MAPPING OF MAIN SOURCES OF POLLUTANTS AND THEIR TRANSPORT IN THE VISEGRAD SPACE

PART I: EIGHT TOXIC METALS

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Report of the expert group on bio-monitoring the atmospheric deposition loads in the Visegrad countries

PROJECT 11007-2006-IVF

Visegrad Fund

www.visegradfund.eu

VÚKOZ	FMFI KU	ÚKE SAV	IB PAN	FEAS SIU

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Printed in 2007

Výzkumný ústav Silva Taroucy pro krajinu a okrasné zahradnictví, v. v. i.,
Průhonice, Czech Republic

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The evaluation of results from the international bio-monitoring campaign 2000 and the preparation for print was carried out in the frame of the project 11007-2006-IVF. The works on the project and the printing of this report was financially supported by:
International Visegrad Fund, Bratislava,
SILVA TAROUCA Institute for Landscape and Ornamental Gardening, Průhonice, Czech Republic,
Institute of Landscape Ecology, Slovak Academy of Science, Bratislava, Slovak Republic,
Faculty of Mathematics, Physics and Information, Comenius University, Bratislava, Slovak Republic,
Department of Ecology, Institute of Botany, Polish Academy of Science, Kraków, Poland,
Faculty of Environmental and Agricultural Sciences, SZENT ISTVÁN University, Gödölő, Hungary.

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Publisher: SILVA TAROUCA Research Institute for Landscape and Ornamental Gardening, Průhonice, Czech Republic
Print: KLEMO spol. s r. o., (Ltd.), Zvolen, Slovak Republic

Cover photographs provided by I. Suchara and B. Godzik

This report should be cited as: Suchara I., Florek M., Godzik B., Maňkovská B., Rabnecz G., Sucharová J., Tuba Z., Kapusta P. (2007): Mapping of main sources of pollutants and their transport in the Visegrad space. Part I: Eight toxic metals.- Expert group on bio-monitoring the atmospheric deposition loads in the Visegrad countries, Průhonice, Výzkumný ústav Silva Taroucy pro krajinu a okrasné zahradnictví, v. v. i., 127 pp.

ISBN 978-80-85116-53-3 (brož.)
ISBN 978-80-85116-55-7 (soubor)
ISBN 978-80-85116-54-0 (2. sv., CD-ROM)

Printing 500

September 2007

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PICTURES (distribution of element content in mosses across the V4 countries and related data) referred in the Part I and in the Part II of this report are available together at the following address: **http://www.vukoz.cz/dokumenty/publikace/MOMSOP_II.zip**

1 INTRODUCTION

Air pollution ranks among important environmental problems occurring in Central Europe and other early-industrialized parts of the world for about two centuries. Increased concentrations of air pollutants and associated high atmospheric deposition loads cause, beyond all doubt, health injuries, diminish forest and crop production, reduce biodiversity, recreational potential of the landscape, cause corrosion of the materials of technical objects, historical monuments and sculptures, etc. Increased deposition levels of nutrients trigger eutrophication, may cause extinction of extremely sensitive plant and animal species, disintegration of ecological stability of ecosystems, and so on. Moreover, atmospheric pollutants can be transported in the air to a long distance and fall down hundreds or thousands kilometres far away from their pollution sources. Toxic and hazardous elements from atmospheric deposition can be bound on surface of soil or forest floor humus particles and thus can become a hidden threat for the local environment, residents, recreational visitors, consumers of local food, etc.

No wonder that the air pollution has become a global issue. Individual countries, their blocks and international associations have introduced air pollution regulation acts, registers of pollution sources and emitted amount of pollutants, institutions dealing with monitoring the air pollution and deposition levels. Governments support projects studying harmful effects of air pollution and introduction of remediation measures.

The Visegrad countries (V4) included a co-operation into the field of environmental protection and risks as a separate article in the official Content of Visegrad Cooperation approved at the Prime Ministers' summit held in Bratislava on 14th May, 1999.

All countries of the Visegrad Group attend the international campaigns on biomonitoring the current levels of atmospheric deposition loads using moss analyses in the framework of the campaigns co-ordinated mainly by the Environmental Monitoring and Data Group, which operates in the Nordic Countries, and later by the co-ordination centre of the international programme UN/ECE ICP-Vegetation, in Bangor, UK. However, the distribution of the atmospheric deposition loads has been presented and commented in national reports, which are usually not so easily available. European surveys summarizing the biomonitoring results obtained from all participated European countries in five-year intervals have been very compressed and only about 10 obligatorily investigated elements had been processed in these surveys.

Considerable amounts of the national biomonitoring data concerning many elements have been obtained. However, none of the reports evaluates the distribution of the atmospheric deposition loads of both the obligatorily and optionally investigated elements in the Visegrad space that has been compiled and presented up to now. Knowledge on the distribution of current atmospheric deposition loads in Central Europe is surely important, for example, for the localization of persistent major emission sources, an effective long-term utilization of landscape, protection of health, proper supporting of landscape remediation programmes, etc. That is the reason why participants of the grant 11007-2006-IVF decided to evaluate the national biomonitoring results in order to reveal current pollution sources and distribution of atmospheric deposition loads of 53 determined elements in the Visegrad space. However, the distribution of only 8 elements in mosses was detected in all V4 countries. In order to economize the limited support for presentation of the obtained results two reports are being edited in parallel. Printed report (Part I) presents evaluation of bio-indicated distribution of 8 toxic elements in the V4 countries. The second report (Part II) presented in CD form evaluates the bio-indicated distribution of atmospheric deposition loads of all 53 investigated elements, mainly on the territory of Czech and/or Slovak Republics. Most of the presented data have never been presented anywhere. These reportrs (Part I and Part II) differ only in number of commented elements. Readers of the Part II will give complete information about the 8 elements discussed in the Part I. Hence the both parts of this report can be utilised independently. The authors wish these reports would contribute to the further protection and improvement of the environment in the Visegrad space.

2 THEORETICAL PART

2.1 Air pollution

2.1.1 Sources of air pollution

Natural and anthropogenic sources of air pollution are being generally recognised. The most common natural sources of air pollution, such as volcanoes, conflagrations of vegetation, formation and spreading of sea spray, weathering and erosion of rocks, etc. are usually less powerful than current anthropogenic sources. Extraction and processing of raw materials, industrial combustion of fossil fuels, industrial production of merchandises and running of the means of transport belong to the most important anthropogenic sources of air pollution. Man indirectly triggers air pollution due to deforestation, ploughing up large areas, farming, launching satellites, making warfare, etc.

Typical major air pollutants are SO_x, NO_x, CO_x, soot, ash and fine particles, fluorine, chlorine, persistent organic pollutants, heavy metals and others. Combustion of coal releases mainly gaseous pollutants SO_2 and CO_2. However, coal, especially lignite, may contain bigger amounts of trace elements. Due to the industrial combustion of enormous amounts of coal in furnaces and coal power plants, significant amounts of various elements and their compounds (Al, Fe, Ba, Cd, Fe, Hg, Mn, Pb, Sb, Zn and others) are emitted into the atmosphere. These elements are mainly associated with suspension of a fine particulate matter. Similar elements and moreover, for example Ni and V are emitted during combustion of fuel oils. Except for gaseous inorganic and organic pollutants some elements, such as As, Sb, Se and V are bound with flying dust and soot particles in the emitted smoke.

Cars emit elements being present in additives of heat resistant oils, particles released by friction of moving car components and during corrosion of metallic parts, paint covers as well as particles from catalytic converters (Cu, Fe, Ni, Zn, Cr, Mo, Pt, Pd, Rh, V, W, Zn, etc.). Very fine or ultra fine particles (PM, UF) released by oil-fired engines cannot be expelled from a human body.

Extraction and processing of raw materials cause dustiness. Soil and dust particles contain high concentrations of typical lithogenic elements (Al, Be, Cr, Fe, Ni, Pr, Si, Ti, U, Y, etc.) Dust from extracted rocks and minerals may contain many elements in various combinations of unexpected health effects. Utilisation of old waste deposits contaminates the surroundings by multi-elementary atmospheric deposition.

Steel, non-ferrous smelters and secondary smelters emit many elements added to noble steels and alloys. Steel works are main sources of the emission of Co, Cr, Fe, Mn, Mo, Ni, W and other elements. Chalcophile and other elements are emitted from non-ferrous smelters and foundries (Ag, As, Cd, Hg, In, Ni, Pb, Se, Sb, Sn and Zn). Production of aluminium is accompanied by increased emission of Al, F, Na. Waste incineration plants emit a good deal of toxic and dangerous air pollutants, such as heavy metals, persistent organic pollutants (POPs), volatile organic compounds (VOC) and other pollutants.

After nuclear weapons tests and accidents of nuclear power plants atmospheric deposition levels of radionuclides (e.g., ^{239}Pu, ^{240}Pu, ^{137}Cs and ^{90}Sr) substantially increased.

Yearly balances of chosen emissions are available in the European Pollutant Emission Register (EPER) available at the following address:
http://eper.ec.europa.eu/eper/documents/EPER%20Review%20report, %20final.pdf.

Registration of important sources of air pollution has been the issue of a great interest of the European Union (http://ec.europa.eu/environment/air/index_en.htm). The EC Regulation no. 166/2006 established the European Pollution Release and Transfer Register (E-PRTR) amending Council Directives 91/689/EEC and 96/61/EC, which deals with about 50 pollutants including some heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn).

2.1.2 Atmospheric deposition and harmful effects

Pollutants present in the atmosphere in gaseous form and adsorbed or included in solid or liquid aerosols are spontaneously deposited on the ground ($\mu g.m^{-2}.year^{-1}$) due to gravitation force of the Earth. The so-called dry deposition occurs mainly in climatic dry regions or dry period without assistance of rains. Coarse particles suspended in the atmosphere are fast deposited through sedimentation (Stokes´ law). This phenomenon appears mainly markedly in the close surroundings of particulate pollution sources. However, deposition speed of gaseous pollutants and of very fine particles (PM) or ultra fine particles (UFP) can be extremely slow. That is the reason why elements associated mainly with fine aerosols (e.g., Hg, Pb) can be transported and deposited thousands kilometres far from their sources. It is considerably difficult to determine the atmospheric dry deposition levels of individual elements. Usually concentrations of pollutants are measured at different heights above the ground and additional physical and chemical parameters of the atmosphere and ground must be determined. Due to low concentrations of pollutants and expensive and time-consuming measurements the dry deposition loads are only rarely measured at special measuring stations. Frequently the dry deposition is assessed through a subtraction of throughfall and wet-only depositions (see later).

Any rain episode can substantially increase the deposition speed of gaseous and particulate matter air pollutants. The wet form of atmospheric deposition prevails in areas affected by increased annual precipitation sums. The total precipitation sums usually significantly and positively correlate with the altitude on the territory of Central Europe. However, air pollutants are washed out from the atmosphere most at the beginning of precipitation episodes and during dense and very fine rain. Also mist can effectively adsorb air pollutants. Aerosol particles and gaseous pollutants with very small deposition speed are more quickly deposited due to the effect of precipitation than through the wet deposition. At measuring stations usually wet-only and bulk atmospheric deposition loads are measured. Concentrations of elements determined in rainwater, caught exclusively during a rain episode (wet-only collectors), are related to the so-called wet-only deposition levels. If atmospheric deposition (wet and dry) is collected for a given period in permanently opened collectors, determined concentrations of elements in the collectors are related to the so-called bulk deposition loads. Content of collectors is usually analysed in daily, weekly, biweekly or monthly periods. Bulk deposition values are higher than wet-only values because the bulks include wet-only deposition altogether with some part of dry deposition. The average interannual variation ranges between 3–9% for dry and about 20% for wet deposition in Europe (Andersson et al. 2007) due to meteorological variability.

For special purposes also throughfall and stemflow atmospheric deposition are determined. Throughfall deposition is determined by the analyses of deposits in collectors situated under tree canopy. Rainwater passing through tree crowns washes off dry deposition, which had been caught on leaves and twigs in the past. The stemflow deposition loads are related to the element contents determined in specimens of water coursing along tree trunks.

More details concerning the determination of individual forms of atmospheric deposition loads can be found, for example, in Manual for the ICP Integrated Monitoring Programme:
(http://www.miljo.fi/default.asp?node=6329&lan=EN).

Direct and indirect harmful effects on human health, ecosystems and materials caused air pollution and atmospheric deposition loads are known mainly for major pollutants. The harmful effects appear when concentration of pollutants exceeds a limit value (maximal permission concentration, critical loads, lower and upper thresholds, etc). These limits may differ for children and adults, for individual ecosystems and materials.

Well known are deaths associated with an acute exposition to high SO_2 concentrations during an urban smoke episode in London in 1952. Recently, composition of air pollutants has changed. Fine particulate matters (UF, $PM_{2.5}$ – PM_{10}), troposphere ozone, nitrogen oxides, hydrocarbons and heavy metals have been under current heath concern:
http://www.euro.who.int/InformationSources/Publications/Catalogue/20070323_1
http://www.euro.who.int/document/E88189.pdf
http://www.euro.who.int/document/e79097.pdf
http://www.euro.who.int/document/e78963.pdf.

