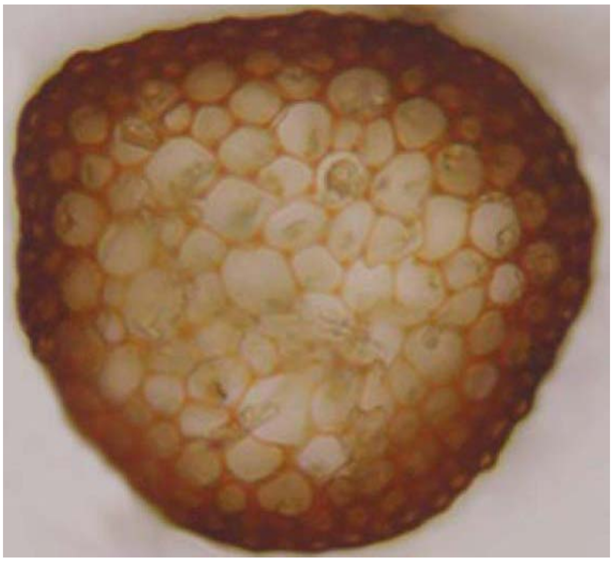
In ectohydric bryophytes, the uppermost leaves and shoot apices have the most rapid conduction of water, so that lower leaves are often supplied last. It was believed that no internal conduction was possible in the absence of a central strand. Although the initial movement of water is clearly ectohydric in most dry mosses, once it has entered the moss it has the opportunity to move apoplastically to reach places where it is needed for cellular metabolism. It is interesting that endohydric bryophytes can be facultatively ectohydric. It is found that *Polytrichum commune* was ectohydric under moderate moisture flux, but under high evaporative flux (*i.e.* dry air) it was predominantly endohydric (Water relations…2010).



1.12. Figure. Cross section of Sphagnum stem with large hyaline epidermal cells and small cortex cells (Water relations…2010)



1.13. Figure. Cross section of Andreaea stem with no central strand (Water relationst…2010)

The natural transpirational stream that carries water from the shoot apices to the atmosphere could be expected to play a similar role to that found in tracheophytes and maintain upward movement (or outward in pleurocarpous mosses) through capillary spaces as long as water was available and internal tension did not exceed that resulting from transpirational loss (Water relations...2009).

Accumulation of HM in mosses

Evidence exists that metals, including both mineral nutrients and heavy metals, move between the annual increments of feather moss and are lost due to leaching, depending on the meteorological conditions and seasonal growth (Brūmelis and Brown...1997).

Mosses *Hylocomium splendens* is widely used to monitor heavy metal deposition since it is assumed to absorb and retain many of the heavy metal ions that fall from above on exchangeable cell wall sites. Theoretically, if these concentrations are due only to exchangeable ions on the cell wall, and assuming 100% absorption and retention, but no vertical movement of metals, then the concentrations in a particular aged segment should be equal to age multiplied by the concentration in the first segment. In the available literature this is never the case and this may be explained by redistribution of elements between segments and losses by leaching. It is not known if the cellular concentrations of metals in feather moss reject short-term readjustment to chemical equilibrium conditions with the environment, or an integrated estimate of past deposition. The relationship between metal transfer and the available pool sizes indicates that recycling can potentially redistribute metals between segments, and also the underlying organic horizon, depending on the conditions of water transfer (Brūmelis and Brown...1997).

The acquisition of mineral nutrients by moss has been reviewed, providing a dynamic equilibrium model based on inputs from both deposition and substratum, losses from dead and damaged tissue and recycling from old to young tissue. It is not known if the upward movement of studied metals observed in the laboratory can be related to natural conditions, and whether results can be extrapolated to other elements. Pb is known to be less mobile than Zn and Cd in laboratory and field conditions.

Although *Hylocomium splendens* probably possesses an internal transport mechanism, upward movement is also likely to occur as a wicking effect, driven by evapotranspiration imposed by the application of water from below only or, episodically, from above. It can be argued that this same type of evapotranspiration occurs in forests in dry periods after rainfall (Brūmelis and Brown...1997).

Mechanism of entrapment of air particles and heavy metals

The metals suspended in air reach the moss surface via physical processes of sedimentation, impaction and diffusion, or via air particulate deposited in precipitation (Onianwa 2000).

Air pollutants are deposited on mosses in three forms as aqueous solution, gaseous form or attached particles.

The accumulation of pollutants in mosses occurs through a number of different mechanisms:

- As layers of particles.
- Entrapment on the surface of the cells.
- Incorporation into the outer wall of cells through ion exchange processes.
- Metabolically controlled passage into the cells (Čeburnis and Valiulis, 1999).

Only accurate quantification of the intracellular fraction will provide information about the metal that affects the cell physiology.

It was distinguished the following metal fractions in terrestrial mosses:

- the inter cellular fraction,comprisedof dissolved elements bathed externally in the cell wall matrix and cell membrane,
- the extra cellular fraction,comprised of elements bound to the cell wall and external surface of the cell membranes,
- the intracellular fraction:comprised of elements contained with intheprotoplasm,

- theparticulate fraction, comprised of unaltered particles originating from the environment and insoluble material from inside the cells (Llamazares *et al*., 2010).

The attachment of the particle is affected by the size of the particle and the surface structure of the mosses. Ion exchange is a fast physiological-chemical process that is affected by the number and type of free cation exchange sites, the age of the cells, their reaction to desiccation, growing condition, temperature, precipitation, pH, composition of the pollutants, and leaching.
In the ion exchange process, cations and anions become attached to the functional organic groups in the cell wall primarily through chelation (Poikolainen, 2004).

The chemical composition of deposition has a large effect on the accumulation of pollutants, because the uptake efficiency of the mosses for individual elements varies considerably. A high proportion of the pollutant load accumulates in mosses through wet deposition. The amount, duration and intensity of the precipitation affect accumulation and leaching. The contribution of dry deposition increases on moving from humid to arid climates. There are considerable differences in the leaching of elements depending on whether they are bound to the cell wall, or accumulated on the surface of the mosses (Čeburnis and Valiulis, 1999).

Uptake efficiency is also affected by competition for free cation exchange sites; for instance, the presence of the sea salts and acidic deposition has been found to have an effect on the absorption of metals by mosses. The type of vegetation and soil dust have also have been reported to cause regional differences in uptake efficiency. In general, the best correlation between the concentrations in mosses and in wet deposition has been found for elements that have a high uptake efficiency from wet deposition (e.g., Pb, Cd, Co, Cu) (Čeburnis *et al*., 1999).

Factors affecting the concentrations of heavy metals in moss

Epiphytic mosses may be considered for common use as biomonitor organisms. This is largely based on their lack of roots when compared with higher plants. Thus, they obtain their mineral supplies only from aerial sources and not from the substratum.

In addition to air pollutants that originate from the anthropologic sources, the concentrations in mosses are affected by many “natural” factors associated with: 1) morphological and physiological properties of the mosses, and 2) the site where the mosses are growing and their immediate environment.

There are natural differences in chemical composition between individual species with different growths and conditions, and between separate parts of the individual moss. There are natural differences in chemical composition between individual species and even among populations of the same species, between individuals with different growth and conditions, and between the separate parts of the individual moss.

Small amounts of nutrients may pass into the mosses from the substrate and nutrients can also be translocated from one part of the moss to another. Mineral particles originating from soil and bedrock also increase Fe, Cr, Al and Ti concentrations in areas which have a sparse vegetation, an arid climate, or exposed mineral soil.

Other factors affecting the concentrations include:

- Stand throughfall.
- Leaching from vegetation layers located above the mosses;
- The nutrient status of the site;
- Snowmelt water;
- Vegetation zone;
- Altitude has an effect due to changes in amount of precipitation, dust or biomass production;
- The sampling and measuring methods employed also have a considerable influence on the analytical results in biomonitoring studies;
- Age of the moss. The finding that older moss parts have higher metal concentration has led to the assumption that the plants provide a historical and interactive recording of the metal supply in the environment (Chakrabortty, Sh. et al. 2006).

The moss method is especially well suited of HM deposition from the atmosphere on a large time time scale (years, decades) or even for reconstructing of historical trends (Čeburnis et *al*. 2002). Åke Rühling and Germund Tyler (1968) analyzed the speciments of three mosses: *Hylocomium splendens, Pleurozium schreberi* and *Hypnum cupressiforme* from herbarium specimens in Lund (Sweden) which had been collected at intervals from the year 1860 to 1968 from the same location. They reported that lead content in the specimens over the year 1860 to 1875 is 20 ppm, in the next 25 years it became almost double. From the year 1900 to 1950 there was not much change, but in the next ten years there was a rapid increase and this brought the average of lead content to 80 to 90 ppm (Chopra and Kumra 2005).

HM impact on mosses

Toxic effects of heavy metals are apparent in a wide range of plant cellular activities that take place in all plant groups, such as protein synthesis,respiration, photosynthesis, mineral nutrition, and membrane structure. Their toxic concentrations have been found to cause membrane damage, ion leakage, and decreased chlorophyll concentrations in vascular plants, in bryophytes, and in lichens. Many of the previously mentioned activities are probably related to the affinity of heavy metals for sulphydryl groups, which results in inhibition of the active sites of enzymes and/or conformational modification of macromolecules.

The mechanism proposed for this inhibition is the replacement of magnesium (Mg) in the porphyrin ring of the chlorophyll molecule by heavy metals. Consequently, cells accumulate protoporphyrin, and chlorophyll synthesis is blocked. Metal ions are known to interfere in this way with chlorophyll biosynthesis and electron transport activities, as well as with other enzymes related to photosynthetic process, either through direct inhibition of an enzymatic step or through induced deficiency of an essential nutrient (Shakya *et al.*, 2008).

1.4 Economic advantages of using mosses in biomonitoring

Air quality can be monitored by measuring the pollutants directly in the air or in deposition, by constructing models depicting the spread of pollutants, or by using bioindicators. Direct measurements are expensive and their use and maintenance are not simple or cheap. Even industrialized nations are unable to afford extensive networks of electronic monitors. They are limited to a few elements or chemical compounds and have no intrinsic relationship with the biological effect of the contaminants (Poikolainen, 2004; Najera et al., 2002).

The models provide information about extensive areas and they can be used to produce predictions of future air quality. However, their accuracy is dependent on the quality of the data used in constructing the models (Poikolainen 2004).

What is more, methods are fast and inexpensive, they only provide a relatively approximate picture of air quality and the deposition of pollutants (Poikolainen 2004).

At this part of this work is presented three different scenarios of mosses as a good bioindicator. Everyone of them is in different point of view, but they all together shows economic benefits of using moss as a tool for biomonitoring.

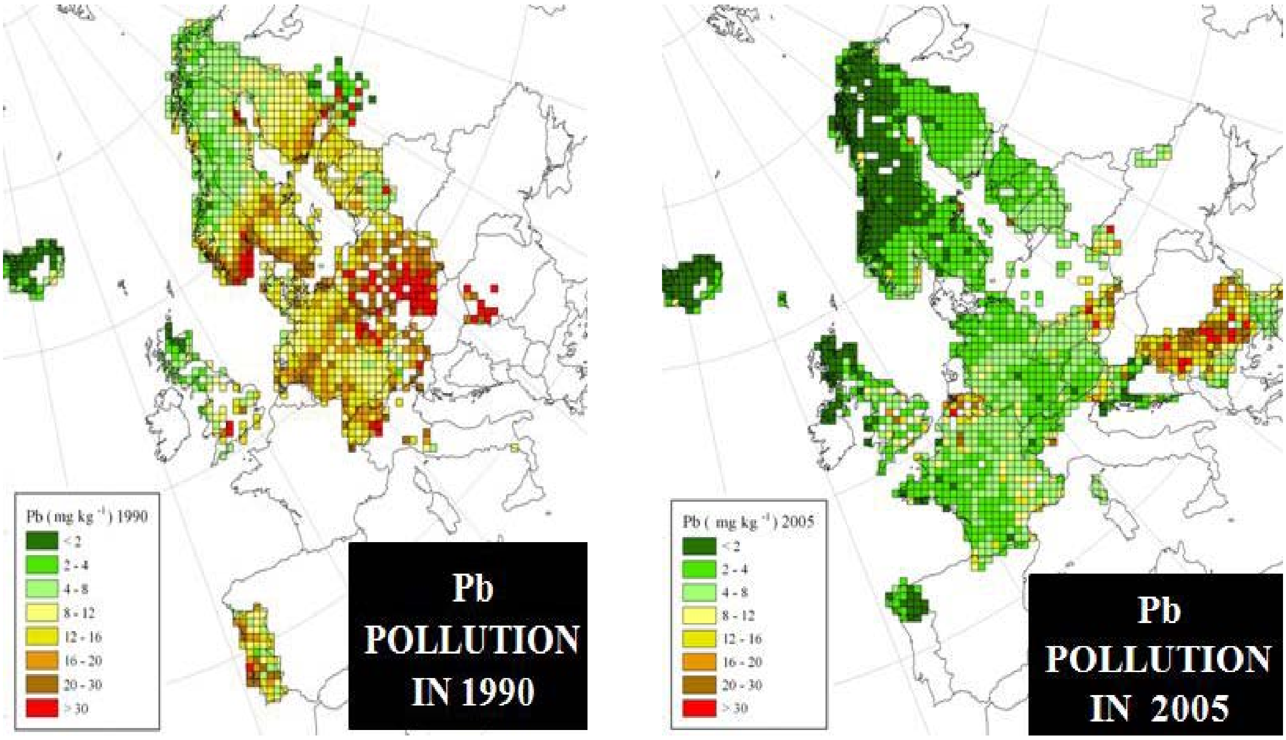
Scenario no. 1. Local and Global surveys

Regional and sub-regional patterns of deposition of aerial metal burden in many parts of the world have been mapped from levels accumulated in mosses. The regions so studied have spanned from small parts of a country to entire subcontinents (Onianwa, 2000).

From many of such studies have been produced contour maps, isopleths and colourcoded maps (Fig. 1.14) depicting variations in regional levels of pollution (Onianwa, 2000).

Mosses provide an effective and cheap method for monitoring trends in heavy metals pollution in Europe at a high resolution. The technique of moss analysis provides a surrogate, time-integrated measure of metal deposition from the atmosphere to terrestrial systems (Harmens *et al.* 2008).

It is easier and cheaper than conventional precipitation analysis as it avoids the need for deploying large numbers of precipitation collectors with an associated long-term programme of routine sample collection and analysis (Harmens *et al.* 2008).



1.14.Figure. Lead concentration in Europe 1990-2005 (An overview...2010).

Therefore, a much higher sampling density can be achieved than with conventional precipitation analysis (Harmens *et al.* 2008).

Scenario no. 2. A lack of equipment

Most air pollution studies in India are based on atmospheric aerosols collected on particulate matter filters. This is an active method that gives an idea of trace-element atmospheric pollution only during the sampling time. It requires long-term sampling at a large number of sampling sites. The measurements require sophisticated technical equipment which is expensive.

There is lack of sufficiently sensitive and inexpensive techniques that permit the simultaneous measurement of many air contaminants. In India, it is difficult to use air samplers in remote areas due to lack of electricity. Biomonitoring is the one and only solution (Chakrabortty and Paratkar, 2006).

Scenario no. 3. To be creative in extremely environment conditions

In Vienna (Austria) was performed an interesting experiment. This was a first-time ever attempt to use mosses (*Hylocomium splendens*) as bioindicators in a tunnel experiment to analyse emissions from road traffic. Moss samples were exposed for four weeks in wooden frames (size 10 cm x 10 cm), covered by a thin plastic net with a mesh size of 1 cm x 1 cm. 17 elements, mainly heavy metals were analysed. Experiment results showed that usefulness of mosses for surveying heavy metals emissions and deposition arising from road traffic sources, even under the extremely adverse conditions of the tunnel environment. This experiment proved, that mosses have considerable potential as easy – to – apply and cost efficient biomonitors of road traffic emissions in tunnels, if the extremly adverse site condition (Zechmeister *et al.*, 2006).

H.G. Zechmeister and his colleagues (2006) consider bioindicators like mosses a suitable alternative to technical particle filters inside tunnels. They are easy to handle, low in costs and valuable information regarding traffic emissions can be obtained.

1.5 General characteristics of the most popular mosses (*Hylocomium splendens*) as a bioindicators in Lithuania and in Europe

Hylocomium splendens is the most widely used bryophyte for biomonitoring in the boreal region (Økland *et al.* 1999). *Hylocomium splendens* (Fig. 1.15), commonly known as Glittering Wood-moss, Stair-step Moss and Mountain Fern Moss, is a perennial clonal moss with a widespread distribution (Hylocomium splendens...2009).

1.15. Figure. Hylocomium splendens (Hylocomium splendens...2009 (b)).

Abundant and often dominant in coniferous forests on water-shedding and water-receiving sites (Mountain fern...2009). It is commonly found in Europe, Russia, Alaska and Canada, north Africa, Australia, and New Zealand (Hylocomium splendens...2009; Plant description...2010).

Hylocomium splendens is generally olive green, yellowish or reddish green; stems creeping, 2 - 20 cm long, stems and branches reddish, often with branches on branches; current year's growth arises from near middle of previous year's branch, producing feathery 'fronds' in step form; forms springy mats. Leaves are 2 - 3 mm long, oval, smooth-edged, wide base, narrows abruptly to tip (Stair - step...2009).

The popularity of *Hylocomium splendens* as bioindicator is due to its wide ecological amplitude and distribution, and to the fact that annual growth segments can be easily distinguished (Økland *et al.* 1999).

Hylocomium splendens modules start as a *growing point* that emerges in spring, and reaches full size as a *mature segment* the next autumn, after a growing period of ca. 1.5 years (Økland *et al.* 1999).

Ruhling and Tyler reported that, *Hylocomium splendens,* have a high capacity to sorb heavy metals from solution mainly via an ion exchange process (Lee, C. K., et *al.* 1994).
In 1995 was made an extended study of heavy metals (using *Hylocomium splendens* as bioindicator) deposition in Lithuania. Concentrations of lead were found in the range of 5–15 μg/g. In general variation of lead concentrations in the mosses in Lithuania is quite small. Only at the sites representing local anthropogenic pollution the concentration of lead was much higher-up to 83 μg/g in the Naujoji Akmene with a very big factory of building materials (mainly cement) (Čeburnis *et al.* 1999).

1.6 Techniques for the Heavy metal determination in mosses

For the analysis of plants, digestion is usually performed either with nitric acid or with a mixture of nitric acid and hydrogen peroxide. The quantity of sample used is about 0.5 g. These conditions do not allow the total digestion of mineral particles and a filtration is necessary (Ayrault, et *al*., 2001).

Contemporary instrumental techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES) or atomic absorption spectrometry (AAS) allow for simultaneous or sequential determination of large number of elements, if only they exceed a threshold concentration, defined by corresponding limit of detetion and by adequate spectral resolution of the instrument. The requirement for the analyzed element concentration to exceed its limit of detection is rarely met in trace analysis. Hence the necessity of concentrating the sample components occurring at trace level (Feist et *al.* 2008).

The following table (1.1) summarizes the relative strengths and weaknesses of each of the techniques, particularly as they may apply to the practical and performance requirements of analysis.

1.1 Table. Summary of elemental analysis techniques (An elementary... 2010)

	Flame AAS	GFAAS	ICP – AES	ICP - MS
Detection limits	Very good for some elements	Excellent for some elements	Very good for most elements	Excellent for most elements
Sample throughput	10 - 15 seconds per element	3 - 4 mins per element	1 - 60 elements/ minute	All elements in < 1 minute
Dynamic range	10^3	10^2	10^6	10^8
Precision				
Short term	0.1 - 1.0 %	0.5 - 5%	0.1 - 2%	0.5 - 2%
long term	2 - beam 1-2 % 1 - beam < 10%	1 - 10% (tube lifetime)	1 - 5%	2 - 4 %
Interferences				
Spectral	Very few	Very few	Many	Few
Chemical	Many	Very many	Very few	Some
Physical	Some	Very few	Very few	Some
Dissolved solids in solution	0.5 - 5 %	> 20 %	0 - 20 %	0.1 - 0.4 %
Sample volume required	Large	Very small	Medium	Very small - medium
Ease of use	Very easy	Moderately easy	Easy	Moderately easy
Capital costs	Low	Medium - high	High	Very high
Running costs	Low	Medium	High	High
Cost per elemental analysis				
High volume - few elements	Low	High	Medium	Medium
High volume - many elements	Medium	High	Low – medium	Low - medium

ICP-MS and ICP-AES systems have similar new sample delay times, which may be up to 60 seconds long. FAAS is much quicker, typically only about 5 seconds. GFAAS systems can take up to 2 minutes to dry and ash the sample prior to measurement.