Increased concentration of the pollutants above may trigger chronic eye, lung and skin irritations, neurological and reproductive disorders, cardiovascular disorders, asthma attacks, chronic bronchitis, premature deaths, lung, stomach and skin cancers, etc. (e.g., Holgate et al. 1999, Peters et al. 2001, Järup 2003, Krzyzanowski et al. 2005, Ming-Ho 2005). Potential harmful effects of heavy metals and air pollution on child and human health in Central and Eastern Europe were investigated frequently (e.g., Fitzgerald et al. 1998, Wcisio et al. 2002, Willeke-Wetstein et al. 2003, Hennighausen 2004). However, except for notoriously known toxic elements such as Hg, Cd, Pb, Ni, Cr, there is still shortage of knowledge concerning the chronic health effects caused by potentially hazardous elements (e.g. Be, Tl, U) and synergistic effects of multi-elementary forms of pollution.

Also biota and ecosystems are damaged by increased air pollution and atmospheric deposition, when safe concentration or critical deposition limits are exceeded (Landis and Ming-Ho 2003). Extinction of epiphytic lichens (“lichen desert”) in industrial areas or in cities, e.g., in central part of London, was stated in the 1960s. Large-scale standing dead coniferous forest in so-called Black Triangle I area (Northwestern Bohemia, Czech Republic) caused mainly by extremely high SO_2 concentrations are commonly known (Hawsworth and Rose 1970, Schulze 1989, Lomský et al. 2002). Some air pollutants cause specific injury of vegetation. Typical marks of damage bioindicators can reveal not only effect of the relevant pollutants but also even exceeding of threshold concentrations. For example, concentration of fluorine >5 $\mu g.m^{-3}$ can cause reddish brown necrotic strips along bifacial leaves of species of *Gladiolus*, *Freesia* and other genera; ozone concentrations >7 $\mu g.m^{-3}$ cause appearance of silvering or bronzing spots at upper side of leaves (e.g., bean and tobacco plants or tulip and ash trees); ammonium concentrations >1 $mg.m^{-3}$ cause dark brown or blackish colouration of tree leaves, etc. (Jacobson and Hill 1970).

Serious financial losses caused by diminished yields and crop quality in the areas caused by a new type of pollution (O_3 and NO_x) have been disclosed recently not only in Northern America but in the whole Europe and in industrialized Asia as well (Emberson et al. 2003, Wang and Hauzerall 2004, Ashmore 2005).

Some pollutants can form in the atmosphere strong inorganic acids (e.g., H_2SO_4, HNO_3, HCl, etc.). Atmospheric deposition of high concentration of protons (H^+) affects as acid rains. Acid rains damage plants and many water animals, trigger degradation (podzolization) of soil covers, release toxic and hazardous elements into soil solution etc. (Hůnová et al. 2005, Hrkal et al. 2006, Brimblecombe et al. 2007). Effects of acid rains have been recently rather diminishing in Central Europe.

On the other hand eutrophication of the environment caused by increased nitrogen deposition is getting fatal for many ecosystems. Atmospheric deposition of plant nutrients, mainly reactive nitrogen compounds (NO_3-N, NH_4-N) has dramatically increased. High nitrogen concentration being available in the environment is blamed for increased accumulation of nitrogen in plants, decreased resistance against diseases and harmful abiotic factors (for example windstorms). Sensitive species are getting dead through nitrogen metabolism disorders (for example species of peat bog, moors and epiphytes). More resistant species grow faster under nutrient rich conditions and win competition with less adaptive species in oligotrophic stands. Critical loads of nitrogen deposition for the most sensitive ecosystems were estimated to be 4–18 kg $N.ha^{-1}.year^{-1}$, while current deposition levels of total nitrogen in Central and Western Europe reach 40–120 $kg.ha^{-1}.year^{-1}$ (e.g., Emmett 2007). No wonder that 70% of native plant species are getting rare or endangered by extinction. Protection of habitats and their biodiversity is one of the important programmes of the EU. For more details see the Directive 92/43/EEC (http://ec.europa.eu/environment/nature/home.htm).

Many metals are common complements of dry and wet atmospheric deposition. Unfortunately, only a few the most toxic metals (Hg, Cd, Ni, Cr, Pb) have been under concern of environmentalists. Increased atmospheric deposition of heavy metals causes surface contamination of plants, soil cover and forest floors. Lichens, mosses, mushrooms and vascular plants can accumulate higher amounts of toxic metals in atmospheric deposition hot spots (http://www.umweltbundesamt.de/whocc/AHR10/III-GP-1.htm). Some plant species, so-called hyper accumulators can extract and accumulate toxic metals in their bodies even in concentrations exceeding 1% of dry weight. Such plants may become a threat for herbivorous animals. For example, the most known astragalus *Astragalus bisulcatus* can poison cattle in Canada and USA through accumulated selenium. On the other hand hyperaccumulators can be utilised for the phytoremediation of highly contaminated waters and soil covers (Brooks 1998).

Deposition of pollutants (heavy metals, acid rain, and reactive nitrogen) can contribute substantially to water contamination and eutrophication as well as endanger water ecosystems (Yaron et al. 1996, Straškrabová et al. 1999, US EPA 2000, Barton et al. 2002, Bergstrom and Jansson 2006, Camargo and Alonso 2006).

Air pollution causes considerable damages of technical constructions and cultural heritage due to increased corrosion of materials. Maps (EMEP grid), national maps and plan of cities for corrosion rates for various building materials and increased risks of copper runoff were created. The trend for steel corrosion has been still declining while corrosion rates for zinc and limestone have been increasing. The reason is the change in the concentration of main pollutants, decreasing of SO_2 and increased concentrations of HNO_3, NO_2 and O_3. For further details see, for example, the following web addresses:
http://www.lisa.univ-paris12.fr/IMA/cult_plaque.pdf
http://www.arcchip.cz/w06/w06_knotkova.pdf.

2.1.3 Air pollution and international conventions

Till the 1960s investigation of air pollution effects was restricted mainly to searching for health or forest injuries being caused by some major pollutants in a working places surroundings at local or national level. However, after proving of transport contribution to the air pollution even far away from pollution sources, the air pollution became an international problem at the end of the 1960s. Then acidification of Scandinavian lakes was stated to be caused by SO_2 emitted in Western Europe. Other harmful, irreversible and global effects of air pollution on climate, terrestrial and ocean ecosystems, technical constructions, historical sights, etc. were successively proved as well. The countries facing the effects of air pollutants, which originated in other territories, called for an international control of air pollution. The first international programmes of air quality monitoring were initiated by WMO (World Meteorological Organization), ECE (Economic Commission for Europe) and UNEP (United Nations Environment Programme) in the 1960s and 1970s. Forming of territorial, continental and global monitoring of air quality was associated with Global Environment Monitoring System (GEMS) operating in the framework of the UNEP programmes in the 1970s. In Eastern European countries the Council for Mutual Economic Assistance (CMEA, 1949–1991) supported the operation of environmental monitoring.

United Nations Conference on the Human Environment held in Stockholm in 1972 started an international cooperation to combat acidification. The Convention on Long-Range Transboundary Air Pollution

(CLRTAP) was adopted at high-level meeting of the Economic Commission for Europe, which dealt with the Protection of the Environment. The convention came into force in 1983. Since that the following protocols have been adopted: in 1984 the Protocol on Long-term Financing of the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollution in Europe (EMEP), the Protocol on the Reduction of Sulphur Emissions or their Transboundary Fluxes by at least 30% (came into force in 1985), the Protocol on the Control of Emissions of Nitrogen Oxides or their Transboundary Fluxes (came into force in 1991), (Gothenburg) Protocol on the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes (came into force in 1992), Protocol on Further Reduction of Sulphur Emissions (came into force in 1998), Protocol on Persistent Organic Pollutants (came into force in 2003), Protocol on Heavy Metals (came into force in 2003) and Protocol on Abate Acidification Eutrophication and Ground-level Ozone. The secretariat for CLRTAP was established at the United Nations Economic Commission for Europe (UN/ECE). A Working Group on Effects (WGE) provides scientific support for the Convention. This group established International Cooperative Programmes (ICPs) for monitoring the effects of air pollution. More details about the structure and monitoring activities of the ICPs can be found in the following chapter 2.1.4.

The European Union (EU) launched a Clean Air for Europe (CAFE) programme not to increase negative impacts of air pollution on human health and the environment (COM/2001 245). This programme is the result of great efforts to improve air quality and decrease harmful effects of air pollution in EU. For example, the following chosen thematic strategies on air pollution have been adopted recently: emissions from the transport sector (Directives 98/69, 98/77, 2003/17/EC), non-road mobile machinery – gaseous pollutants (Directive 2004/26/EC), wheeled agricultural and forestry tractors (Directive 2000/25/EC), CO_2 emissions (Decision 1753/2000/EC), pollution from large combustion plants (Directive 2001/80/EC), volatile organic compounds (Council Directive 1999/13/EC), integrated pollution prevention (Directives 2003/35/EC, 2003/87/EC), air quality directives (Directive 96/62/EC), pollutants in ambient air (Directives 1999/30/EC, 82/884/EEC, 90/656/EEC, 91/692/EEC, 85/203/EEC, 2002/3/EC), heavy metals and polycyclic aromatic hydrocarbons (Directive 2004/107/EC), national emission ceilings (Directive 2001/81/EC), ratification of the Kyoto Protocol (Decision 2002/358/EC), greenhouse gas emission, monitoring and reporting (Decision 280/2004/EC, 93/389/EEC, 99/296/EC, Directive 2003/87/EC, Linking Directive 2004/101/EC), reduction of climate change impacts (COM/2005 459), (COM/2000 88), (COM/2001 580) and the Initiative (INI/2005/2249).

Commission of the European Communities accepted the Communication on Thematic Strategy on Air Pollution and the Directive on Ambient Air Quality and Clean Air for Europe (COM/2005 446), (COM/2005 447 final) on the 21st September 2005. The EU post-2012 strategy on winning the battle with global climate change was issued in the communication (COM/2005 35).

Other European environmental conventions, such as the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention, replacing the Oslo Convention and the Paris Convention), Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention, HELCOM) and the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention, MEDPOL, under the UNEP Regional Seas Programme) also respect air quality control, however this is not the main issue.

2.1.4 Monitoring the air pollution and effects

Measuring of major pollutants (dust deposition, SO_2, Cl, F) was carried out spontaneously in individual countries in Europe. Some national government departments (health service, forestry, agriculture, power industry, etc.) maintained several measuring nets. Different methods and maximum permissive values were used in parallel in accordance with the purposes of the measurements in individual countries or blocks. Later, WHO, WMO, IUFRO, FAO and other international professional organizations tried to harmonize these measurements and interpret their results. However, monitoring system of the block of East European countries was not fully integrated into the measuring net of the EU countries.

After ratification of the LRTAP Convention and introduction of the programmes for checking the observance of the Convention protocols by WGE, the effort for the unification of air quality measurements at chosen stations became stronger. However, while most of European countries accepted a formation of stations measuring air quality in the framework of the EMEP programmes, the East European countries joined slowly. They were running a net of stations GEMS (Global Environmental Monitoring System Programmes for Air and Water) included in the framework of the UN Earthwatch system operated by WHO and UNEP until 1990.

Nowadays, the EMEP steering committee maintains Task Force on Emission Inventory and Projections, Task Force on Measurement and Modelling as well as Task Force on Integrated Assessment Modelling. Measurements of the EMEP stations are scattered over the whole Europe. Processed results, databases and calculations are related to the 150 × 150 km grid of cells.

Since 1985 WGE co-ordinates six international co-operative programmes (ICPs) and Task Force on Health aimed at monitoring the effects of air pollution in the framework of CLRTAP (WGE 2004).

ICP on the Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) monitors anthropogenic effects, mainly major air pollution impact on the development of forest ecosystems in Europe. For example, annual transnational surveys of trees conditions on about 6,000 forest plots are carried out in 16 km × 16 km grid of sampling plots (monitoring level I) and on 860 permanent monitoring plots. Needle and leaf chemistry, soil properties and other optional determinations are performed (intensive monitoring level II) as well. For more general information see http://www.unece.org/env/wge/forests.htm.

ICP on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP Integrated Monitoring) investigates more complexly air pollution effects on ecosystems or catchments. Monitoring has been carried out on about 50 permanently plots in 19 European countries. The effects of major pollutants, some heavy metals and VOCs have been an issue of interest. Current and long-term changes in ecosystems are determined or assessed via models on the basis of many simultaneous physical, chemical and biological measurements. Additional information is available from http://www.unece.org/env/wge/im.htm.

ICP on the Effects of Air Pollution on Materials Including Historic and Cultural Monuments (ICP Materials). The programme was launched in 1985. Specimens of alloys, rocks and other construction materials are exposed to the effect of air pollution at chosen stations in Europe with the aim to determine the rate of corrosion. Effects of major pollutants, rainwater chemistry or particular substances on materials are evaluated after 1, 2, 4 and 8-year exposure, and after that European maps of corrosions are constructed. Damage to cultural heritage objects are under a special interest. For more details see http://www.unece.org/env/wge/materials.htm.

ICP on Modelling and Mapping of Critical Levels and Loads and Air Pollution Effects, Risks and Trends (ICP Modelling and Mapping) deals with the effects of air and deposition concentrations of SO_2, NO_2, O_3 as well as some toxic metals on natural vegetation, soils, waters, and other materials in order to determine critical levels and loads, which are threshold concentrations causing changes in the ecosystems. Twenty-five European countries provided their reports on the national levels of critical loads of chosen pollutants and subsequently European maps of critical loads of acidity for ecosystems were constructed. Further information can be found, for example, at http://www.unece.org/env/wge/mapping.htm.