A measurement period during which the signal is measured for the element(s) and, if necessary, their background points. ICP-MS and simultaneous ICP-AES systems make the fastest measurements; all analytes in a sample can be measured in about 2-5 minutes. Sequential ICP-AES systems take about 10 seconds per analyte line, including the time taken to select the line (An elementary...2010).

The sequence is to measure all the analytes in a sample, one after another, then go to the next sample and measure all the lines again. FAAS generally requires about 4 seconds per measurement, but the sequence is different. All samples are measured at a single analyte line, then the next lamp is selected and all samples are measured again (An elementary...2010).

GFAAS measurement time is less than 5 seconds for a single result at a single analyte line. However, several repeats per sample may be necessary with GFAAS to obtain satisfactory precision.

ICP-MS produces the best detection limits (typically 1-10 ppt), followed by GFAAS, (usually in the sub-ppb range) then ICP-AES (of the order of 1-10 ppb) and finally FAAS (in the sub-ppm range).

ICP-MS typically operates at much lower concentration levels so that linear ranges up to 10 8 can be achieved for some analytes. In standard practice, however, ICP-MS is a technique for ultra-trace to trace levels to ppm levels (An elementary...2010).

Inductively coupled plasma (ICP) is a new, efficient technique for element analysis, but flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS) are still among the most commonly used methods for the determination of Cu, Ni, Pb, Cd, Mo and Zn in biological and food samples.

Prior to FAAS or GFAAS analyses, the samples should be first liquefied to a solution. For this reason, a digestion process is needed for solid samples. Dry, wet and microwave digestion are the main methods for trace heavy metals in solid samples (Guldas, 2008).

Selecting the most appropriate tool for the job can sometimes appear to be a daunting task, especially since there is considerable overlap of capabilities. In fact, all of the techniques may be able to perform your particular analysis at acceptable levels of accuracy and precision (An elementary...2010).

1.7 Possibilities of heavy metal dispersion modelling

Heavy metals in the atmosphere may travel over large distance before being redeposited on soils. Conventional measurements of heavy metal deposition are based on precipitation analysis. Measuring large areas therefore implies deploying large numbers of precipitation collectors with an associated long-term programme of sample collection and analysis (Sience for...2010).

There are a lot of programs for the modelling of polution dispersion: Matlab, VS2DTI, Maple, Mathcad, Mathematica, EMEP, etc.

The Unified EMEP model is a chemical transport model developed at the Air Pollution Section at the Norwegian Meteorological Institute and Meteorological Synthesizing Centre - West.

For HM investigations in EU, were used EMEP model based on Gaussian plume (Science for...2010).

The Unified EMEP model is a limited-area, terrain following sigma coordinate model designed to calculate air concentration and deposition fields. List of pollutants, that are modelled by EMEP is presented bellow:

Main Pollutants**:** The main acidifying and eutrophying pollutants. "All" selects all pollutants in this list.

- Heavy metals: As, Cd, Cr, Cu, Hg, Ni, Pb, Se and Zn. "All" selects all pollutants in this list.

- POP: Persistent organic pollutants. "All" selects all pollutants in this list.
- PM: Particulate matter: PM10, PM2.5 and Pmcoarse (User guide...2010; Open source...2010).

CONCLUSIONS

1. There are a lot of investigations based on biomonitoring. There is no unique specie for biomonitoring in all over the world. Most popular investigation objects are lichens, tree bark and mosses. The best quality of investigation results would be gained if both - lichen and mosses would be used in one experiment.

2. In all over the world it is popular to use terrestrial mosses in experiments of atmospheric deposition of heavy metals. The most important environmental features of mosses as a tool of air pollution investigation are: rootless, large surface, wide - spread population, a habit to grow in groups, long life – cycle (slow growth rate), survival in a high – polluted environment, ability to obtain nutrients from wet and dry deposition, because of their weakly developed cuticle. Mosses can uncover regional - global differences of airborne pollution as well.

3. HM are very dangerous pollutant, mainly comes from industrial human activities. It is important to check air quality on HM due to an impact on all ecosystems. One of the biggest sources of HM pollution is exhaust fumes from the cars.

4. There are some economic advantages of using moss as a bioindicator as well. At this work three different scenario models are presented. Each of them is at different point of economic view. The most popular employment of mosses - national and multinational surveys. It is easy to collect samples, there is no need for: any special modeling programs, any extra employees, extra technical equipment and extra time. What is more, surveys with the help of mosses unite all countries, that means we are having one unify system for biomonitoring in all regions. And this helps to avoid some errors and get more accurate results about present situation on regional and global scale. It is important to note, that it is impractical to use technical equipment for a great extension of territory. Moreover, with one integrated system we can save time and that is very important nowadays.

5. One more economic aspect - not all countries are developed at the same level. For some countries bioindicator can be the only one solution due to a lack of finances or a lack of technical equipment. Mosses are a cheap biomonitoring method, it is even possible to call eco – friendly or sustainable technology - you do not need to use technical equipment in field (money saving), do not need to use energy sources for extra technical equipment (energy saving, costs reduction.

6. Finally, mosses can be creative and economic solution in complicated conditions. Sometimes there are extreme situations, when there are no specific indicators, for example, mosses perfectly fits when it is necessary to check traffic emissions in a tunnel, when for example, tunnels environment is not suitable for other technical devices.

7. Heavy metals in the atmosphere may travel over large distances before being settling down to the environment. Measuring large areas therefore implies deploying large numbers of precipitation collectors with an associated long-term programs of sample collection and analysis. There are a wide variety of pollution dispersion in environment modelling programmes, Matlab, VS2DTI, Maple, Mathcad, Mathematica, EMEP (based on Gaussian plume), etc. For the EU survey EMEP model were used. The Unified EMEP model is a limited-area, terrain following sigma coordinate model designed to calculate air concentration and deposition fields.

2. METHODOLOGY OF HEAVY METAL DETERMINATION IN MOSSES

At this chapter all steps of used methodology (identification of mosses, collection and preparation of samples, HM calculation and statistical data estimation) for experiment of HM determination in mosses are presented bellow.

2.1 Study site

Vilnius is the capital of Lithuania and the biggest transport and industrial centre in Lithuania. Vingis Park, the largest park in Lithuania, is situated at the bend of the Neris River and covers an area of 160 hectares. It was founded in the 15th century (Vingis park...2010).

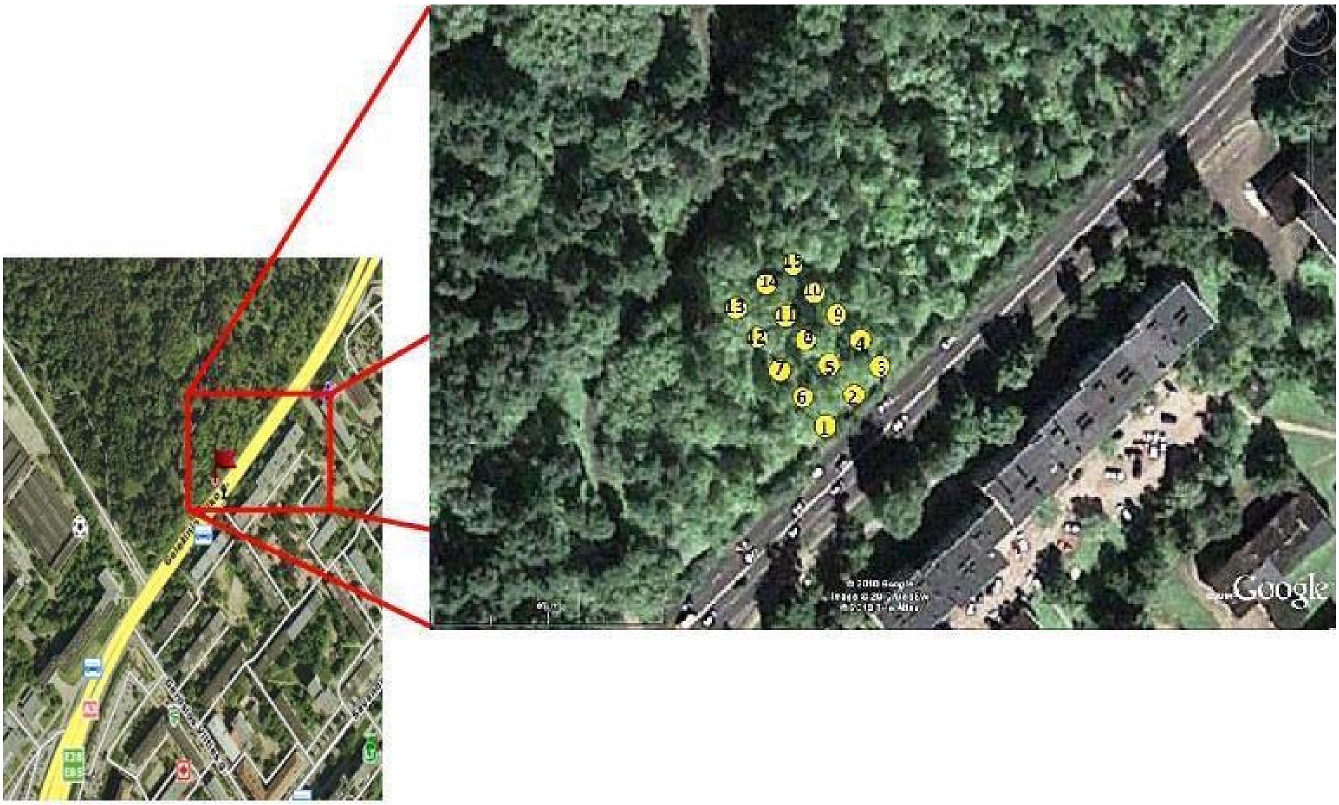
In 1919, after the re-establishment of Vilnius University, the Botanical Garden was established in the former mansion of Vingio Park. In the middle of the 20th century, the Garden was severely damaged by a flood and also by the activities of World War II. A larger part of the Garden having been re-established, was moved to another place. The Park has two entrances: one from M. K. Čiurlionis Street and the other from Birutės Street. Not far from the M. K. Čiurlionis Street entrance to the Park, is a classical chapel, and next to it there is a cemetery for German soldiers (Vingis park...2010; Vingio parkas...2009).

2.1.Figure. An investigation area near Geležinis Vilkas street (by author)

Vingis Park is a favourite place for the residents of Vilnius to take a walk, ride a bicycle or go roller-skating and it is popular with sportsmen. Park is used as a venue for various events and is one of the biggest centers for many recreational human activities. In summer, the park livens up. In its centre, side-shows for children are opened, and there are several cafes, as well as sports equipment rental offices there. (Vingis park...2010; Vingio parkas...2009).

The area of investigations (54°40’28 “ N; 25°14’32 “ E) is situated between the biggest park of Vilnius (Vingis park) and Geležinis Vilkas street (Fig. 2.2).

The place for the moss sampling was chosen according to the high intensive flow traffic (according to Vilnius municipality 4000 – 4300 vehicles per hour) that can cause possible pollution to the atmosphere. Mosses samples were taken from the Vingis park side (2.2 fig.).



2.2. Figure. Vingis park - An area of investigation located in Vilnius region, were collected 15 samples at the distances: 5, 15, 25, 35, 45 meters from the Geležinis Vilkas street. Samples are marked as yellow points by the help of GPS coordinates in Google Earth program. Map, where are marked sample place M 1:1340 (Žemėlapiai...2010; Google maps...2010)

All samples of mosses were taken in this order: 5, 10, 15, 20, 25 meters from the Geležinis Vilkas street, at each distance were taken three samples of mosses, the distance between these samples were 5 meters as well (Fig. 2.2).

Samples of mosses were taken 500 meters from the street as a control samples, in order to evaluate the differences between mosses near Geležinis Vilkas street and 500 meters from pollution source.

Climate conditions of study site

The pollutant emissions are transported to different distances, depending on the geographic area, its geology and the local meteorological factors: fog, wind, rains, thermal inversions (Dobra et *al.,* 2006). For experiments, samplings of mosses were proceed during three seasons (spring, summer and autumn). According to the methodology of mosses sampling for EU surveys, samples should be taken in all seasons, except winter, because in winter mosses are covered with snow.

The climate of Vilnius region is considered as Humid Continental or Hemiboreal by Köppen climate classification. The average annual temperature is + 6.1 °C, in January the average temperature is − 4.9 °C, in July it is +17.0 °C (About Vilnius...2010).

The average precipitation in Vilnius is about 661 millimetres (26.0 in) per year (Lithuanian Hydrometereological...2010).

Dominant wind direction - South - West, speed 2.5 - 4 m/s (Lithuanian Hydrometereological...2010).

In 2010, samples of mosses were taken on 7th of March, the temperature of weather was 6 °C; in summer samples were taken 21st of August, temperature was 27 °C and in autumn - 14th of November ambient air temperature was 9 °C. During all three samplings were no rain and dominant wind was south – west.

2.2 Morphological identification of mosses

Closely related moss species are often difficult to distinguish from each other than other plants, but it is easy to sample and collect (Banienė, 2001; Rowantree et al., 2010).

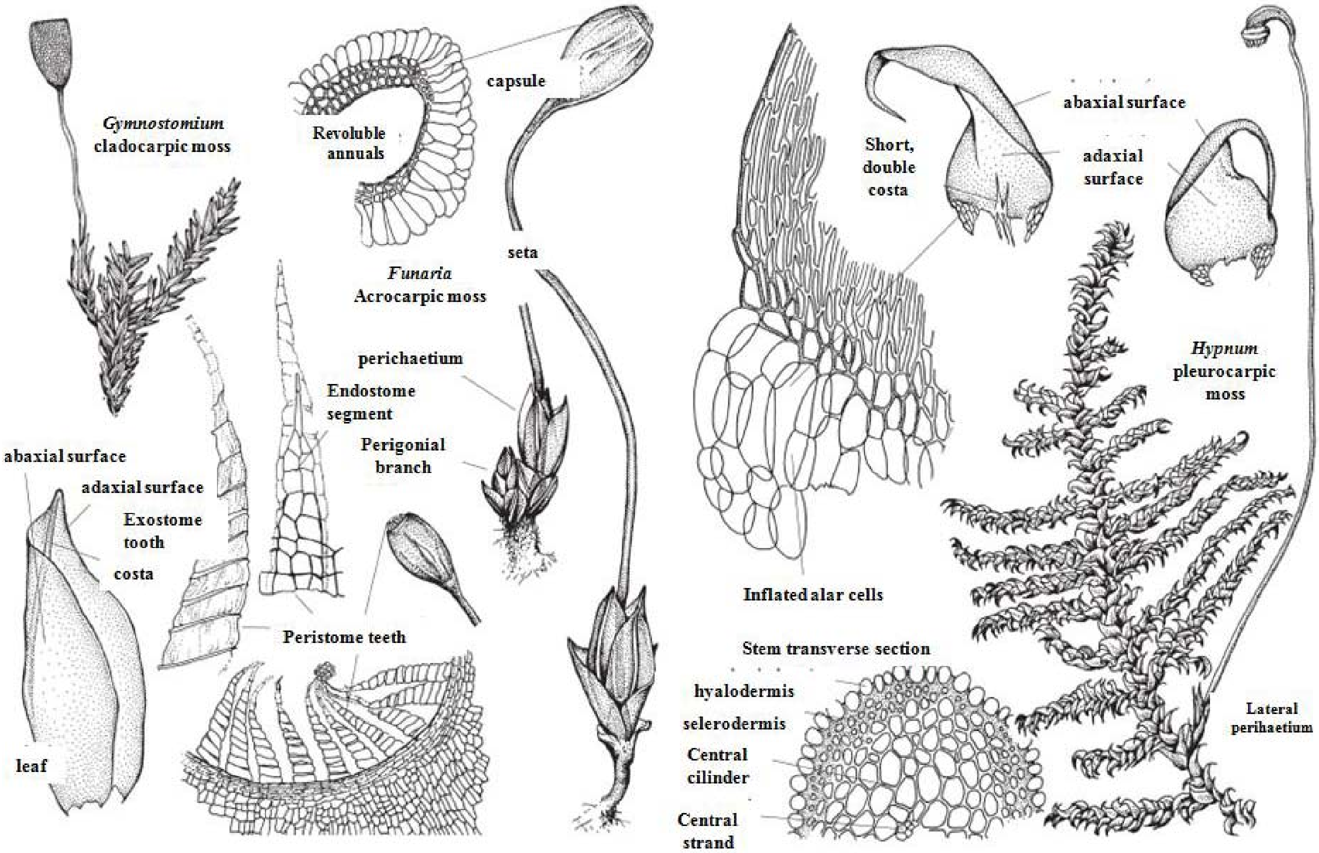
All organisms have characteristics that distinguish them from other kinds of organisms, when enough characteristics are determined, we can identify the organism. There are many popular easy-to-use catalogues of mosses or guides available, that provide photographic illustrations or line drawings of many of common, and sometimes less common, species of vascular and non-vascular plants. In them, plants are grouped by family or genus, or by plant colour (Species identification...2010; Pine barrens...2010).

According to Lithuanian catalogue of mosses, there are approximately 120 species of liverwort, they compound 21 families. In Lithuania grow 350 species of mosses, they all compound 33 families (Banienė, 2001).

Moss plants are difficult to identify due to their morphological features (Fig. 2.3), except when they ambitiously prepare to send offspring moss via spores out into the breeze. The moss plants grow stalks on top of which precariously sit capsules ready to release the spores. Each moss species, though much alike in terms of stems and leaves, tends to have different types of capsules (Tiny Shag...2010).

As mentioned above, the identification of a moss begins with an examination of its general characteristics (fig.2.3): growth habit and mode of branching, leaf characteristics, colour and shape of any capsules (Fig. 2.4) (Tortula muralis...2010).

In the majority of true mosses, capsules consist of three anatomically distinct zones, namely, the basal neck, the median spore-containing urn or theca, and the distal operculum. Capsules with a dehiscent operculum are stegocarpous (Morphology of...2010).



2.3. Figure. General morpohological features of some mosses (Morphology of...2010)

In order to get the results with certainty, it is important to answer a few key questions during identification process:

1. ***Are there any similar species that could cause confusion?***

Usually these will be species in the same genus. Create a list of all species in the genus and check their atlas pages and species descriptions. Then use the photo gallery to view these species, try to compare with other photos (Species identification...2010).

2. Does the distribution fit?

Check the distribution on the specific catalogue, does it fit with your mosses (Species identification...2010).

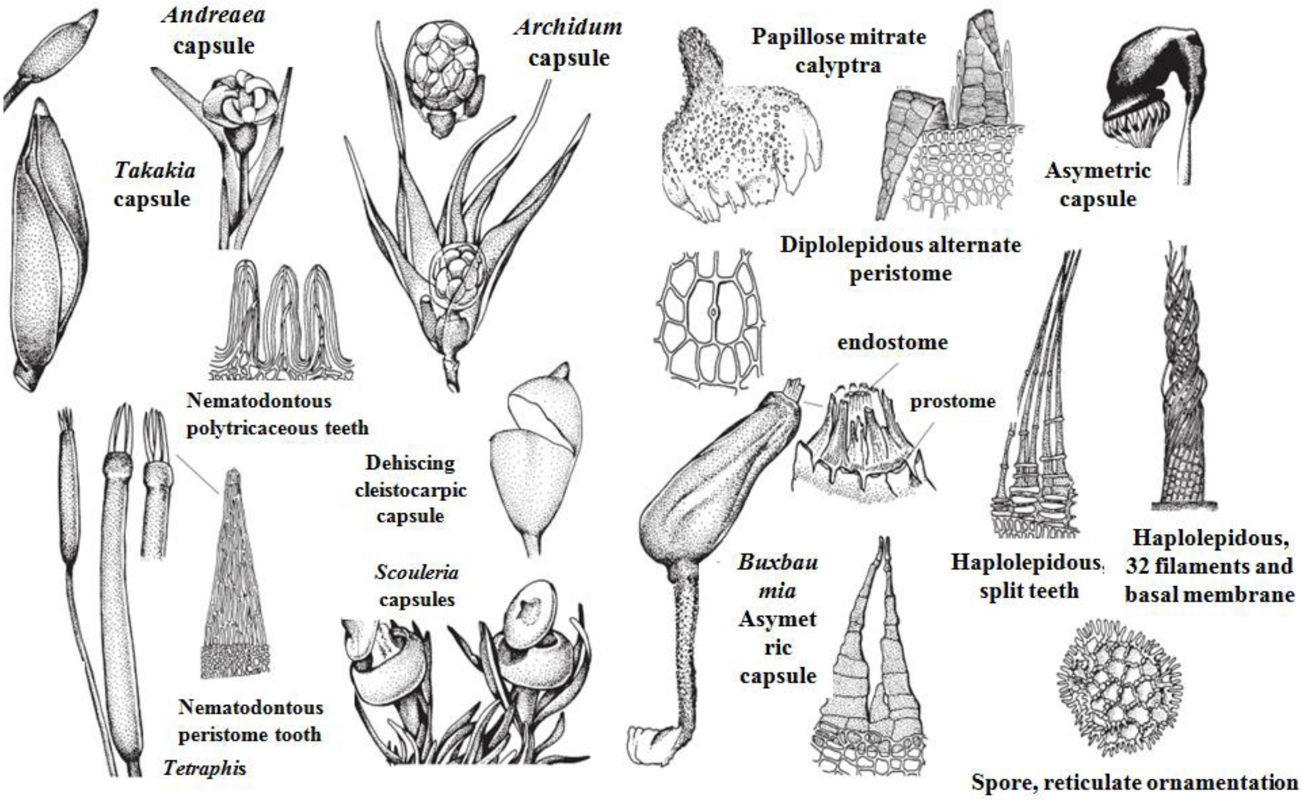
3. Is the habitat correct?

It is important to check the habitat information for the species on specific catalogue of mosses. Habitat is an important aid in plant identification. For example, if your plant was found on a sand dune, then it is unlikely that it is a species that only occurs in cattail marshes or rocky outcrops. This is true even if you have the region of occurrence correct (Species identification...2010).

4. **Is the evaluation correct?**

Often there are similar looking species that are found at other places, so this should always be checked (Species identification...2010).

The considerable variation that occurs in the arrangement and structure in moss morphological features such as: leaves of mosses, structure of stem, capsules (Fig. 2.4) and colour. All these morphological features according to catalogues of mosses, help to identify the speces of mosses by naked eye.



2.4. Figure. General morpohological features of mosses capsule dehiscence and peristomes (Morphology of...2010)

Capsules that lack an operculum and dehisce irregularly due to generalized breakdown of the capsule walls are cleistocarpous (Morphology of...2010).

Identification was made by naked eye by this work author and her supervisor, pictures were sent to Botanical Institute. Identification of mosses were proceed according to Lithuanian catalogue of mosses.

2.3 Samples of mosses preparation and analysis of heavy metal

Most methods in heavy metal monitoring employ mosses as bioaccumulators and involve sample collection followed by laboratory analysis techniques (Stihi et *al.* 2006).

Cleaning of samples

Sampling and sample handling were carried out using plastic gloves and bags. The cleaning procedure is a critical step in the moss technique because it affects the final result. It is important to remove all forest debris (soil, leaves, needles) from samples of mosses.

In the analytical programme for the 2005/2006 EU survey based on the recommendations of Rühling, the following is stated in reference to the cleaning of moss samples: if the samples cannot be cleaned immediately after sampling, they should be placed paper bags and dried and stored at room temperature (20–25°C) until further treatment.

Alternatively, samples can be deep-frozen. Although in some surveys the moss samples were cleaned directly in the field. Most researchers do not usually pick over the moss samples directly in the field, due to the long time that it takes. They usually collect a large volume of moss, place this in a plastic sampling bag and store the bag for an undetermined number of days or weeks, under often undetermined conditions, until the samples are finally cleaned in the laboratory prior to analysis (Aboal et *al.*, 2008).

Calculation of moisture content

Mosses absorb huge amounts from precipitation (rain, snow). That is why is important before digestion of samples of mosses to dry. Before drying mosses were weighted (± 0.01g) and after drying they were reweigted in order to evaluate moisture content. By 2.1 formula moisture content was calculated:

$$Mn = ((Ww-Wd)/Ww) \times 100\% \qquad (2.1)$$

where:

Mn - *moisture content (%) of material (in this case mosses)*;

W_W - *wet weight of the sample*;

Wd - *weight of the sample after drying* (Moisture content...2010).

In order to achieve higher accuracy of this work, all measurements were repeated three times, in results an average of measurements are presented.

Digestion and mineralization of collected samples

Due to reduce a wide range of organic compounds matter interference, that is in mosses tissues, and allow for the conversion of the HM into a form that can be analyzed by AAS, mosses samples should be weighted and digested in muffle furnace E5CK-T, at 450 ^oC, after digestion, samples should be left about 1 h to cool.

Biological materials like moss are highly inhomogeneous. They contain numerous organic compounds of different steps of stability and impurities of sparingly soluble mineral components. Incomplete mineralization of samples during microwave digestion makes analyte transfer difficult for the solution. On the other hand, residues of organic matrix influence electrochemical measurements (Baranowska and Srogi, 2000).

After digestion, mosses should be reweighted again, in order to estimate the mass loss (organic compounds).

After digestion samples should be weight, the quantity of sample should be used about 0.5 g [0.49 - 0.51 g]. For the analysis of mosses were mixed with a mixture of 10 ml nitric acid (65%) and 2 ml of hydrogen peroxide (30%), digestion was performed by microwave of Milestone Ethos in laboratory of Environmental Protection department (VGTU). Digestion proceeded 35 minutes. After mineralization samples were cooled for one hour till 50 - 70 ^oC.

After mineralization solutions were pour into 50 ml flasks, finally, distillate water was pour into flasks, in order to reach the mark of 50 ml.

Mineralization conditions do not allow the total digestion of mineral particles and a filtration was necessary.

HM determination by AAS

HM determination was performed by Atomic absorption spectrometer „Buck Scientific“ 210 VGP. Techniques of GFAAS and FAAS are based on the fact that free atoms will absorb light at frequencies or wavelengths characteristic of the element of interest.

Within certain limits, the amount of light absorbed can be linearly correlated to the concentration of analyte present. Free atoms of most elements can be produced from samples by the application of high temperatures.

In GFAAS, samples are deposited in a small graphite tube, which can then be heated to vaporize and atomize the analyte (Research group...2010).

2.1. Table. General analytical characteristics for the GFAAS and FAAS

Element	**Wavelenght, nm**	**Phon correction**
Chromium (Cr)	357,9	Catode hollow lamp
Copper (Cu)	324,7	Deuterium lamp
Lead (Pb)	283,2	Deuterium lamp
Manganese (Mn)	279,5	Deuterium lamp
Nickel (Ni)	232,0	Deuterium lamp
Zinc (Zn)	213,9	Deuterium lamp

Determination was performed for five HM, that are spread in the atmosphere (Cr, Cu, Pb, Ni, Zn), table 2.1 presents general analytical characteristics for the GFAAS and FAAS.

Calculation of Heavy Metal concentration

HM concentration of an investigative element is calculating accordig to formula 2.2:

$$W(Me) = (C_{Me} \cdot f \cdot V)/W \qquad (2.2)$$

where:

W (Me) - *metal concentration in sample, mg/kg*;

C_{Me} - *metal concentration in solution, mg/l*;

f - *dilution factor*;

V - volume, l; for analysis took 0.05 l;

W - *mass of sample, kg, calculated to dry mass of sample*.

During all this experimental work procedures for the HM analysis in mosses were used specific reagents and instruments:

1. Deyonisated water;
2. HNO_3 , 65%;
3. H_2O_2 , 30%;
4. 2,0 ml, 5,0 ml, 10 ml pipettes;
5. 50 ml Flasks;
6. Paper filters;
7. Analytical weighing - machine VLR - 200;
8. Atomic absorption spectrometer „Buck Scientific“ 210 VGP;
9. Muffle furnance E5CK-T;
10. Porcelaine crucibles;

11. Microwave of Milestone Ethos.

All parts this work experiments were proceeded at the laboratory in the department of Environmental Protection in Vilnius Gediminas Technical University.

2.4 Statistical data estimation of investigative results

After all calculations, it is necessary to perform statistical count of investigative results. For every calculated parameter it is used formula to estimate the average value of results according to formula (Calculating the...2010):

$$\bar{X} = \frac{\sum_{i=1}^{n} X}{n} \tag{2.3}$$

where:

$\bar{X}$ *– the average value of results*;

X – *a single measurement result;*

n – a number of measurements.

Moreover, a dispersion is calculated using 95 % probability (R = 95). Experimental standart deflection is estimated according to the following formula (Calculating the...2010):

$$S_n = \sqrt{\frac{\sum_{i=1}^{n}\left(X_i - \bar{X}\right)^2}{n-1}} \tag{2.4}$$

where:

S_n *– experimental standart deflection;*

$\bar{X}$ *– the average value of results;*

X_i *– a single measurement result;*

n – a number of measurements.

Experimental standart average deflection is calculated using the following formula (Calculating the...2010):

$$S_{\bar{}} = \frac{S_n}{\sqrt{n}} \tag{2.5}$$

where:

S – experimental standart average deflection;

S_n *– experimental standart deflection;*

n – a number of measurements.

Relative standart deflection is estimated according to the formula:

$$S_r = \frac{S_n}{\bar{X}} \tag{2.6}$$

S – relative standart deflection;

S_n – experimental standart deflection;

$\bar{X}$ – the average value of results.

The confiding interval of arithmetic average, which has the probability of 95 % is calculated using the following formula (Calculating the...2010):

$$\bar{X} = \pm t_n \cdot \frac{S_n}{\sqrt{n}} \tag{2.7}$$

where:

X – the average value of results;

t_n – the coeficient of Stjudento, which depends on the probability of confiding interval and the number of measurements;

S_n – experimental standart deflection;

n – a number of measurements.

When we have all calculations, then it is necessary to verify the reliability of results. The results i X is eliminated which does not fit with the clause below (Calculating the...2010):

$$\left| X_i - \bar{X} \right| \geq S_n \tag{2.8}$$

X and S_n are recalculated after results, which were eliminated. Therefore, stimations are performed 3 times with 3 different assumes. Statistical data calculations will be resented at the annex of this work.

CONCLUSIONS

1. Experiment was carried between Vigis park and Geležinis Vilkas street. This site was chosen due to a great possibility to evaluate the relationships between mosses near Geležinis Vilkas street and intensity of traffic flow. During investigation 16 samples in three different seasons were collected, mosses were taken in different distances (5, 15, 25, 35, 45 meters) from the street side and control samples were taken 500 meters from the street.

2. The most difficult part of this work - to identify spieces of mosses. For this work it is important to use all kind of possible tools, such as: specific catalogues of mosses and their morphological features, specific online data basis, to contact with botanists. It is important to pay attention on all morphological features. If it is available - to use microscope to determine specifics of walls and cells. At this work, sample of mosses were identify according to Lithuanian catalogue of mosses by naked eye by author and supervisor of this work.

3. In order to determine the concentration HM in mosses few important steps were made: first of all, mosses were cleaned from litters, soils and all kind of debris. In the literature there are many ways how to treat samples of mosses, we chosen the most popular - to clean and treat samples at the laboratory. After treatment mosses were weighted and dried; calculated moisture content. Later samples of mosses were digested and reweighed, calculated mass - loss of organic compounds. Following step - mineralization process with mixture of strong acidic acid. Proceeded filtration of samples, where it was necessary. Final step - heavy metal determination by AAS. Determination was calculated according Atomic absorption spectrometer „Buck Scientific“ 210 VGP.

4. Due to a higher accuracy and reliability on this work, all measurements of experiments were performed three times, statistical data estimation of investigation results were performed and evaluated according to the presented methodology in Chapter 2.

3. RESULTS AND ANALYSIS OF EXPERIMENTAL INVESTIGATION

At this chapter of thesis, results, such as determination of moisture and mass – loss contents, HM concentrations in mosses are presented.

3.1 Identificated mosses - *Pylaisia polyantha*

Identification was made by naked eye by this work author and her supervisor, pictures were sent to Botanical Institute. All the answers of plant identification showed, that samples of our collected mosses are *Pylaisia polyantha* (Fig. 3.1).

According to Lithuanian catalogue of mosses *Pylaisia polyantha* grows on the bark of several species, most frequently ash and elder, in hedgerows and open woodland, in parks and alleys. It avoids the lower parts of large tree boles, and most frequently colonizes twigs, horizontal boughs and inclined trunks, especially in the upper 10 cm of regularly trimmed hedges. It was lost from some areas when sulfur dioxide polluted the air and acidifi ed bark, but may now is increasing again (Pylaisia polyantha...2009).

3.1. Figure. Sampe of collected mosses Pylaisia polyantha near Vingis park (by author)

The description of mosses habitat perfectly fits to collected samples of mosses.
Collected sample of moss forms slender, creeping, yellowish-green to green, irregularly to pinnately branched, often untidy patches. The seta of moss is a darkish red, the stiffly erect capsule narrowly elliptical in outline, with a conical lid. Mosses samples were compare with a lot of spiecies of mosses in the catalogue and in databases from internet. Morphological description fitted to mosses *Pylaisia polyantha* the best.

The leaves *Pylaisia polyantha* of are erect, often tending to point somewhat in one direction when moist, but are appressed when dry.

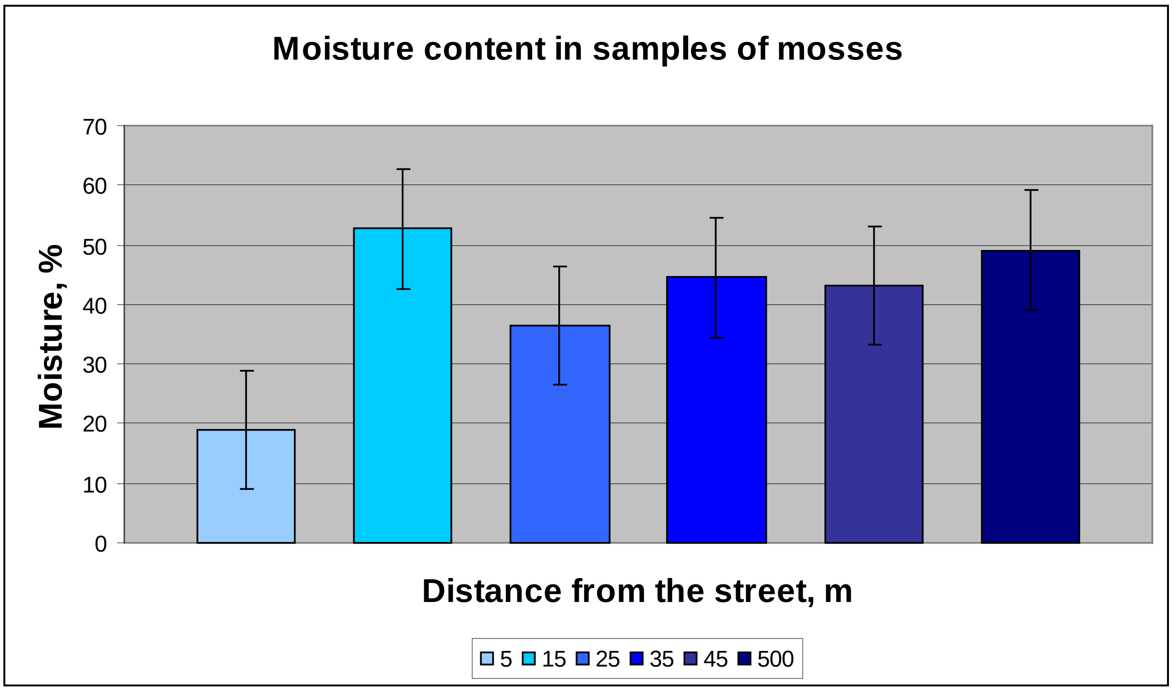
The nerve is very short and double, or absent. Dwarf, fertile branches are abundantly produced, and the most distinctive feature of the plant is its copiously produced capsules, two or more generations of which are typically present.

For example, in late spring the shoots support clumps of old capsules from one season and very young capsules from a later season (Pylaisia polyantha...2009).

3.2 Moisture content in mosses

16 samples were taken from Vilnius Vingis park, near Geležinis Vilkas street. Averages of moisture content in mosses from three seasons were determined (Fig. 3.2).

In mosses which were 5 meters from the street the moisture content was determined – 18.96%.



3.2. Figure. An average results from three seasons of moisture content in samples of mosses

In collected *Pylaisia polyantha* mosses which were found at the distance of 15 meters from the street - the moisture content was 52.65%.

In mosses which were collected 25 meters from the street the moisture content was – 36.44%.

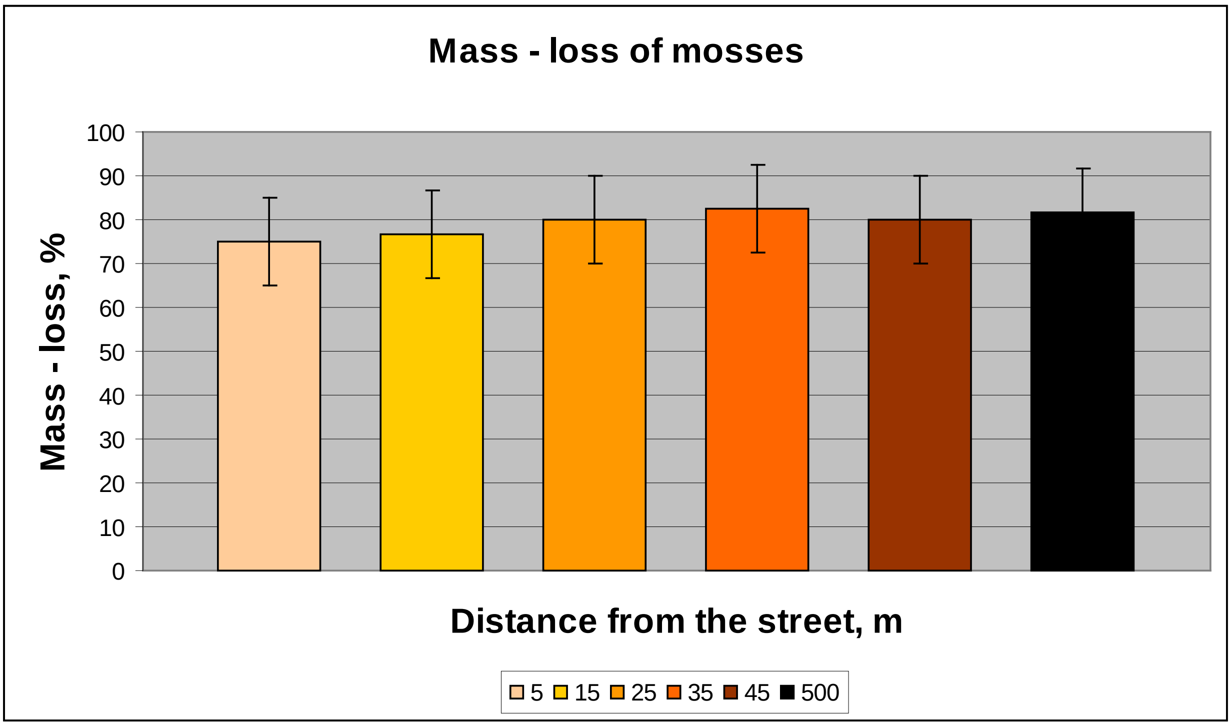
In mosses at the distance of 35 meters from the street the moisture content was 44.55% determined.

In samples of mosses which were collected at 45 meters from the street the moisture content was 43.22%.