ICP on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) monitors damages caused by ozone to semi-natural vegetation, sensitive and resistant clones of plants as models and crops in Europe. Investigation and monitoring of harmful effects of increased deposition of reactive nitrogen on plants and ecosystems in Europe is being introduced. On about 7,000 sampling plots in 28 European countries the concentrations of about 10 mandatory heavy metals are determined in mosses with the aim to monitor trends in atmospheric deposition loads of these metals. More details can be found at the web address: www.unece.org/env/wge/vegetation.htm.

ICP on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters). Objectives of this programme are to assess the degree and geographical extent of the acidification of surface waters caused by acid rains. Chemical parameters, mainly pH, electrical conductivity, concentration of major ions in waters are determined and concentration trends evaluated for about 200 lakes and rivers in 24 European countries. Populations of fishes and invertebrates, and recovery of zooplankton in fresh waters have been monitored since 1992. For further information see http://www.unece.org/env/wge/waters.htm.

Joint Task Force on the Health Aspects of Air Pollution (Task Force on Health). WHO concluded that current levels of air pollutants are still too high and lead to adverse negative effects on the health condition. About 100,000 deaths per one year are associated with long-term exposure to air pollution in Europe. Fine particulate matters like PM_{10}, $PM_{2.5}$, O_3, NO_2, heavy metals (Cd, Pb, Hg), persistent organic pollutants have been under main concern of monitoring (e.g., http://www.umweltdaten.de/uid/manual/healthrisk.pdf). General information about the programme is available at http://www.unece.org/env/wge/who.htm.

WMO established the Global Atmospheric Watch (GAW) programme in 1989: (http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html). This programme monitors the long-term development of atmospheric pollution at regional and global level with regard to climate and environmental changes. About 65 countries are included into the programme on monitoring the air pollution (SO_2, NO_x, HNO_3, H_2O_2, NH_4, CO, VOC, aerosol, Rn, some metals) at 22 stations located on four sites in whole Europe.

The current programme Measuring and Monitoring Air of GEOSS (Global Earth Observation System of Systems) investigates the effects of air pollution (O_3, particles, UV, air quality, etc.) on the atmosphere, hydrosphere, ecosystems and health in America. The U.S. Environmental Protection Agency has been maintained these activities in 61 countries since 2005.

Some other regional campaigns have been under operation in order to check and assess the effects of air pollution. For example, the Arctic Council of Ministers maintains the Arctic Monitoring and Assessment Programme (AMAP). Scientific studies on Arctic haze, acidification pollutants and their effects in the Arctic have been carried out (AMAP 2006).

The Helsinki Commission (HELCOM) works to protect the marine environment of the Baltic Sea against all sources of pollution and eutrophication (1974 and 1992 Conventions). Poland is included into this programme as well. Monitoring of air-borne pollutants (nitrogen compounds, particles, content of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in particles and precipitation) is one of the recommended monitoring activities of the HELCOM activities. For details see: (http://www.helcom.fi/helcom/en_GB/aboutus/).

The Long-term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MEDPOL-II) was launched in 1981 within the framework of the Mediterranean Action Plan (MAP) adopted by the governments of the region, in Barcelona in 1975. The MEDPOL air-borne pollution monitoring and modelling programme was prepared in 1987 with WHO and UNEP as main agencies. Among 10 included countries there are five European countries, particularly France, Italy, Croatia, Greece and Spain. Monitoring programmes are aimed at the determination of toxic metals in aerosol and precipitation as well as at the chemistry and major ions in precipitation.

Global Air Quality Monitoring System (GEMS/AIR) of WHO supports the establishment of a global network of more than 250 monitoring sites in about 80 cities in 40 countries. The system GEMS is a part of the UN Earthwatch System. The GEMS/AIR network in Europe has consisted of almost 22 cities in 20 countries. Very little reporting activities (9 countries) were recognised in the 1990s. The main monitoring programme was the determination of the SO_2 and the concentrations of suspended particulate substances.

Global Atmospheric Watch (GAW) programme of WMO has been under operation since 1989 as an integral part of the Global Ozone Observing System (GO3OS, established in the 1950s) and the Background Air Pollution Monitoring Network (BAPMON, established in the 1960s). The global (baseline) stations have a very extensive monitoring programme while regional stations pursue more flexible and less intensive GAW programmes. Precipitation chemistry (major ions), SO_2, NO_x, O_3, CO_2, CH_4 and aerosol concentrations are determined in the air pollution campaigns in 23 countries.

EUROTRAC Troposphere Ozone Research (TOR) programme (a joint European project with the main aim to study the impact of human activities on the troposphere over Europe) was established in 1983 and it includes 3 subprojects (ALPTRAC: High Alpine Aerosol and Snow Chemistry Study. TOR: Troposphere Ozone Research and TRACT: Transport of Pollutant over Complex Terrain). Twenty-four European countries including Hungary and Poland have been participating in the long-term monitoring programmes of TOR. In this programme O_3, NO_x, CH_4 and CO are the principal air pollutants that have been monitored.

SPAR (Commission for the Protection of the Marine Environment of the North-East Atlantic) in accord with the strategies of the 1992 OSPAR Convention aspires for the protection of marine biodiversity against eutrophication, hazardous substances, oil and radioactive substances. Along coasts in northwestern Europe it monitors major ions and 8 metals in precipitation (25 sites, 10 countries), in aerosols and gases (12 stations, 6 countries).

More information about the international programmes of monitoring air pollution in Europe can be found in Topic reports of the European Environment Agency (EEA).

Besides the international monitoring nets many national and local stations monitoring air quality have been under operation at the same time.

AIRNET is a thematic network established in 2002 for monitoring air pollution impact on health measured in EU-projects (http://airnet.iras.uu.nl/). The information system APHEIS (Air Pollution and Health: European Information System) provides results of monitoring on the effects of air pollution on the health in 26 cities of 12 European countries (http://www.apheis.net/).

2.2 Mosses – bioindicators of atmospheric deposition loads

Mosses have not genuine roots and cannot accept nutrients and water from soil covers. Therefore they must obtain most of nutrients directly from precipitation or from dry deposition of air-borne particles. Lack of any specialised cells for internal conduction of water and minerals does not enable quick transportation and re-translocation of elements in moss body. In order to uptake and bind high amount of dissolved nutrients, leaves and stem of moss plants are not covered by cuticle cover and moss tissue contains substantial amounts of pectins composed by a linear chain of α-(1-4)-linked D-galacturonic acid that forms the pectin-backbone, a homogalacturonan. The polygalacturonic acids can adsorb effectively and firmly free cations from the solutions. That is the reason the adsorption capacity of mosses matrix is very high, about 150-200 meq.$100g^{-1}$(d.w.). The pectins remain in dry moss matter and hence dead dry moss material can adsorb effectively free cations from the solutions. In this way terrestrial mosses can operate as passive samplers of atmospheric deposition loads. Elements dissolved in rainwater or released from dry deposition into dew water penetrate the moss aboveground parts and bind with intercellular parts of tissue or with cell organelles. The distribution of elements within the individual moss segments is relatively homogenous. Total element content in moss closely correlates with element content being determined in bulk deposition collected on the plots where the moss is growing. Since mosses live about three years, and the annual segments of moss plants can be often recognised, element concentration in the moss segments may reflect average levels of atmospheric deposition during last three years. However, some moss species (endohydric bryophytes) have some internal conduction system for more effective transport of water and dissolved nutrients and a thin cuticle on leaves preventing evaporation of water and diffusion of elements from atmospheric deposition. That is the reason that some moss species are less suitable for biomonitoring the atmospheric deposition loads and that different efficiency in element uptake should be tested in interspecies calibration experiments.

Utilization of mosses as cheap and easily available integrators of atmospheric deposition loads was tested in Scandinavia in the end of the 1960s. Common species of boreal forests (*Hylocomium splendens* and *Pleurozium schreberi*) were analysed. A close correlation between concentration of lead and some other heavy metals in moss specimens and in atmospheric deposition (bulks) was found (Rühling and Tyler 1968, 1970). The moss sampling procedure was harmonised in order to eliminate all undesirable effects (throughfall, soiling, litter of trees or little shrubs and grass vegetation, etc.), which could bias the pure effect of atmospheric deposition on elemental composition of the moss samples.

Very promising and effective biomonitoring method of determination of current atmospheric deposition loads was tested on larger territories of the Nordic countries in the 1970s and 1980s (Rühling and Tyler 1971, 1973, 1984, Pilegaard et al. 1979, Rühling et al. 1987). In the course of testing the mosses as effective bio-indicators of atmospheric deposition levels the individual steps of this method, as collection, preparation and analyses of moss samples and interpretation of analytical results were further harmonised and standardised in order to provide comparable results. Special measurements confirmed close relationships of the elements content of moss with elements amounts in annual mean deposition. Few formulas for converting element moss concentration to absolute atmospheric deposition loads of related elements were introduced. For example, element content in dry matter of moss ($mg.kg^{-1}$) divided by four gives a relative good estimation of absolute deposition load of given element ($mg.m^{-2}.year^{-1}$) (Rühling et al. 1987). Later efficiency factors of element uptake and production of moss were determined and more accurate formulas using these factors were used to estimate atmospheric deposition loads. However, investigation of moss production and efficiency factors for individual elements in different climatic and pollution-deposition cadastres would be time consuming. In order to use the efficiency of the biomonitoring system either relative atmospheric deposition are determined or some generalisation of parameters in the formulas is used to estimate easily the absolute deposition loads of the investigated elements. Since the biomonitoring of atmospheric deposition loads of many elements proved to be very effective and cheap the proved moss technique was offered for application in a large European biomonitoring programme in 1990.

The first Pan-European biomonitoring of atmospheric deposition loads of 10 obligatory investigated elements was co-ordinated by the Scandinavian moss experts. 21 European countries were included into this campaign. The pleurocarpous, ectohydric/mixohydric mosses *Hylocomoim splendens*, *Pleurozium schreberi* and *Hypnum cupressiforme* were preferred for use. Twenty-one European countries provided results of determination of As, Cd, Cr, Cu, Fe, Ni, Pb, V and Zn contents in the moss bio-indicators. Results of the first large-scale estimation of the distribution of atmospheric deposition loads in Europe revealed and correctly located the main hot spots of the deposition of investigated heavy metals, for example, at Kola Peninsula, in Black Triangle I and II (Saxony, northern Bohemia, southern Poland, and northern Slovakia) in Central Europe; Ruhr area and Saarland in Western Germany. Constructed isopleth maps showed extent of areas suffering from high deposition loads and directions as well as the impact of long-range transport of pollutants in Europe (Rühling 1994a). Some Scandinavian countries determined in national biomonitoring campaigns 35–40 elements in moss samples. Anyway, only nine obligatorily investigated elements were evaluated in the European monitoring survey. Results for the optionally determined elements are published in the environmental literature.

In the following biomonitoring campaign in 1995/1996 concentrations of 10 obligatorily investigated elements were determined in moss samples collected on about 8,000 plots in 29 European countries. Some countries, for example Scandinavian countries or Germany, except for the authorized elements, determined about 30–35 optional elements in their national biomonitoring programmes. Obtained results for the obligatory elements confirmed distribution of most contaminated zones in Europe, and comparison with the results of 1990 showed diminished metal deposition levels all over the Europe, mainly in the Black Triangle I and II areas in central Europe due to restructuring of industry in eastern European countries after 1990 (Rühling and Steinnes 1998). When the LRTAP Convention (Aarhus, Denmark, 1998) established the Task Force on Heavy Metals, the group of Scandinavian moss monitoring experts offered a biomonitoring method and the obtained results were used for the purpose of the LRTAP Convention. The biomonitoring programme of the determination of current atmospheric deposition loads through moss analyses and the obtained figures of that time were adopted in the programme of UNECE ICP-Vegetation, which was operating since 1987. In 1999 the ICP-Vegetation programme opened a new subprogramme “Heavy Metals in Mosses”. Since 1999 the Centre for Ecology and Hydrology in Bangor, U.K. was arranging co-operation of the next international biomonitoring campaigns.

The new co-ordination centre arranged next international biomonitoring programme for the period 2000/2001. Twenty-eight European countries took part in this campaign. Concentrations of ten authorized elements (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn) were determined in moss samples collected on about 7,000 sites all over the Europe. The results were presented in commented maps. Dot maps indicated content of elements on individual sampling sites and mosaic maps illustrated the determined average concentrations of elements in the moss samples in each square 50 × 50 km of the EMEP grid. Bio-indicated current atmospheric deposition loads in Europe were in accordance with the results obtained in other international measurements of air quality on permanent monitoring stations. Determination of optionally investigated elements in some national monitoring programmes was not included into the European biomonitoring survey. For further details see Buse et al. (2003).

The last international biomonitoring programme in the framework of UNECE ICP-Vegetation 2005/2006 has been evaluated. Similar results as in the preceding biomonitoring campaigns are expected.

Many further moss-monitoring studies were carried out in individual countries out of the activities of the UNECE ICP-Vegetation. The moss technique of the determination of atmospheric deposition loads was successfully applied in the whole world, for example, in America, Asia, Africa and Antarctica (e.g., Daly 1970, Onianwa et al. 1986, Bargagli et al. 1998, Saxena et al. 2001, Allen-Gil 2003, Lee et al. 2005, Osyczka et al. 2007).

Since dried specimens of moss collected in clear area can be exposed in bags of nylon net (moss-bags) elsewhere (Hynninen 1986, Mäkinen 1987, Culicov et al. 2005, Makholm and Mladenoff 2005) and the chosen aquatic bryophytes can be utilised in the same way (e.g., Kelly et al. 1978) the campaigns using moss as bio-indicator became a powerful tool for the determination of deposition rates of various chemical elements, organic compounds, radioisotopes, herbicides, etc. in forests, fields, towns, factory yards, etc. under various environmental conditions (e.g., Mattson. and Liden 1975, Roberts et al. 1979, Baudin-Jaulent and Descamps 1985, Sawidid et al. 1999, Orlinski 2002, Maňkovská 2003, Ötvös et al. 2004, Sucharová and Suchara 2004a, Zechmeister et al. 2006, Fernández et al. 2007 and many others).

In some special campaigns moss analytical results were used for discovering the distribution of deposition loads in the surroundings of point pollution sources, modification of deposition rates by relief, deforestation, land-use, altitude, precipitation and other environmental factors (Gignac et al. 1991, Zechmeister 1995, Šoltés 1998, Økland et al. 1999, Gerdol and Bragazza 2006). Concentrations of 14 elements in the Tatra mountains streams were determined using analyses of aquatic bryophytes (Samecka-Cymernan et al. 2007).

Analyses of herbarium moss specimens were used for retrospective estimation of atmospheric deposition loads of nitrogen and metals as well as the intensity of UV radiation in the past in some European countries (Herpin et al. 1997, Penuelas and Filella 2001, Shotbolt et al. 2007).

Since eutrophication has become a serious environmental problem intensive investigations have been carried our to find a reliable algorithm for the estimation of atmospheric deposition loads of nitrogen compounds from determined nitrogen content in moss specimens (Woolgrove and Woodin 1996, Solga et al. 2005, 2006, Solga and Frahm 2006).

Variability in some metal concentrations in moss samples was positively correlated with metal contents in human blood, urine, hair, etc. in related areas. An accuracy of the assessment of human exposure to metals through the moss analytical data has been an issue of interest in some countries. For example, in some epidemiological studies in Sweden and the Netherlands a distribution of the incidence of some diseases was closely and positively correlated with the distribution of element contents in mosses (e.g., Hellstrom et al. 2004, Wolterbeek and Verburg 2004). The health investigations show that hot spots of high deposition loads of elements revealed through moss analysis may be reliable potential indicator of (hidden) epidemiological risks that needs local prophylactic health screening.

Important partial findings

1. Since the 1990s the air quality in Central Europe has been the issue of high political and environmental interest. Several international conventions aspire for control of the emission of air pollutants and monitoring the contamination of the atmosphere, transboundary transport of pollutants and their deposition loads as well as their harmful effects.

2. Concentrations of air pollutants and their effects have been monitored in local, national and international nets of the stations being located in the whole Europe. Many figures about current air pollution, atmospheric deposition loads and their effects and trends were published in yearbooks and other literature.

3. The national and international monitoring programmes have been dealing exclusively with major air pollutants such as SO_2, NO_x, *PM,* O_3, *CO,* CH_4, *VOC and little with metals (e.g., As, Cd, Cr, Cu, Hg, Ni, Pb and Zn), which are considered to be the most toxic.*

4. Air quality is measured mainly in the cities with high population and in highly industrial regions. On the contrary only few stations operate in rural environment.

5. The biomonitoring programmes using moss as the bio-indicator of current atmospheric deposition loads could serve as the efficient mean for the determination of deposition loads of toxic elements in rural regions where the data from the measuring stations are not available.

3 VISEGRAD SPACE AND AMBIENT AIR QUALITY

3.1 Short introduction to the Visegrad Group

The current Central European countries, Czech Republic, Slovak Republic, Poland and Hungary formed the Visegrad Group at the presidential summit at Visegrad, Hungary that was held on 15th February 1991 in order to co-operate and harmonise political, defensive, economic, social, immigration, cultural, scientific and other activities. Protection of the environment in the Visegrad space belongs to priorities of the Group. Individual countries of current V4 were extensively industrialized after the World War II and some areas in individual countries belonged to the most contaminated sites in Central Europe. After political changes in Europe in the 1990s heavy industry was established or substantially restructured, and sophisticated technologies were introduced. However, some potential toxic or hazardous elements, which are not under current concern of environmental monitoring systems can be emitted from some pollution sources or accumulated in a long-term in deposition loads in some parts of the Visegrad space. Emergence and spreading of pollutants depends on economic and environmental conditions operating in individual countries. Short features of them follow.

Czech Republic (CZ)

a) General

The CZ area is 78,864 km^2 and the population 10,241,138 (2005). CZ consists of historical countries Bohemia (western half of CZ), Moravia (eastern part of CZ) and Moravian Silesia (a small area adjoining the northeastern part of Moravia). Currently, 14 current administrative regions have been in CZ.

b) Geomorphology and climate

The altitudinal range of the CZ territory is 115–1,602 m a. s. l.; Lowlands are situated in the northern part of central Bohemia and in the eastern and south-eastern parts of Moravia. CZ lies in the temperate climatic zone. The warmest parts of CZ copy the position of lowlands (< 250 m a. s. l.) with average annual air temperature in thermophyticum 8–9° C and annual precipitations 450–600 mm. The proportion of lowlands is about 6%. Mountains above 700 m a. s. l. are distributed mainly along the CZ borders and between Bohemia and Moravia. Annual mean temperature and precipitation in the oreophyticum areas is 0.5–4° C and 850–1600 mm, respectively. Mountains cover about 12% of the CZ territory. Downs occur on remaining 82% of the CZ territory. In mesophytic area annual temperature and precipitation are about 5–7°C and 600–850 mm, respectively. Bohemia has more oceanic climate with prevailing western winds, while Moravia's climate is more continental and affected mainly by winds of northeast and southwest directions. More details about climate of CZ can be found in ČHMÚ (2007) some of the following pages can provide more additional details:
http://geography.about.com/library/cia/blcczech.htm maps
http://en.wikipedia.org/wiki/Czech_Republic
http://www.chmi.cz/meteo/ok/atlas/en/menu.html
(http://www.gvm.cz/cooperat/comenius/geograph/surface.htm.

c) Industry

Since the 19th century the territory of the current CZ was highly industrialised. Mainly metallurgical, engineering, glass, chemical and textile industry was operating here. After the World War II steel, metallurgical, power, chemical, engineering, glass, textile, boot-and-shoe, food and other industries developed extensively and concentrated in northwestern (Chomutov and Ústí nad Labem districts), southwestern (Příbram and Plzeň districts), northern (Liberec and Jablonec districts), central (Kladno and Slaný districts) and northeastern (Pardubice district) Bohemia and in northeastern (Frýdek Místek and Ostrava districts) and southern (Brno district) Moravia. Some raw materials were extracted intensively (e.g., metallic ores, coal, uraninite, kaolin, glass sand, coal, limestone, etc.). Coal basins areas in northwestern Bohemia and northeastern Moravia with aggregated power plants and industrial factories belonged to the most polluted areas in Central Europe and they were called "Black Triangle" and "Black Triangle II" (Markert et al. 1996: 97) areas. Further details can be found, for example, at the following pages:
(http://www.energy.rochester.edu/pl/blacktriangle/
http://www.grid.unep.ch/activities/global_change/blacktriangle.php?size=large)
http://perso.orange.fr/cerrm/transconver/English/regions/Ostravan.htm
http://en.wikipedia.org/wiki/Ostrava.

The operation of metallurgical, engineering, chemical and mining industries was dramatically reduced, and industry structure in CZ has been transformed after political changes in CZ after 1989. Recently, motor vehicles, electric power, chemicals, glass and beverage (brewery) production have been important. Nowadays, black coal and lignite, common building materials, glass sand and kaolin are extracted, and the only uraninite pit has been running. Northeastern part of Moravia has left the only significantly industrialised region of CZ, recently. Some additional information can be found, for example, at the following web pages:
http://en.wikipedia.org/wiki/Economy_of_the_Czech_Republic

http://minerals.usgs.gov/minerals/pubs/country/2001/ezhupllomyb01.pdf.

d) Agriculture

After the World War II originally private state farms in the Czech Republic maintained agricultural lands. The country was exceptionally self-sufficient in the production of the main agricultural commodities. However, high portion of arable land (80% of all agriculture lands) and enormous doses of mineral fertilizers affected the environment substantially. After 1989 the land was privatised but the majority of agricultural lands have been hired to private associations. The crop production structure has been dramatically changed. Mainly oil plants and special crops have been cultivated. The area of arable land decreased to about 70%. For more details see the following web pages:
http://www.czech.cz/en/economy-business-science/general-information/economy-development-and-potential/agricultural-industry-in-the-czech-republic/
http://www.fao.org/regional/SEUR/ceesa/Czech.htm.

e) Environmental pollution

The CZ territory was highly contaminated by atmospheric deposition loads mainly in the northern half of the country before 1990. Enormous concentrations of SO_2 and suspended particulate substances were recorded. Industrial regions suffered from high deposition loads, e.g., of SO_4, As, Pb, particulate suspended substances. Heavy acid rains affected mountains considerably. Large deforestation affected the Black Triangle (I) area. After 1990 due to reduction in the industry, desulphurisation of coal power plants introducing more sophisticated technologies as well as the termination of the production and distribution of lead petrol caused that the atmospheric deposition levels of sulphur and majority of heavy metals have been dramatically diminishing. In contrast, enormous expansion of car traffic caused increasing of air pollution by nitrogen compounds, PM, Sb and metals associated with catalysts (e.g., Pt, Pd, Co). The terrestrial and water ecosystems face eutrophication. In order to clean running water sewage water treatment plants have been built. Information about the current state of the environment can be obtained in the reports and yearbooks published by the Czech Ministry for the Environment (http://www.env.cz):
http://www.env.cz/ZP_04_en/aobsah.htm,
http://www.env.cz/AIS/web-pub.nsf/$pid/MZPJZFIKTVXR/$FILE/Report2005.pdf,
http://www.env.cz/www/dav.nsf/rocenka_06/06_titul.htm.

Slovak Republic (SK)

a) General

The area of the country is 49,035 km^2 and the population 5,439,448. SK has 8 administrative regions. People live in 136 towns (with more than 5,000 inhabitants) and 2,717 villages. Proportions of the land use categories are as follows: forest lands 40.6%, arable land 30.2%, meadows and pastures 17%, urban areas 2.6%, water plots 1.9%, gardens 1.6% and other agricultural land 1%.

b. Geomorphology and climate

The Carpathian Mts. stretch across a large territory of Slovakia, particularly from the Alpine mountain range to the West Carpathian Mts. For this Alpine-Carpathian Mts. system a fold nappe structure is a typical, variegated lithologic composition and geomorphologic complexity of the territory (Marsina 1999). The territory of Slovakia is situated in the temperate climatic zone with regular alternation of annual seasons. The climate is modified by a miscellaneous geomorphology. Range of the altitude is from 94 m (Bodrog River) to 2,655 m (Gerlach peak). That is the reason of very different climatic areas on the relatively small SK territory. Mountain ranges occupy mainly northern and central part of SK. Windward and leeward slopes, mountain crests and narrow and wide valleys form a specific mesoclimate. Lowlands are situated in southwestern and southeastern part of SK.

The warmest part of SK lies in the Slovak part of the Danube Lowland (southeastern SK). Mean annual temperatures slightly exceed 10^{o}C and precipitation total is about 500 mm. On the contrary, in the Tatra Mts. the annual mean temperature is under -3^o C and annual precipitation totals average up to 2,000 mm. Wind conditions are very complicated due to broken relief of the country. However, for example, in the Záhorská Lowland and Danube Lowland blow mostly southeastern and northwestern winds. Further details can be found in the Atlas of the Landscape of SK (MŽP SR 2002). For further information see, for example, the following addresses:
http://en.wikipedia.org/wiki/Slovakia
http://en.wikipedia.org/wiki/Geography_of_Slovakia
http://britannica.com/eb/article-9109751/Slovakia.

c) Industry

he country became industrialized in the second half of the 20th century (under the Communist government). The extensive heavy industry including engineering and metallurgical branches were preferred. SK became an important centre of the former Czechoslovakia armaments industry. After political changes at the end of the 1990s the industry has been restructured. However, ceramics, chemical products, machinery, oil products, steel and textiles belong to important products of the current SK industries. Foodstuff production and processing, mainly of traditional food, such as beer or sheep's cheese, is also important branch of the SK industry.

The country is rich in some minerals; nevertheless, some mining activities have been reduced or ended after 1990. Anyway, the extraction and processing of brown coal and lignite, copper, lead, zinc, manganese and iron belong to the important SK production. Additional information concerning the SK industry can be found in the Atlas of the SK Landscape (MŽP SR 2002: 170–174).
http://en.wikipedia.org/wiki/Economy_of_Slovakia
http://minerals.usgs.gov/minerals/pubs/country/1999/9436099.pdf.

d) Agriculture and forestry

The area of arable land covers 30% of the SK territory. Wheat, barley, maize, sugar beet and potatoes are the principal crops of the country. Cultivation of grape has been performed on suitable southern mountain slopes and some tobacco plantations can be seen in the valley of the river Váh. Farming of livestock, including pigs, cattle, sheep and poultry is characteristic for agriculture of SK.