In the control samples which were collected at 500 meters from the street, 49.07% of moisture content was detected.

3.3 Mass - loss of organic compounds

After digestion of samples of mosses, the mass - loss of organic compounds were evaluated (Fig. 3.3).



3.3 Figure. An average results from three seasons of mass - loss in all samples of mosses

In samples of mosses at 5 meters from the street, mass - loss was -74.98 %, this mass – loss was the smallest among all distances from the street.

In collected samples of mosses at the distance of 15 meters from the street mass - loss of organic compounds was 76.62%.

In the samples of mosses at 25 meters from the street, organic compounds composed 79.84% of the total sample.

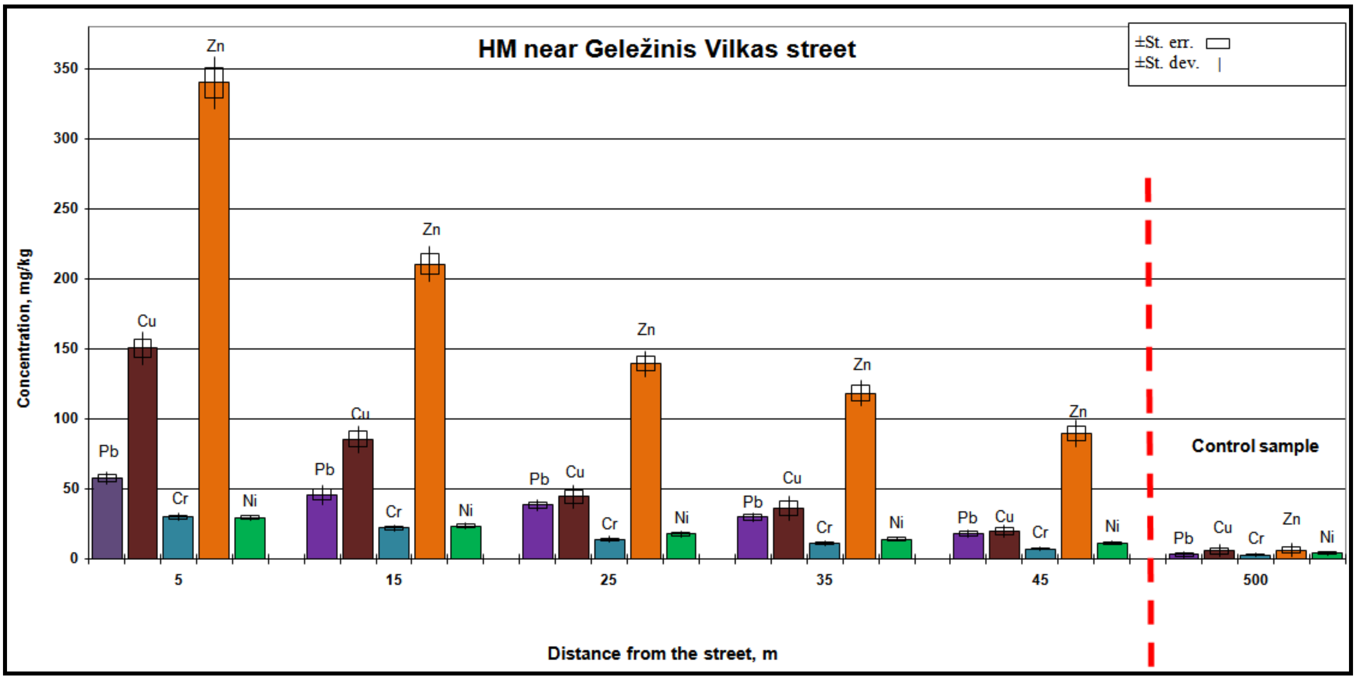
Mass - loss of the sample *Pylaisia polyantha* at 35 meters from pollution source was 82.40%.

In the sample at the distance of 45 meters, mass loss was 79.92% determined. The sample of contrll lost 81.77% of his mass.

3.4 HM concentration in sample of mosses

Five heavy metals (Pb, Cu, Cr, Ni, Zn) were investigated in samples of *Pylaisia polyantha* mosses, along the high intesive traffic Geležinis Vilkas street in Vilnius. Samples were taken in different seasons: spring, summer and autumn.

Statistical analysis of HM concentrations are presented in 3.4 – 3.17 figures bellow. Calculations of HM concentrations were counted for dried mosses.



3.4. Figure. HM concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (spring)

Results of this investigation determined, that heavy metals content in all samples of mosses tender to decrease with the distance from the Geležinis Vilkas street. At the distance 5 and 15 meters from the Geležinis Vilkas street HM concentrations of HM (Fig. 3.4) are considerably high and it reveals that the mosses near intensive traffic are highly polluted.

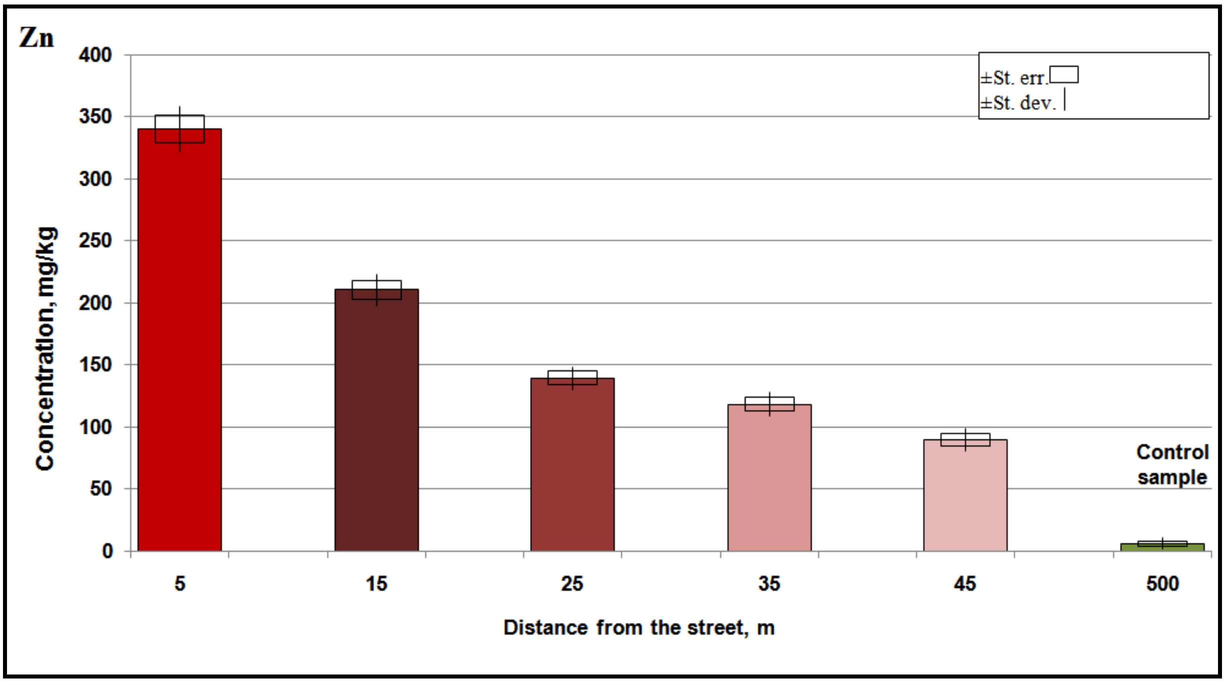
Accumulations of HM in samples of mosses were found in this order: **Zn** > **Cu** > **Pb** > **Cr, Ni**.

Zinc emissions in spring period

Zinc was the highest accumulated metal of all investigated HM in master thesis. According to Blok (2004) the emissions of zinc along roads originating from: wearing of brake lining; losses of oil and cooling liquid; wearing of road paved surface; wearing of tyres; corrosion of galvanized steel safety fence and other road furniture.

At the 5 meters distance from the street was found the highest concentration of Zinc – 339.96 ± 10.72 mg/kg in dried mosses (Fig. 3.5).

In samples of mosses at 15 meter distance from the street, the concentration of zinc was lower 210.47 ± 7.24 mg/kg.



3.5. Figure. Zinc concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (spring)

In 25 meters from the street zinc concentration decreased till 139.47 ± 5.24 mg/kg. In 35 meters zinc concentration decreased 118.44 ± 5.37 mg/kg. The lowest concentration of zinc in samples of mosses was determined at the 45 meters from the intensive traffic – 89.52 ± 5.34 mg/kg.

In sample of control at the distance of 500 meters from the street quite low concentration of Zn were determined – 6.03 ± 2.15 mg/kg.

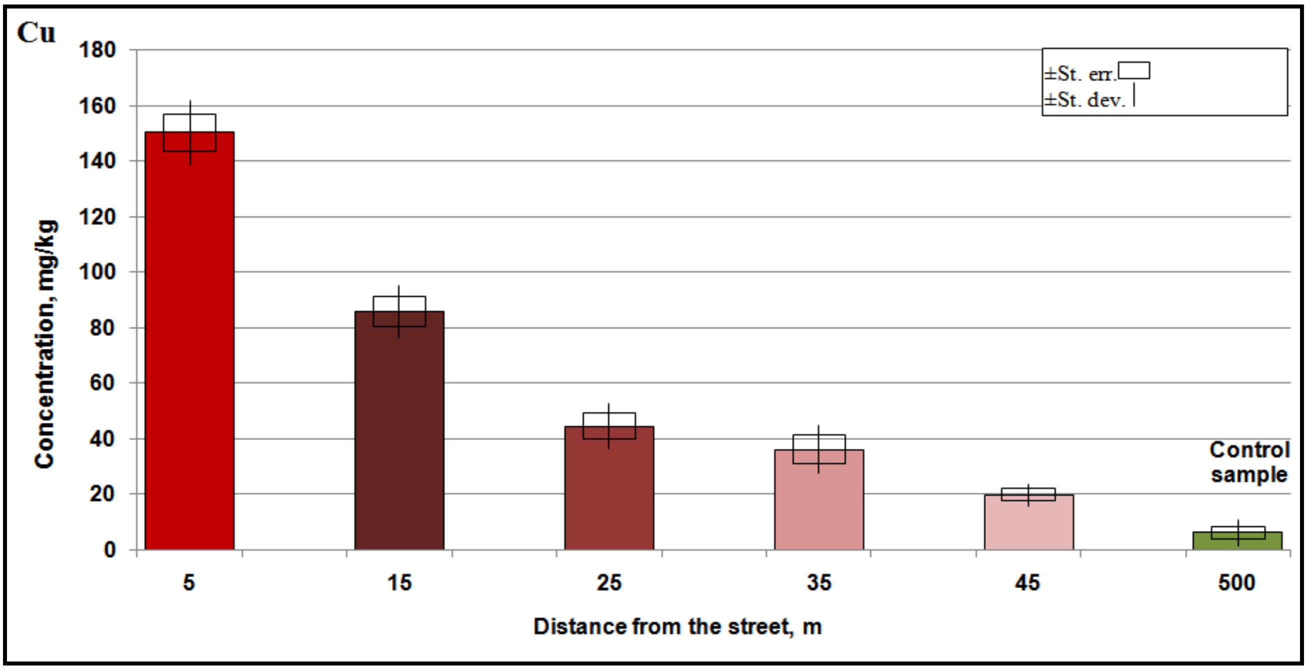
Control sample had 41 times lower concentration of Zinc than the sample at 5 meters from the street. So it is possible to make a conclusion, that HM emission source could be high intensive traffic in Geležinis Vilkas street.

Copper emissions in spring period

Next high accumulated metal, which was determined in samples of mosses, was copper (Fig. 3.6 bellow).

High copper concentrations can originate from the engine as metal wear or as chemical compound dispersed into the oil, also from wearing brass or bronze parts, copper bushings and from bearings, either cooler cores can be as a copper leaching source for diesel cars (Winther and Slentø, 2010).

The biggest accumulations of copper were also found near the intensive traffic. At 5 meter from the street, samples of mosses accumulated 150.43 ± 6.67 mg/kg of Cu.



3.6. Figure. Copper concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (spring)

At 15 meters distance, the highest concentration was found 85.72 ± 5.47 mg/kg. At 25 meters from the street mosses accumulated 44.55 ± 4.80 mg/kg of copper.

With the distance from the road the concentration of Cu decreased significantly, at the 45 meter from the road in samples of *Pylaisia polyantha* mosses were found 19.80 ± 2.27 mg/kg.

In the sample of control 6.03 ± 2.15 mg/kg of copper were determined, that means that concentration at 500 meters from the street is 25 times lower.

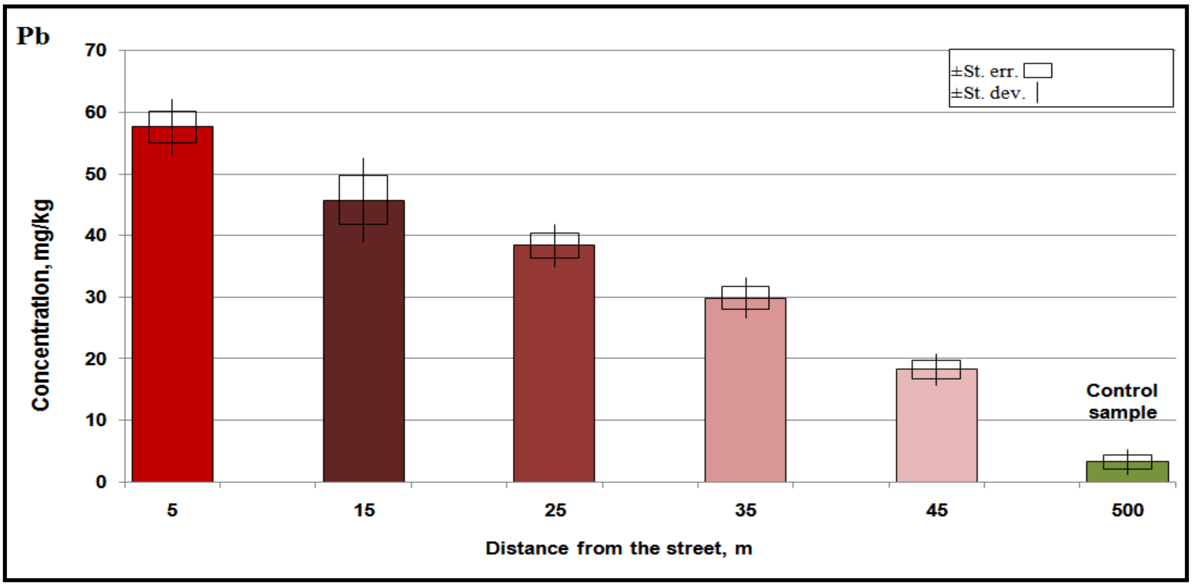
Lead emissions in spring period

Lead levels are quite low in fuels, it may still occur in exhaust gas coming from the fuel and from worn metal alloys in the engine (Winther and Slentø, 2010).

The biggest concentrations of lead (Fig. 3.7) were determined at the distances of 5 and 25 meters from the high intensive traffic street. The highest concentration of lead was determined in mosses of *Pylaisia polyantha* – 57.62 ± 2.59 mg/kg at 5 meters from pollution source.

In the distance 15 meters Pb concentration decreased till 45.78 ± 3.90 mg/kg in samples of mosses. 38.38 ± 2.03 mg/kg concentration of lead were determined at the 25 meters distance from the street.

Concentration of lead were determined at the 45 meters distance from Geležinis Vilkas street – 18.24 ± 1.53 mg/kg.

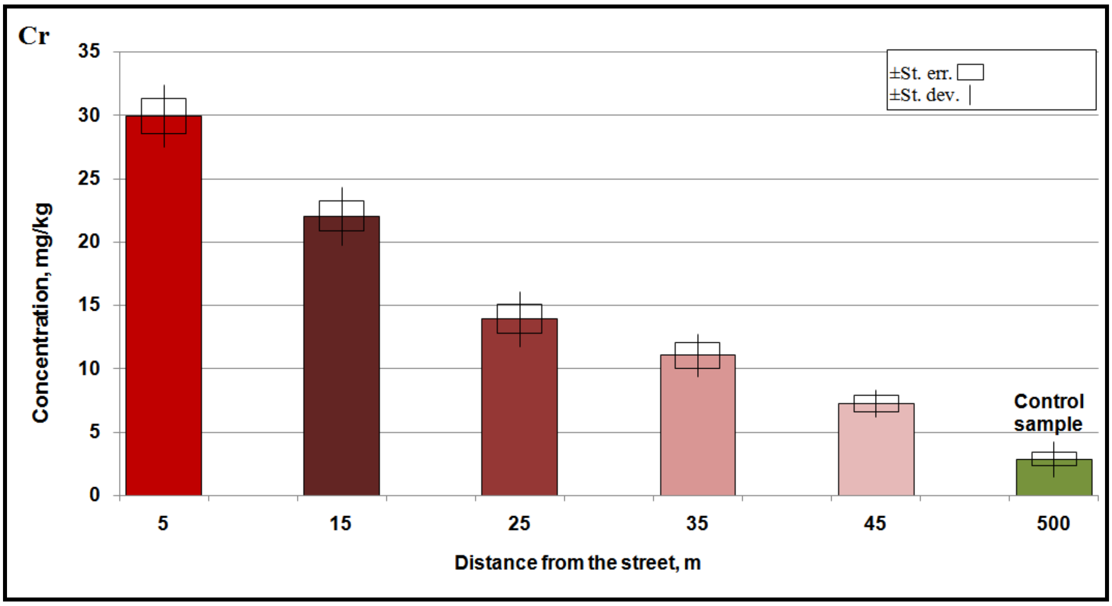


3.7. Figure. Lead concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (spring)

Finally, sample of control (at 500 meters) determined, that lead concentration in mosses is 3.24 ± 1.09 mg/kg, it is almost 20 times lower concentration than at 5 meters from the street.

Chromium emissions in spring period

Chromium mainly occurs in used oil from wearing of e.g. piston rings (Winther and Slentø, 2010).



3.8. Figure. Cr concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (spring)

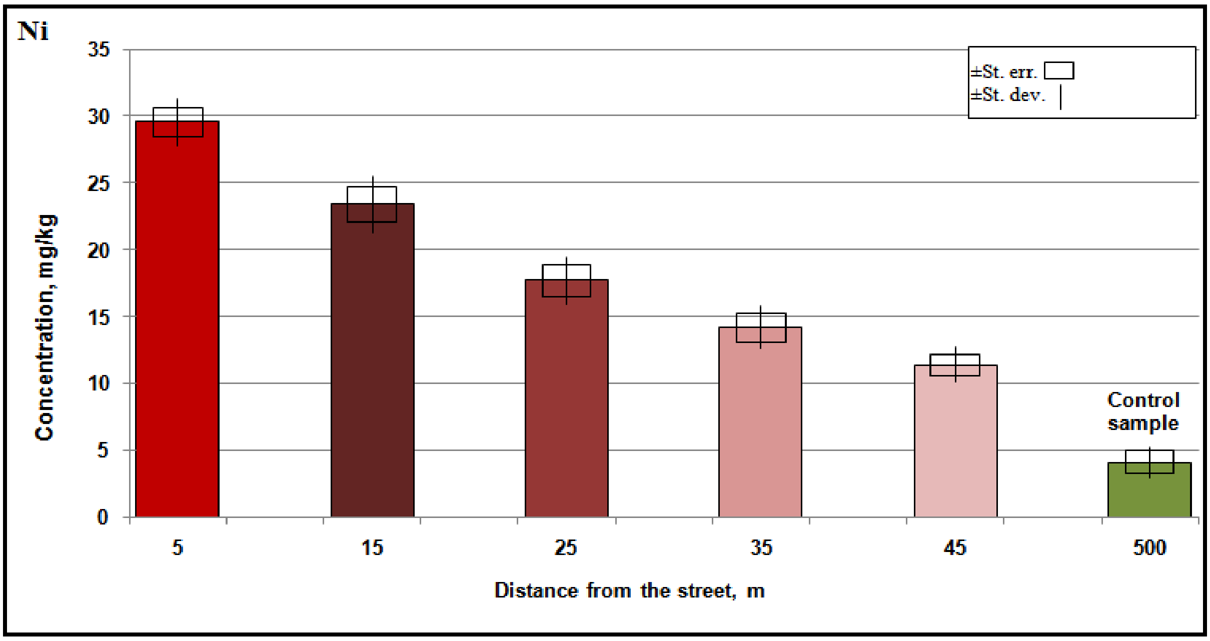
In the distance 5 meters the highest concentration of Cr in samples of mosses (3.8. figure above) was determined 29.95 ± 3.72 mg/kg. Chromium concentration in mosses *Pylaisia polyantha* at the 15 meters distance from the street was 22.05 ± 2.47 mg/kg.