Forests cover approximately 41% of SK. The respective proportions of production, protective and other forests are 72%, 14% and 14% of total forest area. The proportion of coniferous forests is 42.7% of the total SK forest area (spruce 26.8%, pine 7.7%, fir5 %, larch 1.9%, dwarf pine 1.0%, and remaining tree species 0.1%) while deciduous forests cover 56% of total forest area (beech 29.1%, oak 11.3%, others 16%). Since 1987 the health condition of the Slovak forests has been monitored on 111 permanent monitoring plots (www.nlc.org, http://frisweb.fris.sk/CmsLesy). More information can be found at the following addresses:
http://www.fao.org/Regional/SEUR/CEESA/Slovakia.htm.
http://eusoils.jrc.it/ESDB_Archive/eusoils_docs/esb_rr/n09_soilresources_of_europe/Slovakia.pdf.

e) Environmental pollution

About 17,000 regions have been affected by some forms of former or current mine activities in Slovakia. Geochemical mapping of the Slovak territory showed that many of these regions were characterized by a high contamination of toxic elements, such as As, Al, Mn, Cd, Cr, Cu, Hg, Pb and Sb (Maňkovská 1996). Soluble forms of these elements represent increased threat for the environment and health. Exceeded permit concentration limits for some toxic elements were found mainly in soils, waters and river sediments (Čurlik and Šefčik 1999, Rapant et al. 1999, Bodiš and Rapant 1999). Daniel et al. (1996) provide information of natural radioactivity of rocks in SK. In about 50 geographical regions severe injuries of the environment were showed. Heavy metals and other risky elements are spread in the environment through transport of air pollutants, water erosion and mobility of free elements in soil profiles.

Air pollutants affect the health condition of the Slovak forests. Long-lasting air pollution resulted in a large-scale dieback not only of coniferous but also deciduous forests. Observed forest damages are not restricted to the industrial regions but quite large damage to forests has been recorded in the whole country. Due to the effect of prevailing winds of western and southeastern directions, substantial amounts of air pollutants are transported to Slovakia through a long-range transport from southern Poland, Saxony and the Czech Republic. Jagged geomorphology modifies atmospheric transport and deposition of pollutant in mountains. Timber line in the Carpathian Mts. runs relatively high, at about 1,800 m a. s. l. Synergic effects of air pollution and hostile climate may be the reason why in the 1990s about 85% of the SK forests showed the symptoms of damage.

Determination of the proportion of major air pollutants (SO_2, NO_x) in the contamination of forest soils has not been carried out. Most figures for pollution balances are estimated on the basis o emission registers, deposition and transportation estimates. Considering emission and deposition data in Europe, the following main pollution deposition types (PDT) can be recognised (Maňkovská 1996):

A - Acid PDTs

A_1 acid PDT with ash is the most widespread type in Slovakia. Besides the surroundings of all thermal power plants and incinerators, A_1 also affects areas at the altitudes higher than 800 m, which are open to winds and high amounts of precipitation. A_1 is caused mainly by a long-distance transport of SO_2, NO_x, CO_x, ash and O_3. Respecting concentration of given pollutants the A_1 PDT is subdivided into three classes (I high, II medium and III low concentrations). A_1-III class covers virtually the whole Slovakia. Forest plants are affected in a latent way and air pollutants come from regional and remote sources. Larger areas including the surroundings of all SK emission sources and areas at high altitudes (Tatra Mts. National Park, National Park Low Tatra Mts., Beskids and the areas along Czech and Polish borders) are affected by the A_1-II PDT. Forests of this area suffer from chronic injuries. The A_1-I PDT occurs in the vicinity of efficient emission sources, such as Zemianske Kostoľany, Vojany and at high altitudes. Acute injuries of forest trees are manifested in the affected areas.

A_2 acid PDT with F and Cl compounds

This PDT affects around the aluminium plant in Žiar nad Hronom, then in Žilina, Poltár, Lednické Rovne and Hlohovec regions. Phytotoxic effects of F and Cl compounds are strong.

A_3-acid PDT with smelter dust

This PDT affects the area around smelters, for example, Eastern Slovakian Iron Works in Košice, Rudňany, Krompachy, Nižná Slaná, Vajsková, Široká, Istebné, Sereď, Piesok, Brezno and others. High deposition loads of heavy metals and highly toxic compounds of arsenic and antimony bring bout harmful effects on forests.

A_4-acid PDT with substantial effect of organic matter

Areas affected by this PDT were found near cellulose plants in Ružomberok, Štúrovo, Gemerská Vieska, paper mills in Slavošovce and Harmanec, pharmaceutical plant Biotika in Slovenská Ľupča, Bukóza Vranov, rubber plant Gumárne Púchov, plants processing oil products in Petrochema Dubová, Slovenský hodváb Senica, Chemosvit Svit, Sandrik Dolné Hámre, Bratislava, etc. Deposition of hydrocarbons, mercaptans, polychlorinated biphenyls, hydrogen sulphide, carbon sulphide, aromatic hydrocarbons and other organic substances were found in this area.

B - Basic PDTs

SO2 and NOx pollutants and particles of coal and residual oil aerosols locally accompany alkaline dust fallout.

B_1 basic PDT – magnesite

High deposition loads of magnesite dust particles affect near magnesite plants in Lubeník, Jelšava, Hačava, Ťahanovce and Lovinobaňa.

B_2 basic PDT – cement

This PDT affects near cement works in Banská Bystrica, Ladce, Lúčky, Sŕnie, Rohožník, Turňa, Bystré and some other local plots. Deposition of similar type of the pollutants is expected to occur closely to the asbestos-cement plant in Púchov, and lime plants in Tisovec and Nové Mesto nad Váhom.

B3 basic PDT – transport

Approximately 200 m wide belts of the highest deposition levels, both sides along main roads are included in this PDT. Here are present dominant effects of de-icing salts, fume gases and particles of eroded metal parts and tyres, paints, lubricants, etc. and brake cheeks. High loading by engines in mountains increases emissions of cars and vehicles. This PDT occurs mainly along highways and main roads in the Tatra Mts. National Park (the road Liberty) and in the National Park Low Tatra Mts. at the most exposed sites Srdiečko, Tále, Čertovica, Donovaly, etc.

C - Ammonia PDT.

High ammonia emission and deposition is associated with the operation of some chemical plants and farms with concentrated livestock and poultry. The C type of DPT occurs in the surroundings of the chemical plants Chemko Strážske, Duslo Šaľa, nickel smelter in Sereď and PCHZ Žilina. Farms that rear big amounts of cattle are spread everywhere.

For additional information visit the following pages:
http://unfccc.int/resource/docs/idr/slo02.pdf
http://www.un.org/esa/earthsummit/slok-cp.htm.

Poland

a) General

The area of PL is 312,685 km^2 and the population 38,605,000. Currently, 16 administrative regions have been in PL.

b) Geomorphology and climate

PL is the lowland country, territory < 300 m a. s. l. covers 91.3%; average elevation is 173 m (Europe 330 m). The highest peak Rysy (High Tatra Mts.) reaches 2499 m a. s. l., and the lowest site Raczki Elbląskie at the Baltic coast is only 1.8 m a. s. l. Lowlands are situated in northern and central part of PL, mountains in southwestern and southern part of PL. Poland is situated in temperate climate zone, continental influence play some role in eastern part and oceanic one in western part of the country. Years with mainly inflow of humid air masses from the Atlantic Ocean (polar-maritime and maritime) are characteristic for mild winter and cool summer. Dry air masses coming from Asia bring frost and lower amount of precipitation during the wintertime, and heat and drought during summer time. The influence of arctic and subtropical climate is less frequent. Annual amplitude of temperature fluctuates between 18 and 24^{o}C. In summer (July) the highest temperatures were recorded in the Silesia Roztocze and Lublin regions (> 18.5^{o}C) and the lowest in the highest part of mountains (< 10^{o}C). During winter (December) the most worm territory lays in the northwestern part of PL (Świnoujście and Szczecin cities surroundings, about minus 1^{o}C) and the coolest region is situated in northeastern part (Suwałki region, minus 5^{o}C). Pattern of temperature changeability on PL territory have meridian character: in the west temperatures are higher and din the direction to the east. Mean amount of precipitation is 500–700 mm and most of rainfall occurs usually in summer (about 90%). The highest precipitation (> 1500 mm) occurs in highest part of the Carpathian Mt., while the lowest in lowland belt in central PL (Wielkopolska and Kujawy region). More details about the geomorphology and climate of PL can be found at the following addresses:
http://www.pgi.gov.pl/pgi_en/
http://www.igipz.pan.pl/ksig/home.htm.

c) Industry

PL has diverse natural resources, part of which is insufficient (e.g. iron ore, petroleum, and natural gas). Sources of energy: hard coal occurs in three coalfields (Upper and Lower Silesia, and Lublin region); brown coal (lignite) occurs in the southwestern and central part of the country (Turoszów, Bełchatów and Konin districts); petroleum and natural gas occur mainly in the southern part of PL, smaller resources are also in the northern and western regions. Metal sources: the most important copper deposits are located in Lower Silesia (Legnica-Głogów field), zinc-lead deposits in Olkusz district; less significant are iron ore (Staropolskie field, Suwałki district) and nickel ore (Ząbkowice Śląskie district). Of chemical resources the most important are natural sulphur and salts: rock salt (Carpathian Mts. foothills and Kujawy region), potassium and magnesium salt (The Bay of Puck, not exploited). Natural sulphur is present in Tarnobrzeg region. Rock resources are common; they are exploited mainly in the Sudeten and Sudeten foothills (granite, porphyry, basalt, marble, and sandstone), Gory Świętokrzyskie Mts. (sandstone, limestone), Nida Basin (gypsum), Beskids and in the region of Lublin (marl and chalk). Sand, clay, gravel and loam occur in the whole area of the country, and particularly in its northern part. Intensive development of industry took place in Poland in the later part of the 19th century but the extraction and processing of zinc and lead ores as well as salt mining started much earlier, in the 12^{th} century. At that time the occurrence of raw materials decided about the location of industrial works, but at present it is not so important. The largest industrial regions are those of Upper Silesia and Warsaw, with about ¼ of the national production. Other important districts are Poznań, Gdańsk, Staropolski (Old Poland), Krakóv, Rybnik, Bielsko-Biała and Szczecin. The western and southwestern parts of the country are more industrialized. Fuel and energy industry has developed in the regions being abundant in power raw materials (power plants on coal and lignite are in Upper Silesia, Bełchatów and Turoszów; the largest petrochemical works is PKN Orlen in Płock). Zinc metallurgy has had the longest tradition in the region of Góry Świętokrzyskie Mts., and zinc and lead metallurgy in the region of Olkusz. Currently, copper metallurgy is the most important (Legnica-Głogów Copper District); iron metallurgy, based on imported raw materials, has developed in the Upper Silesian Industrial District, as well as in Kraków and Częstochowa. Machine and electrical engineering industry (production of machines and equipment for heavy industry) and the transport means industry concentrate in Upper Silesia. Well-developed chemical industry is located throughout Poland: the largest nitrogen plants are in Tarnów and Kędzierzyn-Koźle; fertilizers are produced in Police, Włocławek and Puławy; organic and economic chemistry works are located in Wrocław, Bydgoszcz, Włocławek, Nowy Dwór Mazowiecki, Warszawa and Oświęcim; rubber works are located in Olsztyn and Dębica, and large pharmaceutical plants, in Poznań, Starogard Gdański, Warszawa and Grodzisk Mazowiecki. Food industry and other industrial branches (timber and papermaking industry, cement industry, ceramic industry (building and applied ceramics) are of smaller importance. For some additional information see the following web page:
http://en.wikipedia.org/wiki/Economy_of_Poland#Industry.

d) Agriculture

About 13% of all the work force is employed in the agriculture. There are about 3 million farms of an average area of 6.6 ha. Most of them are small farms with less than 1 ha (mainly in Małopolska and Lublin region). Larger farms (>20 ha) account only for about 5% of the total number of farms and 44% of their area. They are located mainly in northern and western Poland. The area of farmland covers 16.9 million ha; it has decreased by 1 million ha of what it was in 1996. Arable land accounts for 77.3%, permanent grassland for 15%, pastures for 6.1%, and orchards for 1.6%. Most arable land is in the voivodeships of Wielkopolska, Kujawy-Pomerania, Western Pomerania and Lower Silesia; the largest areas of meadows and pastures are in the voivodeships of Warmia-Masuria, Podlasie and Podkarpacie; orchards concentrate around the largest urban agglomerations and in the Lublin Upland, Małopolska and Podkarpacie. A characteristic feature of the Polish agriculture is the diversity of agricultural production in particular farms. In addition to big modern farms producing food on a large scale, there are under-developed farms. Most farms are in private hands (84% of the agricultural land). Crops are dominated by cereals (8.3 million ha), potatoes (0.8 million ha), industrial crops (0.8 million ha) and fodder crops (0.6 million ha). The most popular cereals are wheat (29% of the crops), rye (19%), barley (13%), triticale (11%), oat (7%) and mixture of cereals (oat with barley) (16%). For more details see the following web pages:
http://en.wikipedia.org/wiki/Economy_of_Poland#Agriculture
http://www.minrol.gov.pl/DesktopDefault.aspx? TabOrgId=1210&LangId=1.

e) Environmental pollution

PL is a country with great environmental contrasts. Its territory was among the most polluted areas in Europe. The most degraded area is the southwestern part of the country, where main mineral resources are located and processed. Until the 1980s, the above standard concentrations of sulphur dioxide and dusts affected more than one half of the country. High sulphur dioxide emissions, originating in both domestic sources and long-range atmospheric transport, resulted in the considerable acidification of the environment. Particularly harmful effects of acidification were noted in the region of the so-called Black Triangle (I), where considerable areas became completely deforested. Much smaller areas were degraded by emissions of dusts containing heavy metals, connected mostly with the extraction and processing of zinc and lead ores (region of Olkusz and Miasteczko Śląskie), copper (region of Legnica and Głogów) and aluminium metallurgy (region of Konin, and formerly also the region of Skawina near Kraków). Since the beginning of the 1990s radical changes have occurred in the industry. Part of the industrial plants employing old technologies were closed or the technologies were changed into less burdensome and more environment-friendly ones. The emissions of sulphur dioxide and dusts have been considerably reduced since the 1990s. Big problems are still posed by sulphur dioxide emissions, generated by large power plants and emissions generated by transport (nitrogen oxides, some specific elements, such as Pt, Pd and Co), because the number of motor vehicles increased from 2.1 million in the 1980s to over 11 million at the beginning of the 21st century. The high deposition of nitrogen compounds has resulted in the eutrophication of the environment.

PL still remains one of the most polluted countries in Central Europe. The annual emission of Cd in the years 1998–2000 was between 50 and 60 tonnes, Cr close to 90 tonnes, Cu close to 400 tonnes, Ni about 250 tonnes, Pb 650-750 tonnes, and Zn over 2000 tonnes (Table 1). Four regions where moss samples were collected in the biomonitoring survey 2000 differ in the level of air pollutions. Southern and southwestern parts of PL, where mineral resources and heavy industry plants are located, the natural environment is degraded the most. Upper Silesia industrial region and Legnica-Głogów copper basin (LGOM) cover about 10% of the country area, and they are inhabited by 20% of the population of PL. 25% of total emissions and 16–31% of heavy metal emission (GUS 2001) originate in these regions.

1. In the Upper Silesia industrial region (Upper Silesia Voivodeship) emission sources comprise following main sources: black coal mines, steel works, power stations, coke-oven batteries, transport, electrical engineering, chemical and food industries. In the late 1990s the emissions of Cd; Cr; Ni; Pb and Zn to the atmosphere from the troublesome industrial plants in this region amounted 2,363–2,609; 3,513–4,387; 288–325; 53,541–146,912 and 57,697–113,483 kg.year^{-1}, respectively (Table 2).

2. In the Legnica-Głogów copper basin (Lower Silesia Voivodeship) the main sources of emission are mining-metallurgy complex and copper mines. Close to LGOM, in the Lower Silesia province electric power stations using brown coal ("Turoszów", and "Turów" in the Polish part of Black Triangle) have been operating. In the late of 1990s the amounts of heavy metal emissions from the troublesome industrial plants in this region were: 105–211 kg.year^{-1} of Cd; 26–37 kg.year^{-1} of Cr; 2–16 kg.year^{-1} of Ni; 1,3704–16,385 kg.year^{-1} of Pb and 2,177–2,899 kg.year^{-1} of Zn (Table 2).

3. Central PL (Mazowsze and Łódź Voivodeships) belongs to the richest regions in Poland. This area is distinct from the previous industry regions (Upper and Lower Silesia) in the central Poland due to mining industry. The amount of heavy metal emissions from the troublesome industrial plants in this region was in the late 1990s much more lower than in the southern and southwestern PL (Table 2). The central PL is abundant in processing industry (electrotechnical and precise products, and electro machines) and food, chemical, rubber, fuel and power industry. For example, there is located the biggest petrol producing complex in Poland "Orlen" in Płock and the power plants in Kozienice, Ostrołęka and Warszawa.

4. In the northeastern part of PL (Podlasie Voivodeship) there is not heavy industry. However, there operate some food plants, wood and paper factories, and electrotechnical and precise factories. It is the cleanest region of PL (Table 2).

Additional information about the environmental pollution can be found on the following web addresses:
http://emissions.ios.edu.pl/kcie/englishMain.htm
http://www.ekoportal.pl/jetspeed/portal/portal
http://www.gios.gov.pl/dokumenty/raport_eng.rar.

Year	Cd	Cr	Cu	Ni	Pb	Zn
1998	55.4	89.8	388.7	251.3	736.0	2,191.4
1999	61.7	89.8	420.9	259.8	745.0	2,377.1
2000	50.4	84.3	374.5	251.4	647.5	2,173.0

Table 1. Total emission amounts (tonne.year^{-1}) of chosen heavy metals in PL for the period 1998–2000, (GUS 2001).

Province *Voivodeship*	**Year**	**Cd**	**Cr**	**Ni**	**Pb**	**Zn**
Norteastern PL *Podlasie*	1998	n.a.	n.a.	n.a.	8	n.a.
	1999	n.a.	n.a.	n.a.	2	n.a.
	2000	n.a.	n.a.	n.a.	n.a.	n.a.
Central PL *Mazowsze*	1998	16	202	38	1 492	1 894
	1999	14	155	1 857	1 035	3 725
	2000	16	164	1 159	1 251	8 723
Central PL *Łódź*	1998	1	7	8	23	118
	1999	3	6	20	25	353
	2000	2	7	14	32	329
Lower Silesia *Dolny Śląsk*	1998	105	37	2	13 704	2 177
	1999	211	23	16	16 385	2 899
	2000	200	26	4	14 199	2 213
Upper Silesia Górny Śląsk	1998	2 363	3 959	319	53 541	57 697
	1999	2 609	3 513	325	146 912	49 322
	2000	2 410	4 387	288	89 853	113 483

Table 2. Amounts of chosen heavy metals ($kg.year^{-1}$) emitted in particular PL provinces in 1998–2000 (GUS 1999, 2000, 2001), n.a. = unavailable data.

Hungary

a) General

HU area is 93,030 km^2 and the population 10,064,334 (01.01.2007). The country has 19 administrative regions and one special region - the city Budapest region.

b) Geomorphology and climate

Hungary is located between 45° 48´and 48° 35´ North and 16° 05´and 22° 58´ East. Approximately more than one half of Hungary's landscape consists of flat to rolling plains of the Carpathian Mts. Basin. The most important plain regions include the Little Hungarian Plain in the west, and the Great Hungarian Plain in the southeast. The highest elevation of the latter is only 183 m a. s. l., which is also the lowest place in Hungary. Transdanubia is a primarily hilly region with a terrain varied by low mountains. These include the very eastern stretch of the Alps, named Alpokalja in the west of the country. In central and southern parts of the Transdanubia there are situated the Transdanubian Medium Mountains and the Mecsek Mts. The highest point of the Transdanubia is 882 m a. s. l. However, the highest point of the country, the Kékes 1,014 m a. s. l., is located in northeast part of HU at a mountain ridge along the Slovak border.

The main waterway the Danube divides the country into two parts. Other big rivers are the Tisza and Dráva, and in Transdanubia the Lake Balaton, a major water body.

Hungary has continental climate, with cold, cloudy humid winters and hot summers. The average annual temperature is 9.7° C. Extreme average monthly temperatures in January and July are -4.0–0 and 19–22° C. The annual precipitation total reaches 500–900 mm. A small area, Pécs, in the south enjoys a reputation of having the Mediterranean climate but in fact the area is only little bit warmer than the remaining parts of the country and receives snow in winter.

Further information can be found at the following pages:

http://geography.about.com/library/cia/blchungary.htm

http://en.wikipedia.org/wiki/Hungary#Landscape

http://en.wikipedia.org/wiki/Geography_of_Hungary.

c) Industry

Hungary is poor in the natural resources being essential for heavy industry and relies strongly on imported raw materials. Industry, only partially developed before the World War II, has been expanding rapidly since 1948 and provides the bulk of exports. Hungary has concentrated on production of steel, machine tools, buses, diesel engines, television sets, radios, electric light bulbs and fluorescent lamps, telecommunications equipment, refrigerators, washing machines, medical apparatus and other precision engineering equipment, pharmaceuticals, and petrochemical products as well. The importance of the textile and leather production has decreased after the World War II, while chemicals have been growing to become the leading industry in the early 1990s in the Eastern region. Food processing, formerly the leading industry, provides a significant portion of exports; meat, poultry, grain, and wine are common export items. In 1992, Suzuki and Opel began production of automobiles in Hungary, the first ever produced here. High-tech equipment (computers, telecommunication equipment, and household appliances) showed the strongest industrial growth in 2001. Industries targets of the

growth in 2003 were the automotive industry, the general industrial and machine tool industry, and the information technology industry. Housing construction was another growing sector in 2002. For more details see the following addresses:
www.nationsencyclopedia.com/Europe/Hungary-INDUSTRY.html
www.britannica.com/eb/article-34842/Hungary+hungary+industry&hl=hu&ct=clnk&cd=11&gl=hu.

d) Agriculture

Hungary, compared to the most European countries, is in a specific position, as more than 85% of its territory is suitable for exploitation of soil fertility by silvicultural and agricultural activities. Nowadays two-thirds of Hungary have been under agricultural use, and the remaining 15% serves for infrastructure. Owing to this the agricultural sector has a considerable impact on biodiversity. Agriculture in Hungary has undergone a considerable recession during the last decade. The economic-political changes caused undoubtedly, agrarian cut backs, loss of domestic and foreign markets and reduction in the agrarian subsidies. Gross production decreased by one-third in the period 1989–1993 followed by a slow increment during recent years. Production volume increased slowly in recent years (by 2–5%, compared to preceding years). The distribution of agricultural areas among sectors has changed. Namely, proportions of forestry areas, reed-beds and fishponds have increased by 0.3%, 2.4% and 0.4%, respectively, whereas the area of uncultivated arable land has increased by 188% in the 1990ies. The extent of uncultivated area has increased by 21%. This was caused by the uncertain ownership due to economical-political changes as well as due to the privatisation.

The additional information can be found at the following addresses:
http://209.85.129.104/search?q=cache:KKtC6xCIcuoJ:ec.europa.eu/agriculture/external/enlarge/countries/hungary/index_en.htm+agriculture+hungary&hl=hu&ct=clnk&cd=8&gl=hu
www.fvvm.hu.

e) Environmental pollution

The territory and the air of Hungary were highly polluted in the period 1949–1990. Oil refineries, chemical factories, heavy industry (metallurgy, mining) emitted many heavy metals and organic pollutants into the air, water and soil. However, Hungary was a poorly polluted country before the World War II. After 1990 the industry started to decline. The disintegration of industry and the effects of introducing the use of unleaded and desulphurised petrol, production of motor vehicles and industrial technologies resulted in the decrease of any elemental and organic pollutants. For more details see Ötvös et al. (2003) and Rabnecz et al (2007).

3.2 Air quality monitoring practice in V4

The Visegrad space countries respect the European Union legislation related with control of the emission limits of air pollutants, checkups of the concentration of air pollutants in the atmosphere and deposition, as well as mitigation of harmful effects of air pollution. However, all V4 countries were included into the block of Eastern European countries before and monitoring the air quality has been arranged differently. The following survey gives some information about the control of air quality in individual countries of the Visegrad space.

Czech Republic (CZ)

a) Air pollution policy

In the 1960s of the past century the Czech Republic (former Czechoslovakia) has built a dense network of stations measuring local air quality both in larger towns (the network is at present managed mainly by the National Institute of Public Health, http://www.szu.cz) and in the country (the network managed by the current Czech Hydrometeorological Institute, (http://chmi.cz). A few new stations were built and included into the international programmes of monitoring the air pollution. The operation of the stations in Košetice and Chopok (currently in Slovakia) was included into the Eastern European GEMS Subsystem. Later, in the 1990s, the CZ stations Košetice (southeastern Bohemia) and Svratouch (northeastern Bohemia) were incorporated into the EMEP international monitoring network. As a new EU member state, CZ fully respects the EU air pollution policy and requirements.

Basic standard for protection of the air quality in CZ is the new Clear Air Act No. 86/2002 Coll. being currently in force. Further details on monitoring, evaluation and maintaining of air quality are specified in the Government Regulation No. 350/2002 Coll. being currently in force. The CZ legislation respects the EU Directive 96/62/EC (evaluation and maintenance of outdoor air quality) and other Directives 1999/30/EC (for SO_2, NO_2, NO_x, suspended particles and lead) and 2004/107/EC (for arsenic, cadmium, mercury, nickel and PAH).

The current networks for monitoring the air quality accomplish the international quality standard EN ISO/IEC 17 025. Mainly the Czech Hydrometeorological Institute and National Institute of Public Health maintain the stations. Some other institutions contribute to the special measuring and research of air pollution (e.g., Forestry and Game Management Research Institute (VÚLHM), Organization for the Rationalization of Power Plants Co. (ORGREZ), Czech Energetic Companies Inc. (ČEZ), Czech Geological Survey, Institute for Water Management, Institute of Chemical Process Fundamentals, J. Heyrovský Institute of Physical Chemistry, Institute of Atmospheric Physics, and Departments of Meteorology of Charles University in Prague and Masaryk University in Brno).

b) Sources of air pollution and emissions

Total emission of greenhouse gasses on the CZ territory has been under international control (EU emission trading scheme, Directive 2004/101/EC scheme for greenhouse gas emission allowance with respect to the Kyoto Protocol 1997), (http://ec.europa.eu/environment/climat/emission/linking_en.htm).