Concentration of Cr decreased till 11.05 ± 2.25 mg/kg in the distance of 35 meters.

At the 45 meters distance from the road Cr concentration was 7.23 ± 2.45 mg/kg. Concentration in 500 meters from the distance was 2.84 ± 0.53 mg/kg determined, it is 11 times lower than in 5 meters from the street.

Nickel emissions in spring period

Nickel is present in fuel and as trace element in steel. It may also be included in virgin engine oil in very small amounts - about 1 ppm (mg per litre) (Winther and Slentø, 2010).



3.9. Figure. Nickel concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (spring)

Ni like all other investigated HM decreased with the distance from the road (Fig. 3.9). The highest concentration at 5 meters from the street was 29.56 ± 1.49 mg/kg.

At 15 meters from the street the highest concentration accumulated in mosses 26.60 ± 0.8 mg/kg. At the distance of 25 meters the concentration decreased to 23.39 ± 1.67 mg/kg.

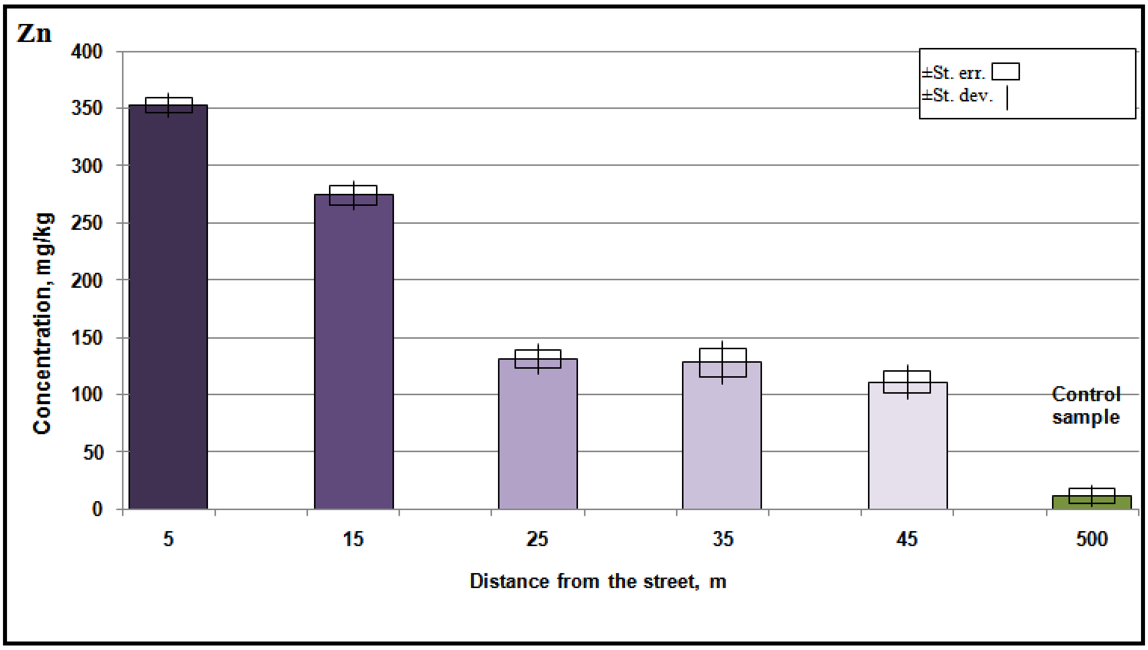
At the 35 meters Ni concentrations decreased till 14.20 ± 2.08 mg/kg, the concentration decreased more then two times (in comparison with 5 meters distance). At the 45 meters distance, the biggest amount of Ni was found 11.40 ± 1.78 mg/kg.

Sample of control showed that in the distance of 500 meters from the street mosses accumulated 4.11 ± 0.84 mg/kg of nickel, the concentrations at control point is lower 7 times than in 5 meters.

Zinc emissions in summer period

At the 5 meters distance from the street was found the highest concentration of Zinc – 352.14 ± 6.52 mg/kg in dried mosses (Fig. 3.10).

In samples of mosses at 15 meter distance from the street, the concentration of zinc was lower 273.75 ± 8.40 mg/kg.



3.10. Figure. Zinc concentrations in mosses (*Pylaisia polyantha*) near Geležinis Vilkas street (summer)

In 25 meters from the street zinc concentration decreased till 131.55 ± 7.83mg/kg. In 35 meters zinc concentration decreased 128.01 ± 11.98 mg/kg. The lowest concentration were determined at the 45 meters from the Geležinis Vilkas street – 110.74 ± 10.15 mg/kg.

In sample of control at 500 meters from the street small concentration of Zn were determined – 7.49 ± 7.133 mg/kg, it is .47 times lower than near (in 5 meters) pollution source.

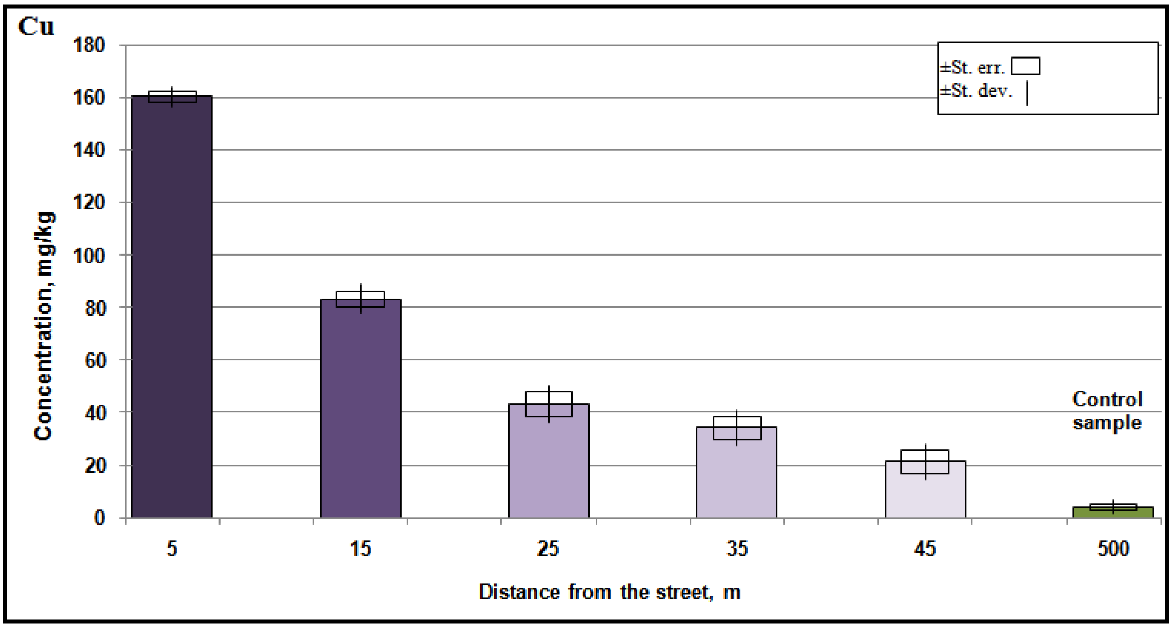
Copper emissions in summer period

Next high accumulated metal, which was determined in samples of mosses was copper (Fig. 3.11).

The biggest accumulations of copper were also found near the street. At 5 meter from the road mosses accumulated 160.11 ± 2.15 mg/kg of Cu.

At 15 meters distance, the highest concentration was found 83.33 ± 2.93 mg/kg. At 25 meters from the street mosses accumulated 43.12 ± 4.49 mg/kg of copper.

With the distance from the road the concentration of Cu decreased significantly, at the 45 meter from the road in samples of *Pylaisia polyantha* mosses were found 21.26 ± 4.47 mg/kg.

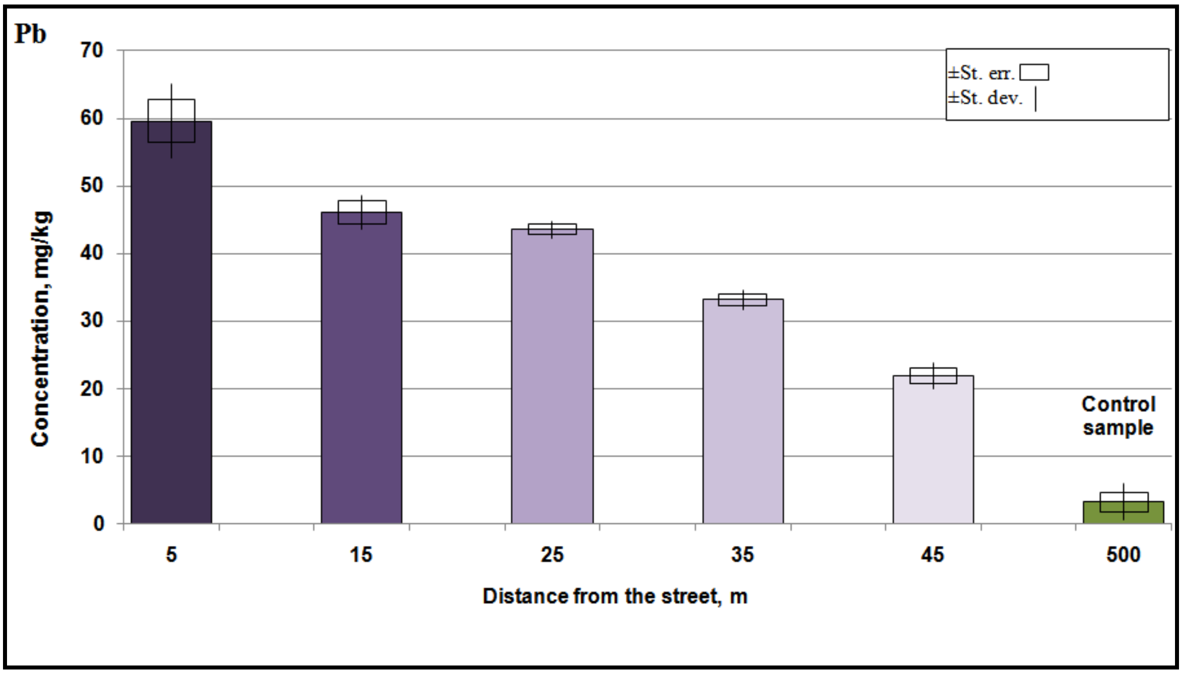


3.11. Figure. Copper concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (summer)

In the sample of control at 500 meters from the street 4.02 ± 1.15 mg/kg, it is 40 lower than in 500 meters.

Lead emissions in summer period

Lead levels are quite low in fuels, it may still occur in exhaust gas coming from the fuel and from worn metal alloys in the engine (Winther and Slentø, 2010).



3.12. Figure. Lead concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (summer)

The biggest concentrations of lead (Fig. 3.12) were determined at distance 5 – 25 meters from the high intensive traffic street. The highest amounts of Pb were accumulated in 5 meters – 59.614 ± 3.14 mg/kg.

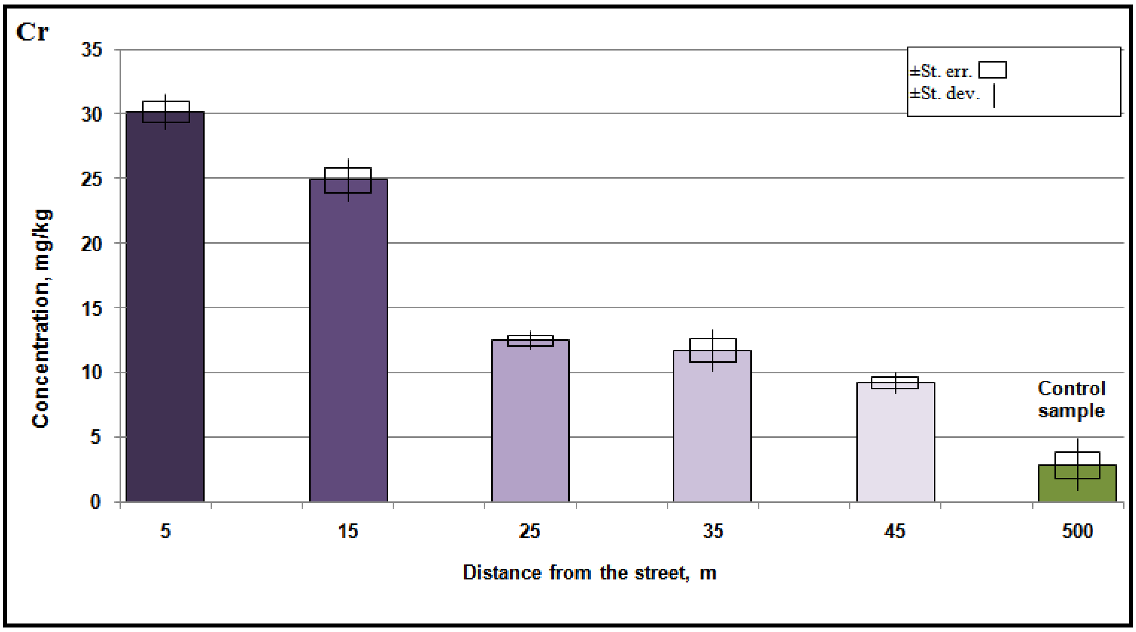
In the distance 15 meters Pb decreased till 46.111 ± 1.70 mg/kg. 38.381 ± 2.03 mg/kg concentration of lead were determined at the 25 meters distance from the street.

Concentration of lead was determined at the 45 meters distance from Geležinis Vilkas street – 21.860 ± 1.09 mg/kg.

And, finally, sample of control (at 500 meters) determined, that lead concentration in mosses is 3.134 ± 1.48 mg/kg and that is 19 times lower than in 5 meters from intensive traffic.

Chromium emissions in summer period

In the distance 5 meters the highest concentration of Cr (Fig. 3.13) was determined 30.17 ± 0.78 mg/kg. The concentration of Cr in mosses was determined at the 15 meters distance from the street were – 24.88 ± 0.97 mg/kg.



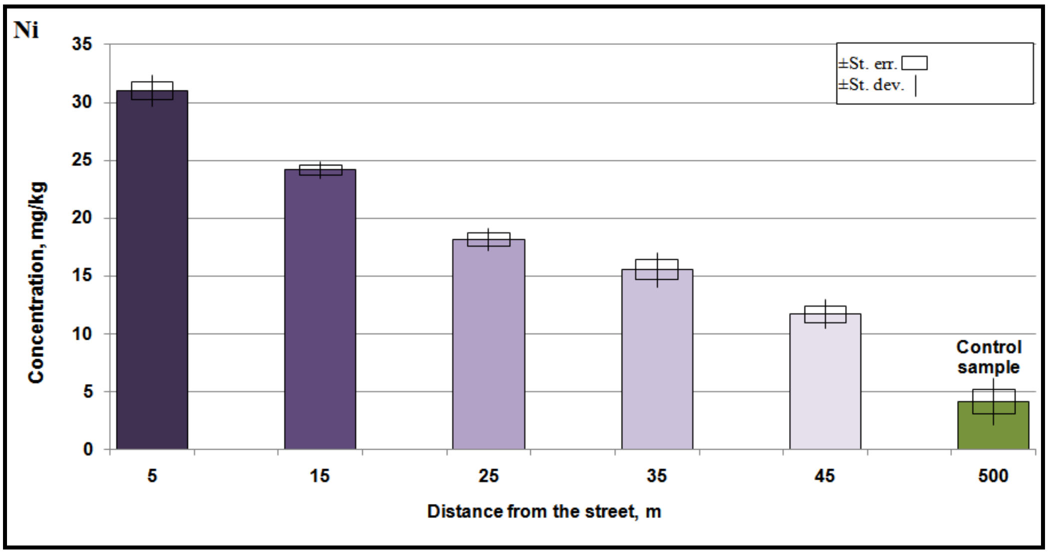
3.13. Figure. Chromium concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (summer)

Concentration of Cr decreased till 11.70 ± 0.91 mg/kg in 35 meters. At the 45 meters distance from the road Cr concentration was 9.17 ± 0.46 mg/kg.

Concentration in 500 meters from the distance – 2.85 ± 1.02 mg/kg were determined, 11 times lower than in 5 meters from the street.

Nickel emissions in summer period

Ni like all other investigated HM decreased with the distance from the road (Fig. 3.14). The highest concentration at 5 meters from the street was 31.03 ± 0.79 mg/kg.



3.14. Figure. Nickel concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (summer)

At 15 meters from the street the highest concentration accumulated in mosses 24.15 ± 0.40 mg/kg. At the distance of 25 meters the concentration decreased to 18.12 ± 0.57 mg/kg. At the 35 meters Ni concentrations decreased till 15.52 ± 0.87 mg/kg, the concentration decreased more then two times (in comparison with 5 meters distance). At the 45 meters distance, the biggest amount of Ni was found 11.66 ± 0.73 mg/kg.

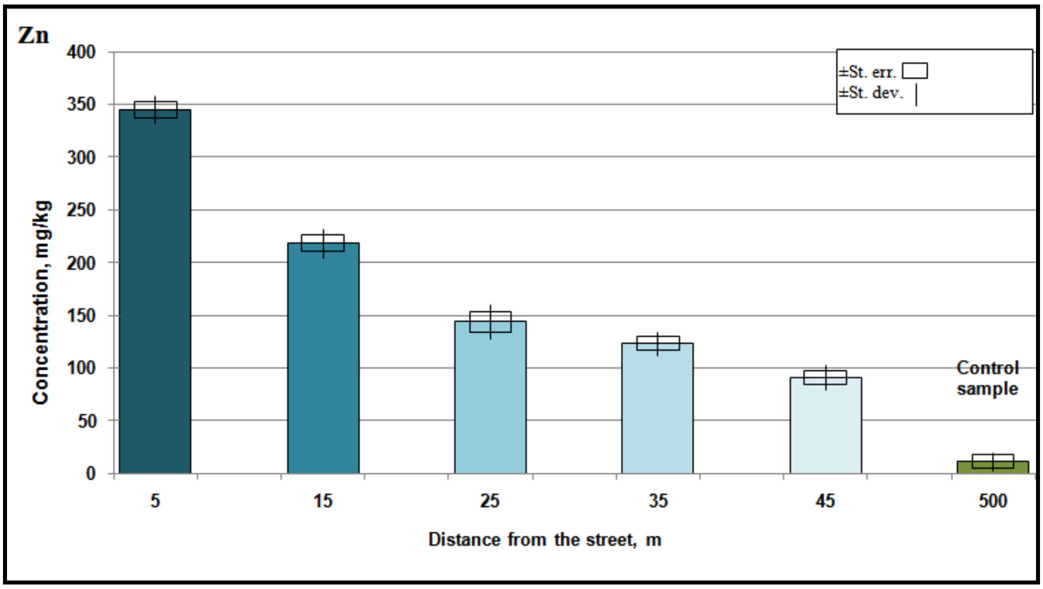
Sample of control showed, that in the distance of 500 meters from the street mosses accumulated 4.10 ± 1.06 mg/kg of nickel - 7 times lower concentration than in 5 meters.

Zinc emissions in autumn period

At the 5 meters distance from the street was found the highest concentration of Zinc – 344.65 ± 7.84 mg/kg in dried mosses (Fig. 3.15).

In samples of mosses at 15 meter distance from the street, the concentration of zinc was lower 217.82 ± 7.81 mg/kg.

In 25 meters from the street zinc concentration decreased till 143.71 ± 9.52 mg/kg. In 35 meters zinc concentration decreased 123.19 ± 6.38 mg/kg. The lowest concentration were determined at the 45 meters from the Geležinis Vilkas street – 90.88 ± 6.86 mg/kg.