Generally, air pollution sources in CZ are divided according to the emitted amounts of registered pollutants (suspended particles, SO_2, NO_x, CO, PAH and others) into four categories, and the pollution sources are listed in the registers REZZO1–4. Position of current pollution sources in the CZ administrative districts and basic characteristics of individual sources are available at the CHMI pages :
http://www.chmi.cz/uoco/data/emise/gnavemise.html.

Since 1996, yearly balances of emissions (SPM - Suspended Particulate Matter, SO_2, NO_x, VOC, NH_3) counted by the registers REZZO1–4 data are available for CZ administrative territories at the following address: (http://www.chmi.cz/uoco/emise/embil/emise.html).

More information on the air pollution in CZ provides the information system at the CHMI address: www.chmi.cz/uoco/isko/schisko/schiskoe.html (in English).

c) Stations measuring air quality

Five owners run about 230 stations measuring ambient air quality. The stations with manual operation measure, e.g., concentrations of SO_2, NO_2, PM_{10} and O_3 and at about 60 spots with heavy metals (Al, As, Cd, Pb, Cr, Ni, Be, Hg, Mn, Fe, Cu, Zn, Sb, V) in the atmosphere. At 15–20 stations also concentrations of special organic pollutants (VOC, POPs) are determined.

Automated determination of $PM_{2.5}$, NH_3, Hg and some meteorological readings are registered at about 95 stations in the network of automated air pollution monitoring (AIM).

About 75 urban stations have been under operation. The National Institute of Public Health maintains 44 stations and the Czech Hydrometeorological Institute 32 stations. The concentrations of SO_2, NO_x, PM_{10} and As, Cr, Cd, Mn, Ni, Pb in particulate matter are monitored in 27 cities.

Atmospheric wet-only, bulk or throughfall deposition of major ions, such as SO_4^{2-}, NO_3^-, H^+, F^-, Cl^-, H^+, NH_4^+, K^+, Na^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Fe^{3+}, Al^{3+}, As^{3+} are determined at approximately 20 spots.

The analytical results have been gathered in the Air Quality Information System ISKO, (IIS) operating since 1992.

Position and distribution of the measuring stations in the map of CZ is available at the following addresses:
http://www.chmi.cz/uoco/isko/tab_roc/2005_enh/cze/pdf/map.pdf (in Czech) and
http://www.chmi.cz/uoco/isko/sitsta/sitstae.html (in English).

The chosen stations are included in special long-term European research projects, for example, EUSAAR (European Supersites of Atmospheric Aerosol Research) or ACCENT (Atmospheric Composition Change – The European Network of Excellence).

d) Data of air quality

Primary and evaluated analytical data are available in the information system and some, mainly up-to-date air quality are presented on-line at the web page www.chmi.cz. For example, figures concerning the current levels of atmospheric pollution are available at the following address:
http://www.chmi.cz/uoco/act/aim/aregion/aim_region.html.

Effective limit values for the protection of health, ecosystems and vegetation accepted in CZ can be found at: http://www.chmi.cz/uoco/isko/projekt/creu-ang.html (in English).

Tabular yearbooks of analytical results for individual station and given year are edited since 1997. Details can be found at the following addresses:
http://www.chmi.cz/uoco/isko/tab_roc/tab_roc.html (in Czech) and
http://www.chmi.cz/uoco/isko/tab_roc/tab_roce.html (in English).

Annual evaluation of measured air pollution data in CZ and comparison with the previous period is available at the following pages:
http://www.chmi.cz/uoco/isko/projekt/hodn02/kval02.pdf (in Czech).

Annual measurements are also presented in the form of maps, for example, of emission densities, concentration fields of investigated pollutants in air, distribution of wet and dry atmospheric deposition in CZ. For further information see the following addresses:
http://www.chmi.cz/uoco/isko/groc/gr05cz/sezobr.html (in Czech) and
http://www.chmi.cz/uoco/isko/groce/gr05e/asezobr.html (in English).

e) Monitoring of air pollution effects (ICPs)

CZ is a member of all International Cooperative Programmes (ICPs) monitoring the air pollution effects and operating in the framework of CLRTAP activities.

Forest health state has been monitored (ICP-Forests/Forest Focus) in CZ since 1986 through harmonised manuals. The EU Regulation No. 3528/86 supported the programme ICP/Forests, in 2004 it was changed for a new programme (ICP/Forest Focus) established by the EU Regulation No. 2152/2003. About 146 monitoring plots in national network 16 × 16 km and 150 plots of the 8 × 8 km grid have been observed recently (former Level I monitoring). Defoliation and growth parameters of about 14,000 trees (29 species) are monitored and further stand parameters are determined, and satellite scenes are evaluated. About 16 monitoring plots in CZ were included into the Level II monitoring. Soil, soil water and leaf analyses are carried out and on some chosen plots for micrometeorological measurements, determination of atmospheric deposition and other investigations. Determined deposition loads on the monitoring plots (H^+, NH_4^+, NO_3^-, SO_4^{2-}, F^-, Cl^-, PO_4^{3-}, Al^{3+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{4+}, Pb^{2+}, Na^+, Zn^{2+} are included into the database of air pollution of the meteorological institute ČHMU. Annual reports of the ICP-Forests/Forest Focus are available in hard copies (e.g., Boháčová et al. 2007) or for 1994–2006 in electronic versions (http://www.uhul.cz/zelenazprava/1994.php).

The programme ICP-Integrated Monitoring is co-ordinated and fulfilled at the meteorological station CZ 01 Observatoř Košetice (southeastern Bohemia) in the sub-programmes Meteorology, Air Chemistry, Precipitation Chemistry, Throughfall, Runoff Water Chemistry, Soil Chemistry, Heavy Metals and POPs in compliance with the updated manuals for integrated monitoring (Finnish Environ. Inst.) Besides meteorological and radiological measurements and running water and soil water analyses the ambient air quality (SO_2, SO_4^{2-}, NO_2, NH_4^+, NO_3^-, NH_3, PM_{10}, $PM_{2.5}$, O_3, VOC, aldehydes, Cd, Pb, Ni, Ca, Cu, Fe, Mn and Zn) and atmospheric depositions bulk (Mn, Zn, Fe, Pb, Cd, Ni), bulk and throughfall (H^+, NH_4^+, NO_3^-, SO_4^{2-}, F^-, Cl^-, PO_4^{3-}, Al^{3+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{4+}, Na^+, Zn^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+}) and wet-only (H^+, NH_4^+, NO_3^-, SO_4^{2-}, F^-, Cl^-, PO_4^{3-}, Al^{3+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{4+}, Na^+, Zn^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+}). POPs (DDT, DDE, DDD, PCB, PCDD/F, etc.) are monitored in air, precipitation, brook water and sediments, soils, litter, needles and bryophytes. The station Košetice is included into the international monitoring programmes GAW and EMEP as well.

The second station of ICP-IM CZ02 Lysina has been operating in southwestern Bohemia and the Czech Geological Survey (ČGS) maintains it. The station is also included into the hydrochemical monitoring programme GEOMON (see Fottová 2003).

More information is available, for example, at the following addresses:
http://www.chmi.cz/uoco/struct/odd/ook/doc/kosetice_0.pdf
http://www.recetox.muni.cz/obr/File/reporty/tocoen-report-194-id530.pdf
http://www.emep.int/assessment/czech.pdf.

Programme ICP-Modelling and Mapping was oriented toward the improvement and utilisation of analytical results obtained within the international programme GEOMON in the monitored catchments Uhlířská, Jizerské Mts. (northern Bohemia) and Červík, Beskids (northeastern Moravia), recently. Dynamism of air pollutants in atmospheric deposition, throughfall and stemflow (pH, NO_3^-, NH_4^+, SO_4^{2-}) and effect of their content in brook water was investigated. Determination of pollutants in stemflow in the catchment Na Lizu in Šumava Mts. (southern Bohemia) has been carried out recently.

Critical loads of chosen air pollutants have been determined for CZ. Recently, critical loads of Cd, Pb and Hg with respect of ecotoxicological effects of view (forest ecosystems) have been estimated. The Manual ICP-MM (htt://www.icpmapping.org) has been used.

The Czech Geological Survey has accomplished the ICP-MM programme. Additional information about the mapping critical loads can be found in Skořepová et al. (2006).

Programme ICP-Waters is oriented in CZ in a long-term towards monitoring water acidity and chemistry (pH, conductivity, NO_3^-, SO_4^{2-}, F^-, Cl^-, Al^{3+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{4+}, Na^+, Si^{4+}, Be^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and Ni^2 in lakes (Černé, Čertovo, Laka, Prášilské, Žďárské, Plešné) and their tributaries in the Šumava/Bohemian Forest Mts. (southwestern Bohemia). The figures are available since 1983, for time before introduction of the ICP-Waters in CZ. The Czech Geological Survey arranges the measurements. Special monitoring of biota including zoo-benthos is provided by experts from several other institutes and universities. For details about the ICP-Water programmes in CZ and previous results see, for example, Veselý et al. 1998a, 1998b, Majer et al. 2003).

Two CZ stations have monitored trends in material corrosion since 1987. Both stations (no. 1 Prague, central Bohemia, urban-industrial pollution and no. 3 Kopisty/Most, northwestern Bohemia, industrial pollution) are included into the ICP-Materials programme. The corrosive trends were tested at carbon steel, zinc, Portland limestone and glass specimens. The results are correlated with measured or received pollution data for SO_2, HNO_3, PM_{10}, Cl^-, HNO_3^-, SO_4^{2+}, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+. Recently, ozone concentrations are taken in account. In the past maps of corrosive rates for steels, zinc, sandstones and Portland limestone in CZ were processed. In 2001, Czech Geological Survey was asked to construct maps of corrosive rates for copper, bronze

and aluminium materials in CZ. The Research Institute for the Protection of Materials, Ltd. (SVÚOM) is responsible for carrying out the ICP-Materials programme in CZ. For additional information see the following page:
http://www.svuom.cz/index.php?zobraz=home&lang=en.

CZ is included into the subprogramme "Heavy Metals in Mosses", which was declared in the framework of the programme ICP-Vegetation in 2004. However, collection of moss samples all over the country and determination of element content in moss as indicator of atmospheric deposition levels has been carried our since 1991. Current Silva Tarouca Research Institute for Landscape and Ornamental Gardening is responsible for fulfilling these monitoring activities in CZ. More details are described in Chapter 3.3.

The activities in the Task Force on Health Programme are focused mainly on the study of the effects of fine particles PM on health in CZ. Several summaries and pilot studies were carried out. The PM particles emitted mainly from traffic and possibly from home furnaces became a serious risk, especially for urban populations. WHO tightened limits for concentrations of several air pollutants including PMs. The indoor and outdoor concentration of PMs and associated concentrations of As, Cd and Pb were measured in pilot investigations in the home for old people in the town Kladno. Effects of PM concentrations on health were assessed and certified.

Slovak Republic (SK)

a) Air pollution policy

Now, in SK there have been operating 29 stations measuring local air quality and 5 regional stations, which are included into the EMEP international monitoring network. The Slovak Hydrometeorological Institute - SHMI (http://shmu.sk) manages the network. Except for the national network the keepers of crucial emission sources are obliged to control and monitor themselves the air pollution level of such source. These stations are operated independently from the SHMI. According to the new Clean Air Act operators of these local stations have to provide representative data to the SHMI, but SHMI does not guarantee the quality of these measurements. As a new EU member state, SR fully respects the EU air pollution policy and requirements. According to the framework Directive "Council Directive 96/62/EC on Air Quality Management and Assessment", the member states are obliged to provide an assessment of ambient air quality throughout the territories of the member states.
SHMI is responsible for implementation of the new EU air quality directives and for performing air quality assessment according the requirements stated. Since 1 January 2003, SK has fully transposed the EU AQ legislation, which came into force under the Clean Air Act No. 478/2002 Coll. and the Decree No. 705 about Air Quality.

b) Sources of air pollution and emissions: The system of the registers on the emission amounts has similar principles as in CZ due to the introduction of this system in the former Czechoslovakia in the 1980s.
The Air Act No. 35/1967 initiated the registration of main pollutants emitted from stationary sources. The register system EAPSI (Emission and Air Pollution Source Inventory) consists of three subsystems (EAPSI 1 major sources, EAPSI 2 middle sources and EAPSI 3 small sources).

Due to changes in legislation on the protection of air quality a new module NEIS (National Emission Inventory System) was invented in a project of the Ministry for the Environment and SHMI in 1997. The programme is supported by regional and district authorities and selected operators.

Major sources (heating output over 5 MW and selected technologies): In the register 967 sources of air pollution were registered in 1999. Except for basic data characterizing each source the emissions of CO, NOx, SO2 and particulate matter for the individual sources are calculated by using the emission factors. Since 1996, these values for selected sources have been substituted by the data provided by the operators using the recalculations from the results of measurements. Emission data from technologies are provided by the individual sources based on their own findings. Currently into the NEIS register 843 major stationary sources are included. Emissions from combustion processes and technologies of individual sources are further summarised at the level of area administrative units. New system NEIS contained 843 major point sources (SPIRIT et al, 2006).

Medium sources (heating output 0.2–5 MW and selected technologies): NEIS registered 12,082 medium sources in 2005.