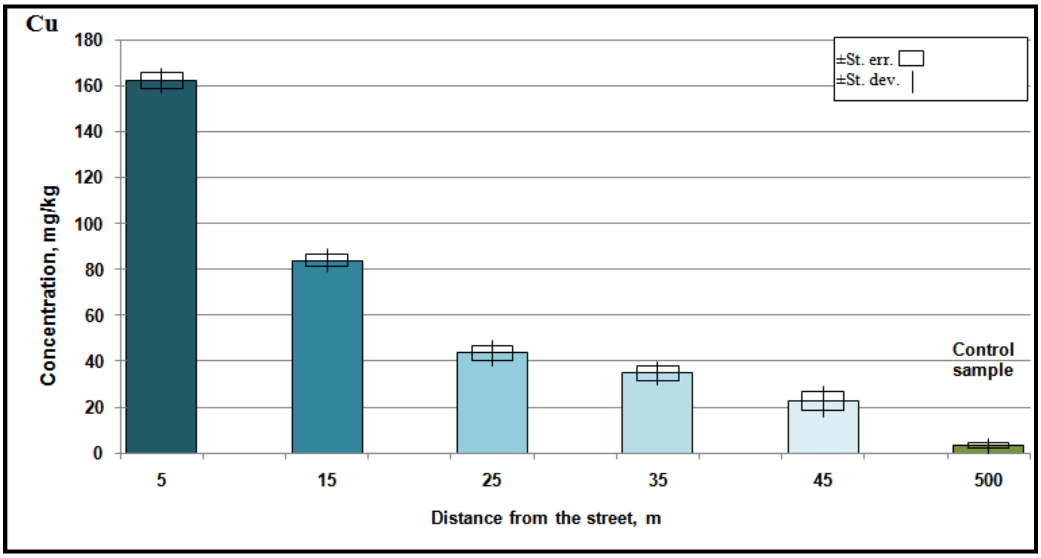


3.15. Figure. Zinc concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (autumn)

In sample of control at 500 meters from the street small concentration of Zn were determined – 6.17 ± 6.13 mg/kg – 56 times lower concentration than in 5 meters.

Copper emissions in autumn period

Next high accumulated metal, which was determined in samples of mosses was copper (Fig. 3.14). The biggest accumulations of copper were also found near the street. At 5 meter from the road mosses accumulated 161.92 ± 3.53 mg/kg of Cu.



3.16. Figure. Copper concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (autumn)

At 15 meters distance, the highest concentration was found 83.83 ± 2.68 mg/kg. At 25 meters from the street mosses accumulated 43.52 ± 3.40 mg/kg of copper.

With the distance from the road the concentration of Cu decreased significantly, at the 45 meter from the road in samples of *Pylaisia polyantha* mosses were found 22.41 ± 4.10 mg/kg.

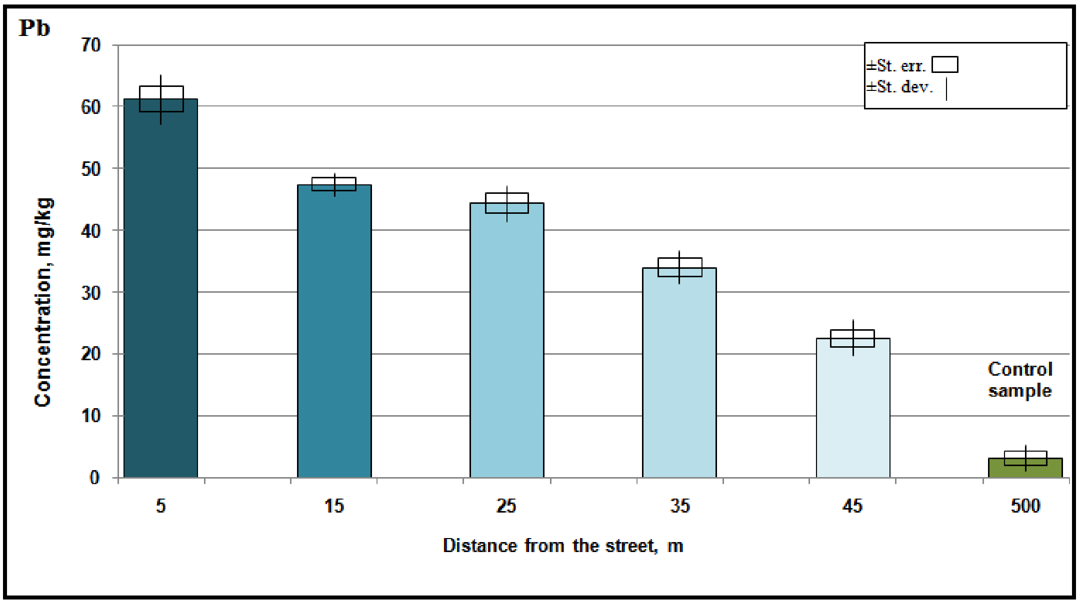
In the sample of control at 500 meters from the street was 3.15 ± 1.15 mg/kg determined and that is 50 times lower than in 5 meters from the street..

Lead emissions in autumn period

The biggest concentrations of lead (Fig. 3.17) were determined at distance 5 – 25 meters from the high intensive traffic street. The highest amounts of Pb were accumulated in 5 meters – 61.23 ± 1.99 mg/kg.

In the distance 15 meters Pb decreased till 47.42 ± 1.01 mg/kg. 44.33 ± 1.64 mg/kg concentration of lead were determined at the 25 meters distance from the street.

Concentration of lead was determined at the 45 meters distance from Geležinis Vilkas street – 22.550 ± 1.39 mg/kg.

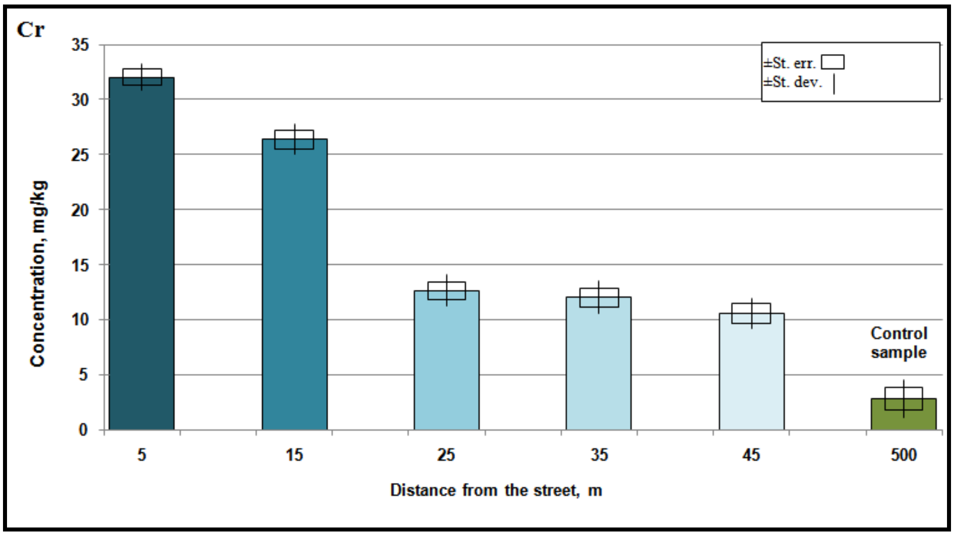


3.17. Figure. Lead concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (autumn)

And, finally, sample of control (at 500 meters) determined, that lead concentration in mosses is 3.611 ± 1.08 mg/kg – 17 times lower than at meters from pollution source.

Chromium emissions in autumn period

In the distance 5 meters the highest concentration of Cr (Fig. 3.18) was determined 32.04 ± 0.75 mg/kg. The concentration of Cr in mosses were determined at the 15 meters distance from the street were – 26.37 ± 0.85 mg/kg.

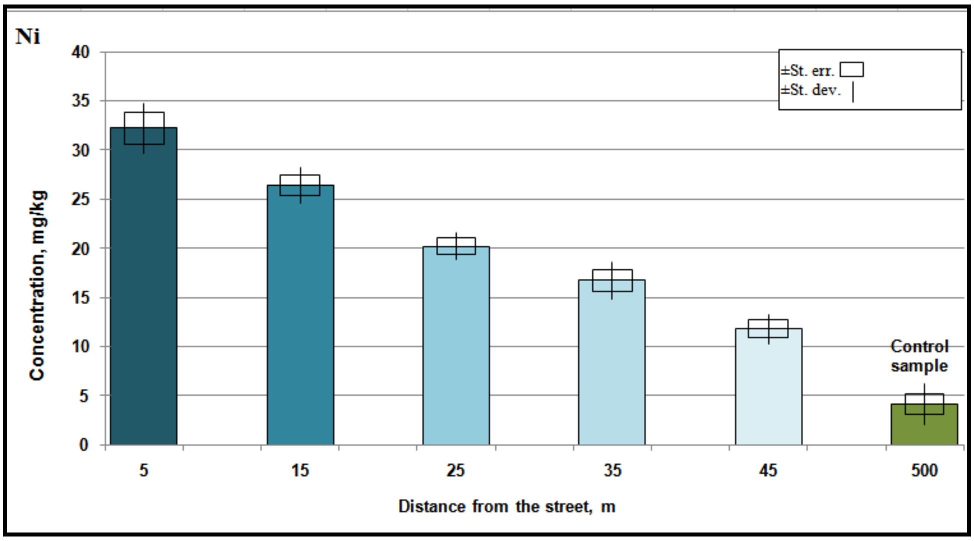


3.18. Figure. Chromium concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (autumn)

Concentration of Cr decreased till 12.01 ± 0.85 mg/kg in 35 meters. At the 45 meters distance from the road Cr concentration was 10.57 ± 0.92 mg/kg. Concentration in 500 meters from the distance – 2.85 ± 1.02 mg/kg was determined.

Nickel emissions in autumn period

Ni like all other investigated HM decreased with the distance from the road (Fig. 3.17). The highest concentration at 5 meters from the street was 32.23 ± 1.62 mg/kg. At 15 meters from the street the highest concentration accumulated in mosses 26.41 ± 1.05 mg/kg.



3.19. Figure. *Chromium concentrations in mosses (Pylaisia polyantha) near Geležinis Vilkas street (autumn)*

At the distance of 25 meters the concentration decreased to 20.21 ± 0.90 mg/kg. At the 35 meters Ni concentrations decreased till 16.71 ± 1.14 mg/kg, the concentration decreased more then two times (in comparison with 5 meters distance). At the 45 meters distance, the biggest amount of Ni was found 11.76 ± 0.92 mg/kg.

Sample of control showed, that in the distance of 500 meters from the street mosses accumulated 4.102 ± 1.06 mg/kg of nickel – 8 times lower concentration than in 5 meters from the street.

DISCUSSION

During practical part of this master thesis high concentrations of HM were detected. According to the EU surveys based on mosses (in 2005), HM concentration, for example, lead (figure 1.14 in Chapter 1) concentrations are significantly lower (Pb 2 – 8 mg/kg in 2005 in Baltic states), than in our results of investigation.

But is important to note, that surveys in Europe were conducted with different species of mosses and with specific methodology, in which is written, that: *the sampling points should be located at sites representative of non-urban areas of the respective countries. In remote areas the sampling points should be at least 300 m from main roads (highways), villages and industries and at least 100 m away from smaller roads and houses* (Harmens et *al*., 2010).

That means that EU surveys monitor background pollution and in our case we can make a conclusion, that so high concentrations of HM in mosses were influenced by pollution of intensive traffic at Geležinis Vilkas street, that could be the main logic reason why we got higher concentrations of HM than in EU surveys.

4. MATHEMATICAL MODELING OF HEAVY METAL DISPERSION BASED ON GAUSSIAN PLUME MODEL

Modeling of environmental processes and contaminant transport is essentially second nature now to the modern engineer and scientist. The scope of engineering problem that can be addressed by modeling is truly infinite. There are models or package programs for almost every conceivable task be it wastewater treatment, optimizing the routes for municipal solid waste haulage trucks, identifying the optimum location for a sewage outfall (to maximize mixing and dilution) or, air quality modeling. Question to your favorite Internet environmental engineering forum will also show up locations of software availability. Traditional physical models of hydrosphere systems have almost been replaced by computer models, primarily because of the lower cost involved and the ease with which problems can be run and rerun with different data at quick speed (Vaitiekūnas and Vaišis, 2009).

The Gaussian plume model is a (relatively) simple mathematical model that is typically applied to point source emitters, such as coal-burning electricity-producing plants. Occassionally, this model will be applied to non-point source emitters, such as exhaust from automobiles in an urban area (Gaussian plume…2011).

4.1 The Gaussian Plume Model

In a Gaussian plume, the spatial distribution of concentration along a transverse axis is Gaussian in shape. The following steady state 3-dimensional model describes the concentration at any point in a coordinate system where the wind is moving parallel to the x-axis (4.1 formula) (Gaussian plume…2011).

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

Where C - concentration of contaminant (g/m^3);

x, y, z = distance from origin in x, y, z coordinates (m);

H= effective stack height (m);

Q= rate of emission of gas (g/s);

σ_y, σ_z= horizontal and vertical plume standard deviations (m), each a function of x;

u= wind speed at effective stack height (m/s).

A plume is the region of space containing the gases and particulates released from a smokestack as fuel is burnt (Gaussian plume…2011).

The Gaussian Plume Model is the most commonly used model to make the calculations needed to predict the movement of a pollutant in complex situations. In order to do this, several assumptions need to be made. It is assumed that certain things will stay the same, i.e., remain in a "steady state." For example, meteorological factors such as temperature and wind speed and direction are assumed to remain fairly constant over the time period when the prediction is being made (Gaussian plume…2011).

Some limitations of the model - as a result the Gaussian plume model will only work well over short distances of up to 50 km from the source of the pollutant to the receptor. The receptor could be a measuring instrument, but it might well be a neighborhood in the path of the pollutant flow. The model will also not work well in areas where the terrain is very complex or in a coastal area where sea and land-breezes can cause dramatic changes in meteorological conditions.

Fuel is burned and a plume of emissions is produced. This may look like smoke and could contain one or more pollutants (Gaussian plume…2011).

Because the plume is hot, it will rise, since hot air is less dense. The plume will rise to a certain point and this is called the "**effective stack height**". The effective stack height depends on three main factors: the exit velocity of the gas from the stack, the temperature of the plume, the temperature of the surrounding air.

After the plume reaches the effective stack height, the plume starts to disperse in three different directions.

1) The plume can move **downwind**. The amount that the plume moves is directly proportional to the wind speed and in the direction of the prevailing wind.

2) The plume can move in a **cross-wind** direction. This is determined by the Gaussian Plume equations.

3) The plume can move in a **vertical** direction, either up or down. This is also determined by the Gaussian Plume equations (Gaussian plume…2011).

One of the key assumptions of this model is that over short periods of time (such as a few hours) steady state conditions exist with regard to air pollutant emissions and meteorological changes. Air pollution is represented by an idealized plume coming from the top of a stack of some height and diameter. One of the primary calculations is the effective stack height. As the gases are heated in the plant (from the burning of coal or other materials), the hot plume will be thrust upward some distance above the top of the stack - the effective stack height. We need to be able to calculate this vertical displacement, which depends on the stack gas exit velocity and temperature, and the temperature of the surrounding air (Gaussian plume…2011).

Gaussian Plume Model Simulations

For calculations an excel sheet from Environmental protection Agency of United States was used. It is complicated to use any kind of modeling program for mosses, because they do not have root and absorb all atmospheric pollution directly from the atmosphere. We decided for this work to use Gaussian plume model and automobile is presented as a smokestack in this calculation.

What we were concerned about in this model - the concentration of heavy metal downwind from the vehicle (in this case vehicle is a stack). As the pollutants are emitted from the smokestack, they mix with the air and are carried downwind, away from the stack. How far they are carried depends on a number of input parameters, which we must enter to the calculations:

1. the height of the stack above the ground (in meters);
2. the diameter of the opening of the stack (in meters);
3. the velocity of the gas emitted from the stack (in meters per second);
4. the temperature of the gas as it exits the stack (in degrees Celsius);
5. the rate at which pollution is emitted from the stack (in grams per second);
6. the atmospheric stability in terms of one of six categories:
   6.1. very unstable;
   6.2. moderately unstable;
   6.3. slightly unstable (for calculation we have chosen slightly unstable atmosphere);
   6.4. neutral;
   6.5. somewhat stable;
   6.6. stable.
7. the number of wind velocities that you wish to investigate;
8. the wind velocities;
9. the number of distances downwind to calculate (for this case 5, 15, 25, 35, 45 and 500 meters were selected);
10. the actual distances downwind.

The atmospheric stability categories accounts for the fact that a parcel of air changes temperature as it changes in altitude.

With this input data, we can calculate the concentration of the pollutant (in units of micro-milligrams per cubic meter, or $\mu g/m^3$) at various locations downwind from the stack, usually measuring from 0 kilometers (the base of the stack) down to 100 km from the stack (Gaussian plume…2011).

4.2 Input data

In order to make mathematical model more similar to exhaust fumes from vehicle, the input data was selected as much as possible similar to vehicle (an average of stack height and stack diameter were taken from exhaust fumes pipe of passenger car). The input data is presented in the 4.1 table bellow.

4.1. Table. Inputdata for mathematical modeling of HM dispersion

Input data	Value
Stack height, m	0.3
Stack diameter, m	0.1
Emission rate*, g/s	
Zn	0.006
Cu	0.009
Pb	0.007
Gas exit velocity, m/s	1
Gas exit temperature, °C	200
Atmospheric condition	3 – slightly unstable
Ambient temperature °C	
Spring	6
Summer	27
Autumn	9

* Emission rate was calculated to all HM individually, calculation formula is presented bellow.

In order to get different results from each HM, we need to calculate emission rate (g/s), for this calculation we need to know each HM emission factor.

Emission rate from vehicles per 1 hour:

60 km/h – allowable speed at Geležinis Vilkas street, we take, that for 100 km vehicle uses 10 l of petrol.

This means, that per 1 hour 1 automobile emit 6l/h, moreover, according to Vilnius municipality investigation, traffic intensity at Geležinis Vilkas street is 4000 - 4300 vehicles per hour, from this we can say that, total fuel consumption per hour at investigation area can be:

$$6 \text{ l/h} * 4300 = 25800 \text{ l}$$

Then we need to find out the density of fuel (at this model only petrol fuel was modelled).

$$\rho_{petrol} = 770\ kg/m^3 = 770\ g/l$$ (Kokių būna...2011)

Next step – to find total emissions per 1 hour at investigation area:

$$25800\ l * 770\ g/\ l = 19866000\ g = 19866\ kg$$

In order to make more specific calculation for each HM, we need to use individual emission factors for each HM from table 4.2 bellow.

4.2. Table. Heavy metal emission factors for vehicles in mg/kg (Road transport…2011).

Type of vehicle	**Zinc**	**Copper**	**Lead**
Passenger cars, gasoline	1	1.7	1.3

Emission rate (X) of each HM is possible to calculate from proportion, e.g.:

1kg fuel emits 0.001 g of Zinc

19866 kg of fuel emits X g of Zinc

X = 19.866 g/h = 0.006 g/s

In the literature gas exit temperature varies from 150 – 300, we decided to use an average 200 °C.

Gas exit velocity we decided to take constant - 1m/s.

Atmospheric conditions were slightly unstable selected, because in this model we tried to make as practical as possible and atmospheric conditions cannot be ideally stable.

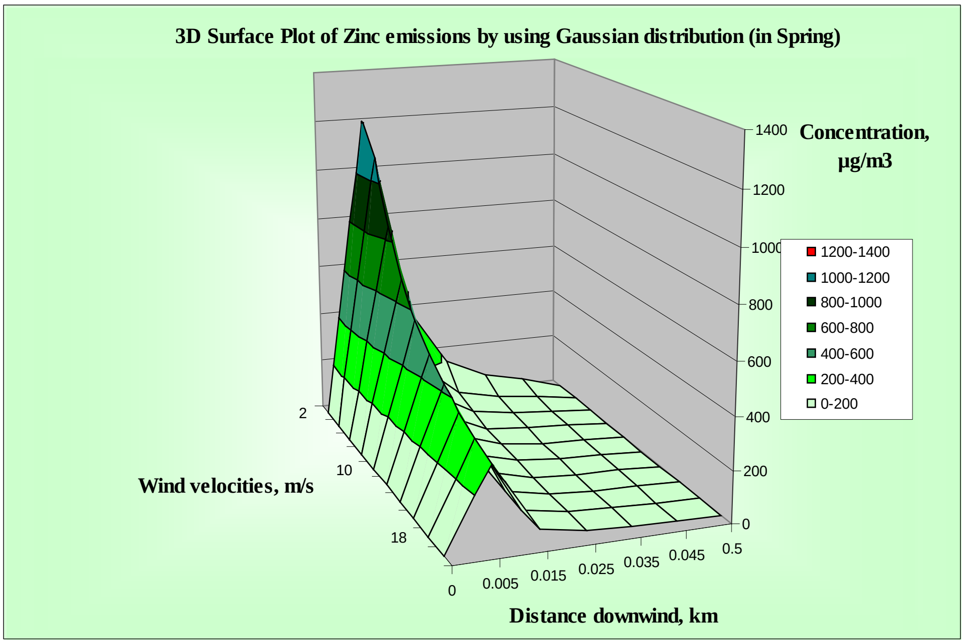
Results from modeling are presented bellow.

4.3 Modeling results

Zinc emissions in spring

From the 4.1 figure is apparent, that the highest emission concentration is at 5 meters from the source, this congruous with the results from collected samples of mosses, moreover, concentration tender to decrease from the source in both (real and modeled) cases.

According to the Lithuanian Hydrometeorological Service under Ministry of Environment, an average of annual wind speed in Vilnius is 4 m/s.



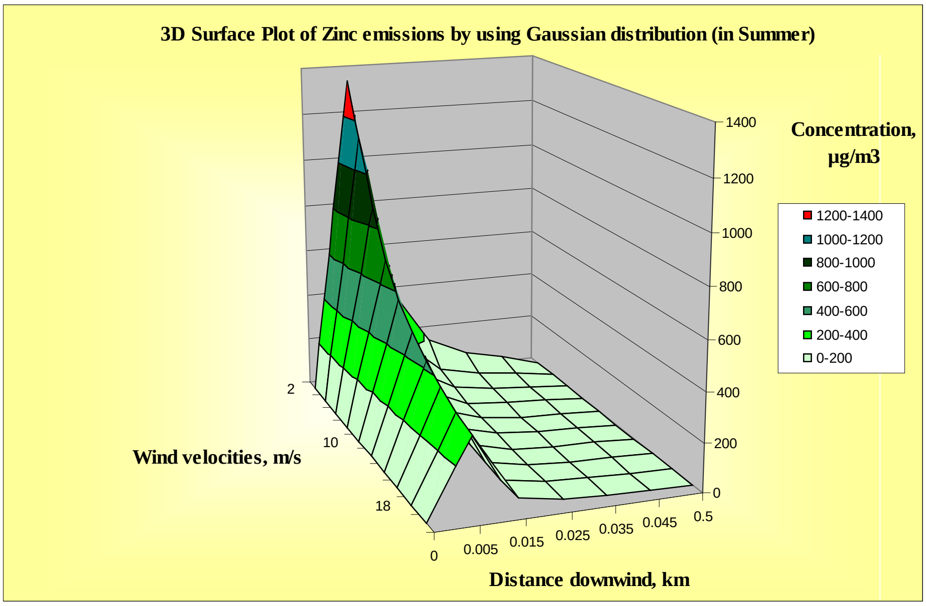
4.1. Figure. 3 D surface plot of Diffusion of point – source pollution of Zn based on Gaussian distribution (Spring)

From 4.1. figure is observable, that accumulation of HM has a strong relationship with the speed of wind. The highest concentrations of HM near emission pollution source in the atmosphere were detected when wind speed was low.

Zinc emissions in Summer

Here situation is almost the same like in diffusion of Zn during spring period. HM had a tendency to decrease with the distance from pollution source.

Wind relationship with concentration is also found the same. But what was interesting, during summer modeling, one more relationship was found. The concentration is tender to increase with the higher temperature. This relationship is presented in 4.4 figure, where concentration at 5 meters reaches more than 1200 µg/m^3 (in red color).



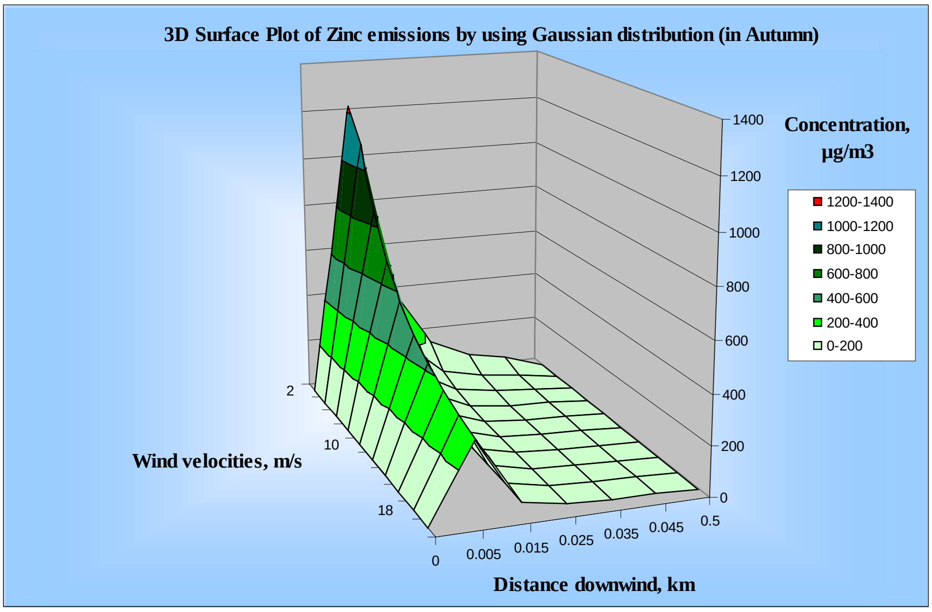
4.2. Figure. 3 D surface plot of Diffusion of point – source pollution of Zn based on Gaussian distribution (Summer)

This tendency is similar to results of analyzed samples, where HM concentration where slightly higher in summer period than spring.

Moreover, the highest concentrations of Zn were found during summer period in practical investigation (see Chapter 3).

Zinc emissions in autumn

Situation in autumn was almost the same like in spring. This was due to similarity of ambient temperature (spring 6 °C and autumn 9 °C).

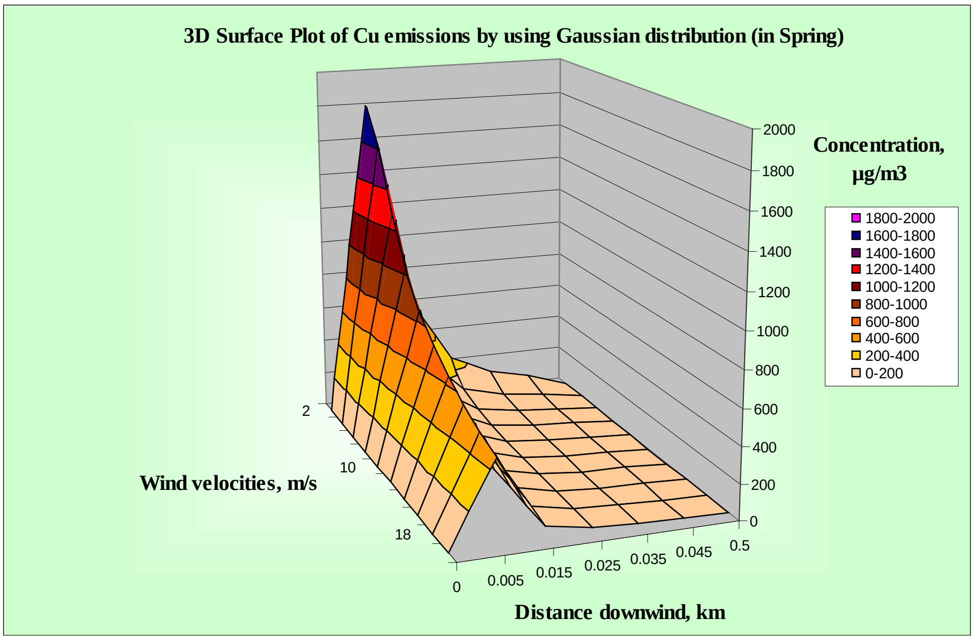


4.3. Figure. 3 D surface plot of Diffusion of point – source pollution of Zn based on Gaussian distribution (Autumn)

Figure 4.3 also presents strong relationship between wind speed and HM concentrations near pollution source. Lowest concentrations were modeled where the speed of wind is high.

Copper emissions in spring

From the 4.4 figure is apparent, that the highest emission concentration is at 5 meters from the source, this congruous with the results from collected samples of mosses, moreover, concentration tender to decrease from the source in both (real and modeled) cases.



4.4. Figure. 3 D surface plot of Diffusion of point – source pollution of Cu based on Gaussian distribution (Spring)

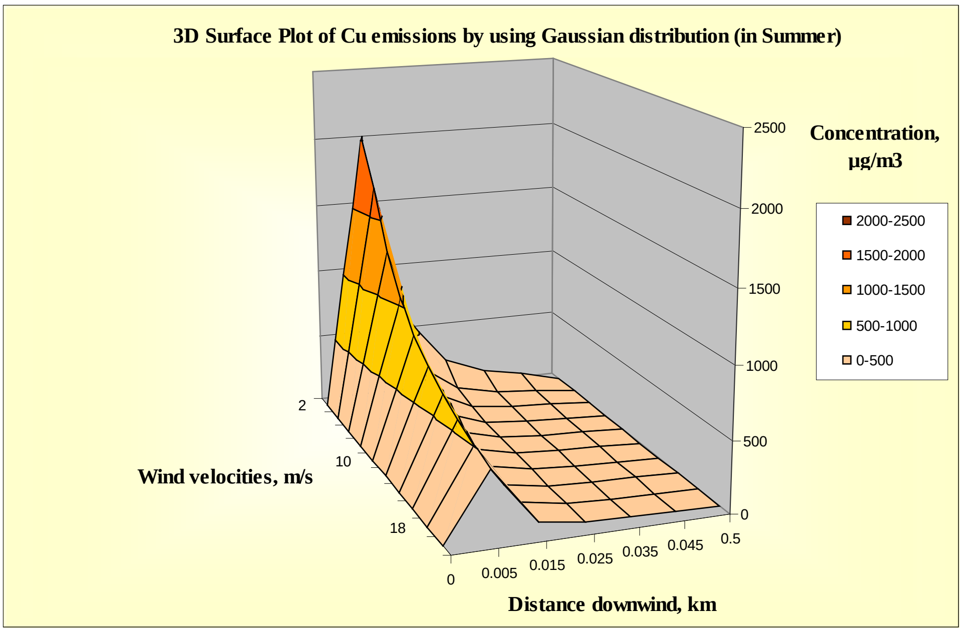
Only one difference was found in modeled results, that Cu concentrations in the atmosphere are higher than Zinc, this discrepancy is due to calculation of emission rate, where we used emission factors to each HM individually. Emission factor for Cu is higher than Zn and this coefficient influenced our calculation.

From 4.4 figure is evident, that the highest concentration of Cu – 1800 µg/m^3 is at 5 meters from the pollution source, when the wind speed is 2 m/s.

The lowest concentration of Cu at 5 meters from pollution source was only – 460 µg/m^3, when the wind speed is 20 m/s.

Copper emissions in summer

As it was expected the concentration of Cu increased due to the higher temperature in summer (4.5 fig.). Strong wind relationship is also detected like in modeling before -the highest concentration of copper was modeled at 5 meters from the source – approximately 1840 µg/m^3, when wind speed is low – 2 m/s.

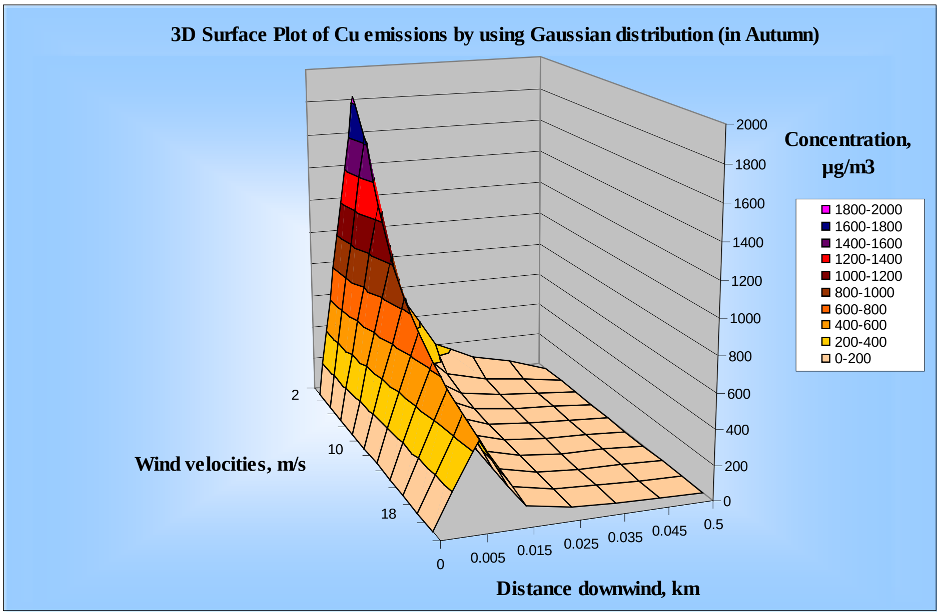


4.5. Figure. 3 D surface plot of Diffusion of point – source pollution of Cu based on Gaussian distribution (Summer)

The lowest concentration – 0.07 µg /m^3 was found at the farthest point from pollution source, when speed of the wind reached 20 m/s.

Copper emissions in autumn

Situation in autumn was almost the same like in spring. This was due to similarity of ambient temperature (spring 6 °C and autumn 9 °C).



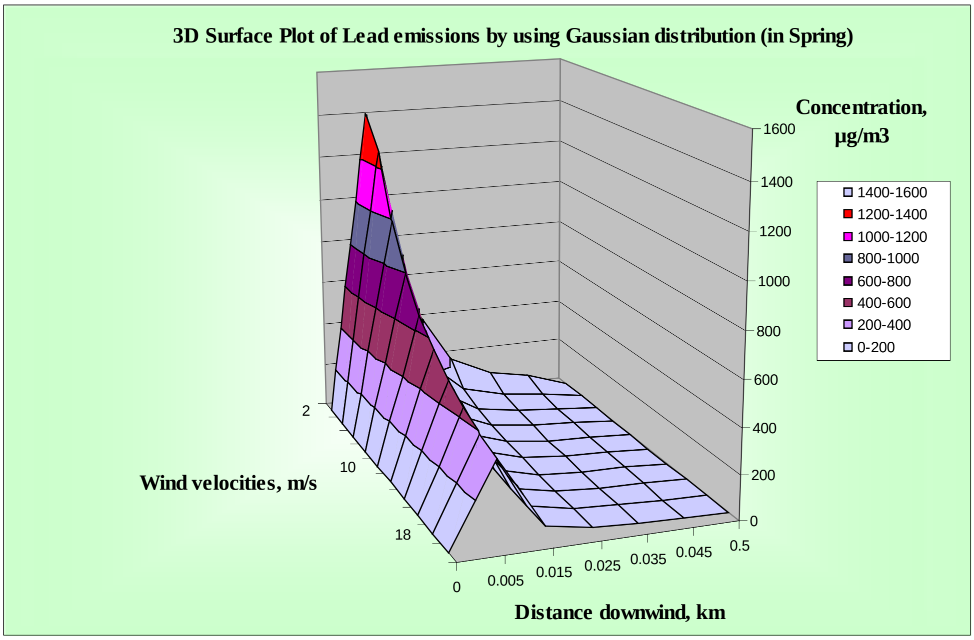
4.6. Figure. 3 D surface plot of Diffusion of point – source pollution of Cu based on Gaussian distribution (Autumn)

The highest concentrations were modeled at the distance of 5 meters and the lowest at 500 meters from pollution source, these pollution dispersion results (with distance concentration of HM decreased) are the same like in investigated samples of mosses (Chapter 3).

Lead emissions in Spring

Lead concentration in spring had the same relationships like all modeled HM before (4.7 fig.).

The highest concentration were found at the distance of 5 meters, the lowest at 500 meters in control point of investigation.



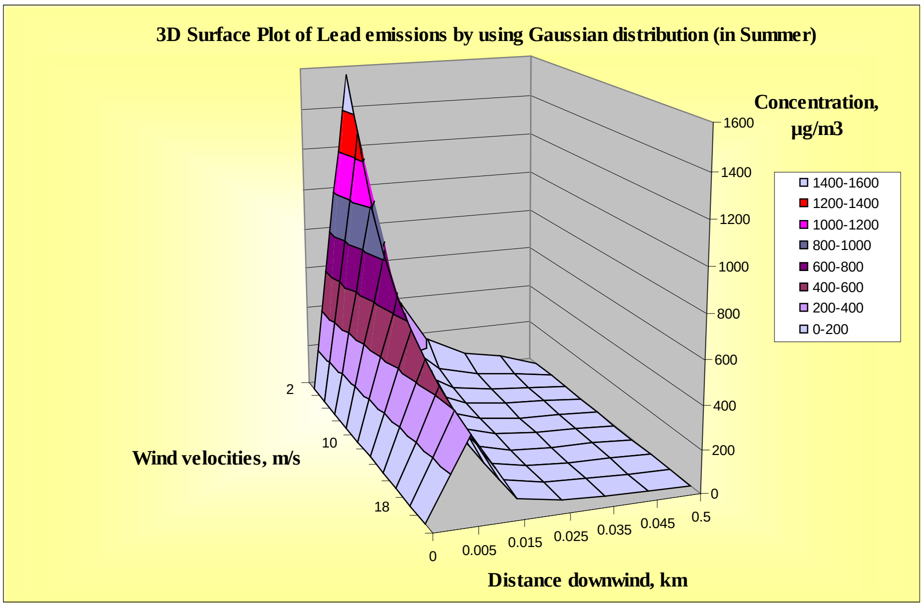
4.7. Figure. 3 D surface plot of Diffusion of point – source pollution of Pb based on Gaussian distribution (Spring)

Due to calculated emission rate with specific emission factor, lead took second place of highly polluted metal. According to the real investigation, lead in mosses was determined only in third place – after Zn and Cu.

Lead emissions in summer

The highest concentration 1600 µg /$m^3$of Pb was determined at 5 meters from the pollution source (4.8 fig.), when wind had the slowest speed.

Concentration was determined higher than in spring or autumn modeling, due to higher temperature of ambient air.

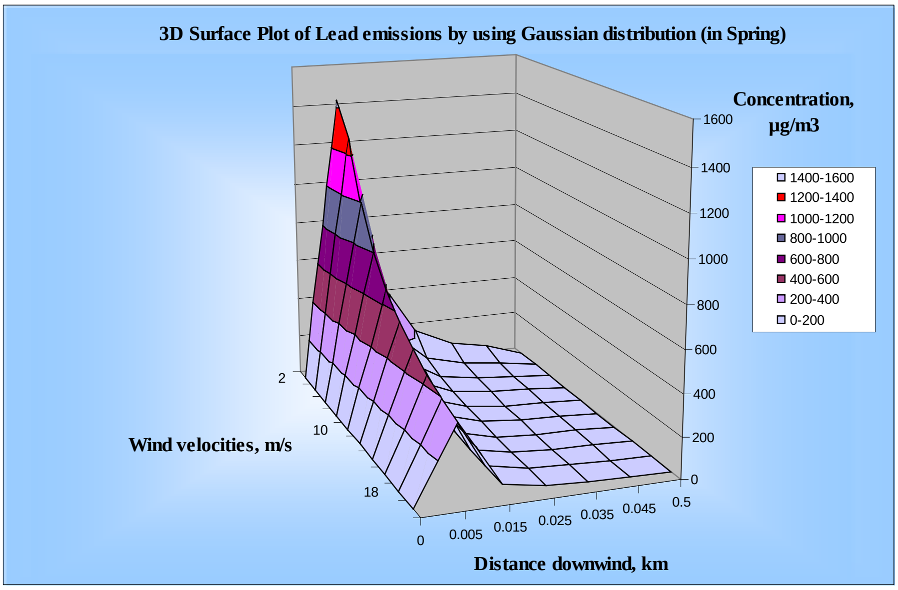


4.8. Figure. 3 D surface plot of Diffusion of point – source pollution of Pb based on Gaussian distribution (Summer)

In comparison with practical results from chapter no. 3 it is possible to find one more similarity, such as concentrations of lead increment in summer.

Lead emissions in autumn

Situation in autumn (4.9 figure) was almost the same like for all modeled HM.

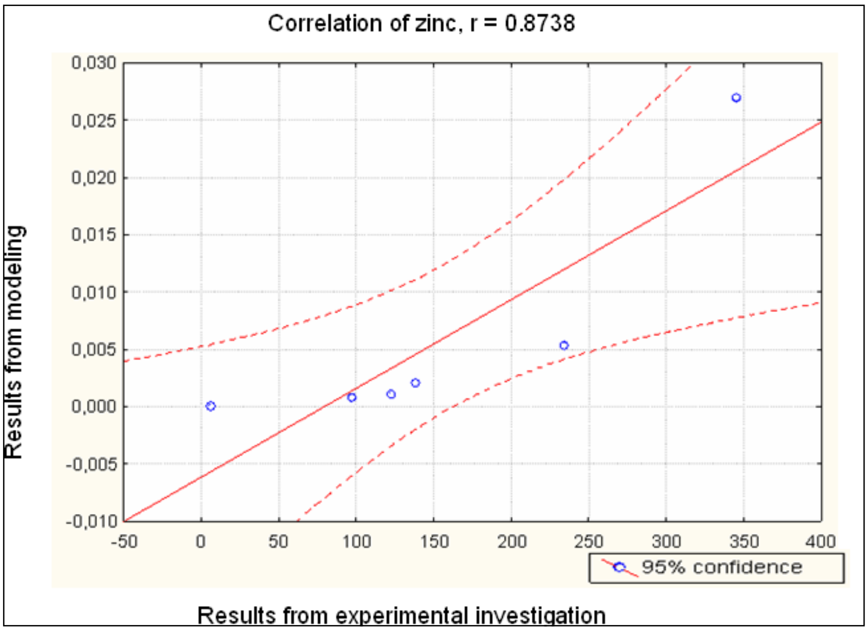


4.9. Figure. 3 D surface plot of Diffusion of point – source pollution of Pb based on Gaussian distribution (Autumn)

Concentration was determined lower than is summer, but higher than in spring. All these changes cause differences of temperature. Concentration of HM had tendency to decrease with the distance from the from pollution source, in our case from the street.

The highest concentration (like for all HM) of Pb was 1200 – 1400 µg /m^3, when the wind speed was 2m/s.

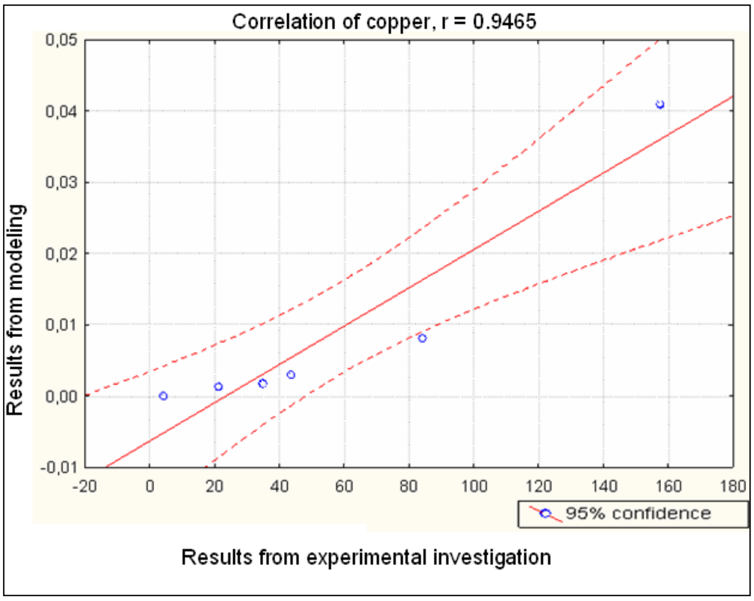
Second step, after all modeling, correlations between data from chapter no. 3 and chapter no. 4 results were performed by the Excel and software STATISTICA (4.10 - 4.12 figure). For determination of correlation Pearson coefficient was used.



4.10. Figure. Correlation between investigated and simulated results of Zinc

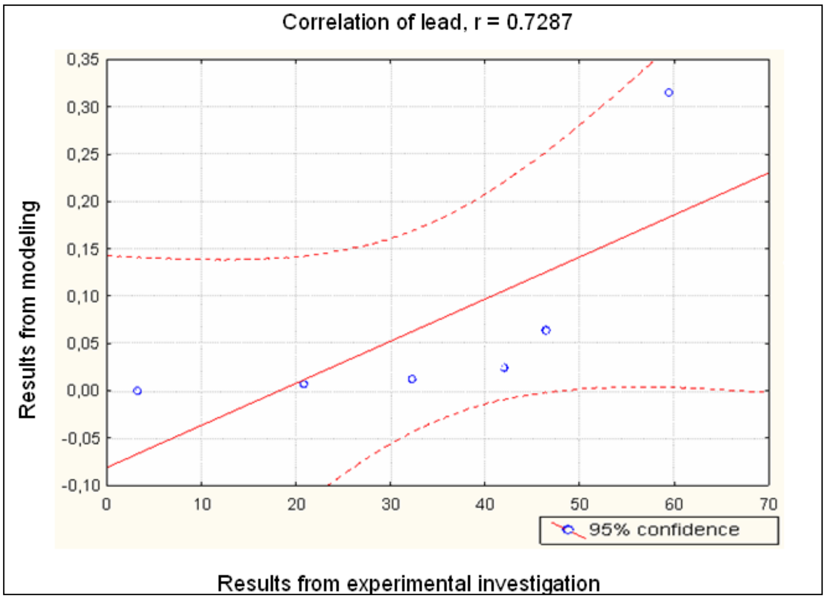
The correlation was zinc was calculated high – r = 0.8738.

The highest correlation between experimental modeling results was calculated for copper, r = 0.9465.



4.11. Figure. Correlation between investigated and simulated results of Copper

Correlation for lead between experimental and modeling results was the lowest for copper, only - r = 0.9465



4.12. Figure. Correlation between investigated and simulated results of Lead

To sum up, correlation between practical data and modeling results was found. This show, that real results and modeling results has strong relationships, moreover, this helps to prove, that high concentrations were determined due to pollution from intensive traffic.

Comparison of real and modeled results

After modeling, real results from Chapter 3 and modeled results from Chapter 4 were compared. The hypothesis of this calculation would be – traffic influences concentration in mosses, therefore in order to get clear result of transport impact, from all concentrations at different distances we should make a subtraction of background pollution, for this case :

Concentration in mosses - concentration of control sample = Concentration of HM caused by transport.

From this we can make an equation:

$$C_{\text{in mosses}} = K \cdot (C_{\text{modeled results}})^{n} \quad (4.2)$$

Where

$C_{\text{in mosses}}$ – Concentration of HM in mosses from modeling results;

K – Coefficient, which converts results from mg/m^3 to mg/kg;

n – Empirical coefficient;

After calculations we got, that convert coefficient K = 300 and n = 0.346. All results and formulas for calculations are presented in 4.3 table bellow. For control sample errors were not calculated, because values of control sample performed as background pollution of HM in formula above.

4.3. Table. Comparison of real and modeled results of Zinc

Distance	(t, v)	Real results from experiment	Modeled results, mg/m3	Error	Converted results from modeling
m	°C; m/s	mg/kg	**mg/m^3**	**%**	**mg/kg**
		d	**e**	**f**	**g**
				f= (d-g-m) ·100 /(d-m)	$C_{in\ mosses} = K \cdot (C_{modeled\ results})^n$
Spring period					
5	6; 4	339.96	1.08857	-1.85908	339.83347
15		210.47	0.22379	3.70181	196.59083
25		139.47	0.08475	-5.51755	140.49345
35		118.44	0.04389	0.20111	111.89152
45		89.52	0.02674	-13.3082	94.26109
500		6.33	0.00023	-	-
Summer period					
5	27;4	352.14	1.13358	-1.11259	344.63114
15		273.75	0.22480	24.97441	196.89790
25		131.55	0.08489	-16.9061	140.57256
35		128.01	0.04393	4.10017	111.92373
45		110.74	0.02675	5.19154	94.27753
500		5.08	0.00023	-	-
Autumn period					
5	9;4	344.652	1.09489	-2.15008	340.51526
15		217.816	0.22394	4.78291	196.63470
25		143.71	0.08477	-6.11661	140.50475
35		123.188	0.04390	-0.01084	111.89612
45		90.877	0.02675	-18.4616	94.263436
500		6.17	0.00023	-	-

From 4.3 table, we can see, that modeled results are quite similar to investigation results, differences vary 0.01 to 25 %.

DISCUSSION

In order to evaluate investigation results, a mathematical model based on Gaussian plume was performed. All data analysis were made in three main steps: mathematical modeling, calculation of correlation and, finally, in order to make sure that results from mathematical modeling and results from chapter no.3 can be compared, we decided to make one more - error calculation for just for Zn.

Zinc was chosen, because in real results (of Chapter 3) Zn concentrations were the highest in mosses.

Simulation model showed few strong important relationships from conditions of the atmosphere. First one would be wind speed – the slower speed – the higher concentration near emission source was detected. Second one would be - the higher temperature – the higher concentration of pollutants, especially near pollution source was detected. That is why all models from summer period had the highest concentration of HM.

On the other hand, model does not include rain and snow precipitation. What is more, emission factors for all simulated HM were calculated and other input data was chosen according to an average for one passenger automobile, which is the main reason why we cannot expect accurate results.

It is important to note, that mathematical model was prepared for one passenger car, in order to get main relationships between HM dispersion and atmospheric conditions.

It would be very inaccurate results if we try to model for all 4300 vehicles, because all vehicles has different technical characteristics, such as old or new car, type of vehicle (passenger, bus, etc.) engine and fuel type, different speed, different situations in traffic (peak hours, etc.).

CONCLUSIONS

1. For monitoring of heavy metal atmospheric deposition it is popular to apply terrestrial mosses. The most important environmental features of mosses as a good tool of air pollution deposition reflection are: mosses do not have any roots, their surface is large, they grow in wide-spread population in groups, they have long life cycle, they survive in the high-polluted environment, they are able to obtain nutrients from wet and dry deposition and clearly reflect the atmospheric deposition. All these environmental characteristics prove that mosses are a good tool in airborne pollution monitoring, especially in HM monitoring.

2. Sampling and chemical analysis of mosses were fast and not complicated, it was easy to collect samples, and there was no need for any special equipment (one more advantage for using mosses as bioindicator). Chemical analysis was performed in Vilnius Gediminas Technical University, at laboratory of Environmental Protection department.

3. *Pylaisia polyantha* - specie of moss was identified according to Lithuanian catalogue of mosses. Morphological description (such as color, form of capsules and leaves, habitat) and pictures of mosses perfectly fitted to our collected moss.

4. Samples of mosses accumulate high amounts of precipitation, according to the calculations, moisture in *Pylaisia polyantha* mosses were 13.82% - 60.07 %. Results of moisture content shows that it is important to take a big amount of samples during sampling process, because after drying of mosses, the sample can be lost due to underweight. According to the measurement, the ratio of mass - loss in samples of mosses was 73.28% - 83.18%. Calculation proves that mosses consist of large amount organic compounds.

5. Investigation results of this work clearly present a strong traffic-related gradient - HM concentrations in samples of mosses tender to decrease with distance from the Geležinis Vilkas street. At the distance 5 and 15 meters from the Geležinis Vilkas street HM concentrations were considerably high and it reveals that the mosses *Pylaisia polyantha* near intensive traffic are highly polluted. Accumulations of HM in samples of mosses *Pylaisia polyantha* were found in this order: Zn > Cu > Pb > Cr, Ni. According to the literature research all determined HM clearly represents traffic pollution: *Zn* - originating from: wearing of brake lining, losses of oil and cooling liquid, wearing of road paved surface,

wearing of tyres, corrosion of galvanized steel safety fence and other road furniture; *Cu* concentrations come from the engine as metal wear or as chemical compound dispersed into the oil, also from wearing brass or bronze parts, copper bushings and from bearings, either cooler cores can be as a copper leaching source for diesel cars; *Pb* - may still occur in exhaust gas coming from the fuel and from worn metal alloys in the engine; *Cr* - used oil or from wearing of. piston rings; Ni comes from fuel and virgin engine oil.

6. Sample of mosses were collected three times in different sessions (spring, summer, autumn). There were no significant changes in HM concentrations between these periods. Results of different seasons vary 3 – 10 mg/kg for all determined HM. This not significant variation could be due to short period of investigation.

7. The highest concentration accumulated in samples of *Pylaisia polyantha* was Zinc, in 5 meters distance from the street the biggest concentration was found during summer season - 352.14 ± 6.52 mg/kg. At the distance of 15 meters from the street the highest concentration was also detected in summer season – 273.75 ± 8.40 mg/kg. At 25 meters from intensive traffic 143.71 ± 9.52 mg/kg in autumn season. The highest concentration of Zn at the 35 meters from intensive traffic flow was 128.01 ± 11.98 mg/kg determined. At 45 meters from the street mosses contain 110.74 ± 10.15 mg/kg of zinc and this was the highest concentration, which was determined in summer season. In sample of control at 500 meters were determined 6.325 ± 2.13 mg/kg of Zn.

8. The biggest accumulation of Cu was also found near the street. At 5 meter from the road mosses the highest concentration of copper was found in autumn season - 161.91 ± 3.53 mg/kg. At 15 meters from the street the highest concentration in mosses were 85.72 ± 5.47 mg/kg. At 25 meters from intensive traffic the highest concentration of Cu was 43.52 ± 3.40 mg/kg in autumn season. At 35 meters – 36.07 ± 5.07 mg/kg of copper from spring investigation. With the distance from the road the concentration of copper decreased significantly, at the 45 meter from the street in samples of *Pylaisia polyantha* the highest concentration were 22.405 ± 4.47 mg/kg found from autumn investigation. In sample of control at 500 meters were determined 6.03 ± 2.15 mg/kg of Cu (from spring investigation, it is the highest concentration from all seasons).

9. The biggest concentrations of lead were determined at distance 5 – 25 meters from the high intensive traffic street, the highest concentrations of lead were found during autumn season.

The highest amounts accumulated in 5 meters – 61.23 ± 1.99 mg/kg. At the 15 meters from the intensive traffic flow, the highest concentration of lead was 47.42 ± 1.01 mg/kg. In 25 meters – 44.33 ± 1.64 mg/kg. At the 35 meters from the street the highest concentration of lead in samples of mosses was 33.92 ± 1.50 mg/kg. At 45 meters distance, the amount of Pb accumulated in mosses was 20.88 ± 3.81 mg/kg. Only the highest concentration of lead in control sample was found during spring investigation – 3.24 ± 1.09 mg/kg.

10. The biggest concentration of Cr was also found mostly near the street. The biggest concentration at 5 meters was 32.04 ± 0.75 kg/mg during autumn investigation. At the distance of 15 meters highest concentration of Cr was 26.37 ± 0.85 mg/kg in autumn season. At the distance of 25 meters the highest Cr concentration decreased till 13.93 ± 1.13 mg/kg during spring investigation. The highest concentration of chromium at 35 meters from intensive traffic – 12.01 ± 0.85 mg/kg (in autumn). At the final distance from the road, the biggest Cr concentration was 10.57 ± 0.92 mg/kg. In a control sample at 500 meters from the road the highest concentration of Cr was 2.85 ± 1.02 mg/kg (summer).

11. The highest concentration of Ni at 5 meters from the street was 32.23 ± 1.62 mg/kg (in autumn). At 15 meters from the road the highest concentration of nickel was 26.41 ± 1.05 mg/kg during autumn investigation. At 25 meters from the street the highest concentration of Ni in samples of mosses was 20.21 ± 0.90 mg/kg (autumn). In 35 meters from intensive traffic the highest concentration was determined in autumn investigation – 16.71 mg/kg. At the distance of 35 meters from the street, the biggest amount of Ni was found 11.76 ± 1.14 mg/kg (during autumn experiments). In the sample of control the highest concentration of Ni was determined in spring period – 4.11 ± 0.84 mg/kg.

12. At the final chapter – mathematical modeling based on Gaussian plume is presented. Modeling was performed only for the three main pollutants (Zn, Cu and Pb), where some more clear changes were expected. HM emission dispersion from pollution source was calculated only for one vehicle. This was done in order to reach as clear as possible relationships between environment conditions and dispersion of different HM emission from vehicle exhaust fumes pipe. It was not logic to calculate total pollution, caused by high intensive traffic, because there are no accurate data about different types of vehicles, for example: engine type, fuel type, old or new vehicle, what was the speeding of vehicle and other factors, which could have an influence to the final results. From our modeling based Gaussian plume, we detected, that concentration of HM tender to decrease with the distance

from pollution source, that is the same tendency like in practical our results. Moreover we found out strong relationship between wind speed and HM concentration, the slower speed, the higher concentration near pollution source. Other interesting relationship was detected during temperature changes – the higher temperature – the higher concentration near pollution source. Accumulation order of HM was different from real results – Cu < Pb < Zn. This is due to inaccurate calculation of different HM emission rates, for this calculation individually emissions factors (the higher emission factor – the higher emission rate) were used.

RECOMMENDATIONS

1. This work proves that mosses can be a suitable biomonitoring tool for heavy metal investigations in the atmosphere; therefore they should be used in future. It would be recommended to perform a longer biomonitoring in order to get more information about air quality and HM accumulation in mosses from transport and other pollution sources. This could help to detect, control and determine more accurate relationships of HM dispersion and accumulation in mosses.

2. What is more, according to the investigation results (Chapter 3), air in Geležinis Vilkas street is highly polluted with HM. Government should pay attention on traffic intensity (maybe to direct some amounts of vehicles to other streets) in that part of Geležinis Vilkas street, because this street is between people living area and the biggest park in Lithuania – Vingis park.

3. There are no special program for modeling HM dispersion and accumulation of pollutants in mosses. It is hard to apply a model for mosses, due to their morphological properties such as rootless. For future modeling should more developed model for mosses, where extra data analyzed and included, for example, rain and snow washouts, changes of wind direction, relief and nature of investigation area –than model could reflect more accurate results.

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1 APPENDIX

List of presented papers

Participation in conferences:

Participated at 13th Conference of young Lithuanian scientists „MOKSLAS – LIETUVOS ATEITIS“, a poster presentation - INVESTIGATION OF ATMOSPHERIC POLLUTION ON HEAVY METALS APPLYING MOSSES AS BIOINDICATOR.

Participated at 8th International Conference „Environmental Engineerig“, a poster presentation - DETERMINATION OF HEAVY METALS IN MOSSES (*PYLAISIA POLYANTHA*) ALONG THE HIGH INTENSIVE TRAFFIC FLOW IN GELEŽINIS VILKAS STREET.

2 APPENDIX

List of publications

Publisheв articles:

Blagnytė, R.; Paliulis, D.; 2011. Research into Heavy Metals Pollution of Atmosphere Applying Moss as Bioindicator: a Literature Review **-** *Aplinkos tyrimai, inžinerija ir vadyba, 2010. Nr. 4(54), P. 26-33.*

Blagnytė, R.; Paliulis, D.; 2011. DETERMINATION OF HEAVY METALS IN MOSSES (*PYLAISIA POLYANTHA)* ALONG THE HIGH - INTENSIVE TRAFFIC FLOW IN GELEŽINIS VILKAS STREET (VILNIUS, LITHUANIA) **-** *Selected paper at 8th international conference May 19–20, 2011, Vilnius, Lithuania.*

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