Small and mobile sources **(***sources of the output below 0.2 MW):* The emission balance is based on the data about the selling of solid fuels for households and retail users. Since 1990 emissions from mobile sources are calculated annually. It is based on the number of individual types of cars, the amount of kilometres driven and the consumption of individual fuel types. Apart from road transport, inventory of mobile sources includes the railway, air and shipping transport as well.

c) Stations measuring air quality

SHMI has monitored the level of air pollution since 1971, when the first manual stations in Bratislava and Košice were put into operation. In the course of the following years the measurements were gradually disseminated into the most polluted towns and industrial areas. In 1991 a modernization of the air quality-monitoring network was launched. The manual stations were gradually substituted by automatic ones, which enable the continuous monitoring of pollution and made possible to evaluate changes depending on time and the extremes of the short-run concentrations.

The EU countries applied two different principles for the delimitation of countries into respective zones. The first approach is based on the administrative principle, where the zones more or less copy the boundaries of administrative units. The second one takes into account the spatial distribution of pollutants and the zones are delimited according to the level of air pollution.

In SK, the delimitation was based on the administration principle. In accordance with the Air Protection Act the territory of SK was divided into 8 zones and 2 agglomerations. The delimitation of these zones is identical with the higher administrative units – regions. In the Bratislava and Košice monitored zones the urbanised areas of these cities were excluded and they were treated as specific monitoring categories – urban agglomerations. The air quality is monitored in the largest cities, where different types of emission sources contribute to the air pollution level.

In the course of the last ten years the air quality-monitoring network has been developing. The number of the monitoring stations has changed from year to year, and in the last three years the measurements of the particulate matter (PM) were gradually substituted by the measurements of the particulate matter concentrations with the aerodynamic diameter less than 10 µm (PM_{10}). In 3 stations measurements of $PM_{2.5}$ were put in operation.

In 1999 in the framework of EMEP seven stations were deployed (Chopok, Mochovce, Topoľníky, Milhostav, Liesek, Stará Lesná, Starina) on the SK territory for regional monitoring of the level of basic pollutants (SO_2, NO_x, HNO_3, O_3, Pb, Cu, Zn, Mn, Cr, V, Ni, Cd). The current SHMI monitoring networks subsume 29 local stations and 5 regional stations (included into the EMEP network). Most of them have measured the level of pollution caused by the basic pollutants. In the year 2005 measurements of benzene were carried out at 4 automatic stations, and at 12 stations there were performed the measurements by a passive 2-weeks sampling. The monitoring of heavy metals (Pb, Cd, As, Ni) pollution was performed in 21 localities on the whole. At one station, besides the mentioned pollutants, H_2S concentrations are being determined as well. Distribution of the measuring stations is available at:
http://www.shmu.sk/?page=224
http://enviroportal.sk/pdf/spravy_zp/svk01e_ovzd.pdf.

d) Data of air quality

Results of the monitoring of air quality in SK are available in the form of yearbooks published by the Slovak Hydrometeorological Institute (SHMU), for example:
http://oko.shmu.sk/rocenky/Air_pollution_in_the_Slovak_Republic_2004.pdf.
Yearly reports of SHMU are available also at the SHMU pages, for example, report for 2000-2006 (MŽP SR and SMHÚ 2001, 2005) at http://oko.shmu.sk/rocenky/SHMU_Sprava_o_kvalite_ovzdusia_SR_2000.pdf.

More results of measuring concentration of pollutants in the air are available at the web pages of SHMU http://oko.shmu.sk/, http://oko.shmu.sk/Vysledky_merani.html.

e) Monitoring of air pollution effects (ICPs)

SK is included into the following UN ECE ICPs programmes: Forests, Waters, Vegetation and Modelling and Mapping.

In SK, B. Maňkovská from Forest Research Institute (FRI) in Zvolen has performed extensive studies included into the programmes of ICP-Forests and ICP-Vegetation during the last decade. The programme "Monitoring of metal atmospheric deposition in the Slovak Republic using analysis of mosses" was carried out with the activities of ICP-Forests in parallel. In the framework of ICP-Forest activities multi-elementary analyses of soils, plants, mosses, tree bark, humus and other environmental matrices are being done. Sophisticated equipment for atomic absorption spectrometry (AAS) was used and AQ/QC rules were kept. (http://www.fris.sk/CmsLesy/CMS98/Cms_6.html). FRI Zvolen was involved into the international programmes of monitoring the metal atmospheric deposition in Europe co-ordinated by a group of Scandinavian experts in 1990 and 1995, and the co-ordination centre of the ICP-Vegetation programme at Bangor in 2000 and 2005. Results of determined distribution of heavy metals in mosses were presented mainly in the form of isopleths maps in the Geochemical Atlas of Slovakia (Maňkovská 1996).

The ICP-Forests programmes have been carried out in SK since 1987. The activities of the monitoring at the Level I and Level II are performed. The national network includes 111 permanent forest plots distributed in a grid of approximately 16 × 16 km. FRI Zvolen did the needed measurements. Since 1992 Lesprojekt Zvolen has been establishing a new monitoring network of 4 × 4 km. However, the network has not been completed yet. For more information see the following addresses:
http://frisweb.fris.sk/CmsLesy
http://www.fris.sk/CmsLesy/Projekt/projekt.htm, http://www.sl.kvl.dk/upload/manual_1.pdf.

Experts from the Slovak Hydrometeorological Institute (SHMI) in Bratislava and Forest Research Institute (FRI) in Zvolen perform ICP-Waters programmes in SK.

Poland (PL)

a) Air pollution policy

There is a network of stations measuring air quality in PL. In compliance with the EU regulations they are located mainly in large towns (urban stations) but part of them are rural stations. After accession to the EU, monitoring stations have been adapted to meet the EU requirements but the system is still under development. The present measurement system was established in the 1990s; the former network (operating since the beginning of the 1960s) measured mostly the magnitude of dust deposition and concentrations of sulphur dioxide and nitrogen oxides. Provincial Sanitary and Epidemiological Stations operated it. Air pollution monitoring is one of the tasks realized within the framework of the State Environmental Monitoring Programme, which includes 3 thematic blocks: 1. Pressures 2. State 3. Assessment and Prognosis. The scope of monitoring and evaluation methods is determined by the needs of the country ecological policy and requirements of international agreements, of which the most important are: Convention on Long-Range Transboundary Air Pollution and Framework Convention on Climate Change.

The basic standard for the protection of air quality in PL is Clean Air Act No. 86/2002. Respective obligations of the country are regulated by the Act on Environmental Protection of 2006 (Official Journal No 129, Item 902). Polish legislation is in conformity with the provisions of the EU Directives 96/62/EC (evaluation and maintenance of outdoor air quality) (country regulation OJ EU L 296, 21.11.1996) and Directives 1999/30/EC (for SO_2, NO_2, NO_x, suspended particles and Pb) (country regulation OJ EU L 163, 29.06.1999), 2000/69/EC (for C_6H_6 and CO) (country regulation OJ EU L 313, 13.12.2000), 2002/3/EC (for O_3) (country regulation OJ EU L 67, 09.03.2002), 2004/107/EC (for As, Cd, Ni, Hg and PAHs) (country regulation OJ EU L 23, 26.01.2005).

b) Sources of air pollution and emissions

Air pollution sources in PL are registered in PL individual administrative districts (16). Characteristics of individual sources are available at the page:
http://www.gios.gov.pl/index_mapa.php?nr=1.

The Statistical Publishing Establishment, Warszawa publishes the hard copies of GUS (Central Statistical Office) report "Ochrona Środowiska" ("Environment") for individual years. Central information on emissions in PL is available in the UNECE/EMEP database including the official Polish emission data. The National Emission Centre in the Institute of Environmental Protection in Warsaw maintains the national data in co-operation with other institutes and the Polish Ministry of Environment. In 2001/2002 the development of national pollution release and transfer register in PL was agreed (new Environmental Protection Law, 2001). Former pollution reporting register system was related to fees for environmental use. Law introduced some new district registers in 2001/2002.

Emission of greenhouse gasses on the territory of PL has been under international control (Kyoto protocol).

c) Stations measuring air quality:

There have been four stations operating in the EMEP network in PL (PL01 Suwalki, from 1991; PL02 Jarczew, since 1985; PL 03 Śnieżka since 1991; PL 04 Łeba, since 1993). The EMEP station PL 05 Diabla Góra operated from 1978 to 1994. The Institute of Meteorology and Water Management maintains these EMEP stations except for the station PL 05 (Institute of Environmental Pollution). All EMEP stations fulfil the basic EMEP programme and some of them have monitored additional parameters. Some of these stations have been also operated as a part of international programmes as EGAP, GEMS, Air, BAPMON, GAW/WMO, and COMBINET/HELCOM.

Measurement stations, operating within the State Environmental Monitoring system, are located in 12 urban agglomerations (number of citizens > 250,000) (Białystok, Bydgoszcz, Górny Śląsk, Kraków, Lublin, Łódź, Poznań, Rybnik-Jastrzębie, Szczecin, Trójmiasto, Warszawa and Wrocław) and in 7 province capitals (Gorzów Wielkopolski, Kielce, Olsztyn, Opole, Rzeszów, Toruń, Zielona Góra). Monitoring stations and procedures are under control of the Provincial Inspectorates of Environmental Protection (PIEP). The system of automatic measurement of air pollution was launched in the 1990s.

Concentrations of sulphur dioxide are measured at 98 stations located in 12 urban agglomerations and 7 provincial capitals, nitrogen dioxide at 103 stations, while dusts PM_{10} at 103 stations automatically, and at 150 stations manually. Monitoring of $PM_{2.5}$ dust is carried out at 2 stations only (Kraków, Łódź). Lead (Pb) concentrations in the air are measured in 9 agglomerations and 6 provincial capitals; in total data are collected from 43 stations, most of which are situated in the Upper Silesian Agglomeration. In addition, benzene concentrations (C_6H_6) are measured at 22 stations and concentrations of carbon oxide (CO) at 30 stations.

Monitoring of tropospheric ozone is carried out at 25 urban and 20 rural stations (only a half of these stations provide full measurement series, allowing the statistical processing of data).

Wet depositions of air pollutants (basic cations and anions, and heavy metals) are measured at 22 stations. The Institute of Meteorology and Water Economy in Wrocław supervise that system.

The distribution of measurement stations and information on the structure and tasks of the State Environmental Monitoring System are available as a hard copy in the State Inspectorate of Environmental Protection reports (Library of Environmental Monitoring, in Polish) and at the Internet addresses:
http://www.gios.gov.pl/index7.php?temat=7
http://www.gios.gov.pl/index7.php?temat=168.

Access to data of air pollution in individual provinces is possible through the following links:
http://www.gios.gov.pl/index_mapa.php?nr=1.

For example, there are the links to the provinces databases where the biomonitoring moss plots were located in 2000:
http://www.wios.warszawa.pl/index.php?akcja=glowna (Mazowsze Province)
http://www.wios.bialystok.pl/ (Podlasie Province)
http://www.Kraków.pios.gov.pl/ (Małopolska Province)
http://www.katowice.pios.gov.pl/ (Upper Silesia Province)
http://www.wroclaw.pios.gov.pl/ (Lower Silesia Province).

d) Data of air quality

The results of measurements carried out by the Provincial Inspectorates of Environmental Protection PIEPs are collected in the state database (JPOAT), administered by the Chief Inspectorate of Environmental Conservation. The data measured in the National Network of Basic Stations are gathered in the Central Database of the Institute of Environmental Protection in Warsaw running as a part of the State Environmental Monitoring Programme coordinated by the Chief Inspectorate for Environmental Protection. The Institute regularly edits annual Report Air pollution in Poland and Annual Report on Concentration of Air Pollutants in Poland for Environmental Protection. Institute for Occupational Medicine, Lodz supervises 537 urban stations measuring SO_2 (394), NO_2 (483). Stations measure also deposition of particulate matter and some determine concentrations of hydrocarbons.

In 2000, for example, the annual mean $N\text{-}NO_3$ deposition in lowlands was 3–4 $kgN.m^{-2}.year^{-1}$ and in Sudeten Mts. about 10 $kg.m^{-2}.year^{-1}$. Mean wet deposition of ammonium was 3–4.7 $kg.m^{-2}.year^{-1}$. Reaction of wet deposition was 4.5–4.6 and deposition levels of H^+ from 20 $mg.m^{-2}.year^{-1}$ in the northern regions to 20 $mg.m^{-2}.year^{-1}$ in southern Sudeten Mts.

Regional air quality monitoring data are prepared and presented usually by the regional inspectorates of protection of the environment (WIOŚ).

For additional information see, for example, Olendzyński et al. (2002) and Skotak et al. (2002), and. the following sources:
http://www.emep.int
http://eea.eu.int
http://www.emep.int/assessment/poland.pdf
http://www.mos.gov.pl/mos/publikac/environment.html.

e) Monitoring of air pollution effects (ICPs)

PL is involved into the following International Cooperation Programmes:

UNECE ICP-Forests: Monitoring of forest health started in Poland in 1989. It is a subsystem of the State Environmental Monitoring coordinated by the Chief Inspectorate of Environmental Protection. The Forest Research Institute and the Bureau of Forest Management Planning and Geodesy are responsible for the programme. About 1,400 Permanent Observation Plots - POPs I (First-Level Monitoring) were established in pine, spruce, fir, oak, beech and birch stands; more than 400 of these plots (in the 16 × 16 km grid) are part of the European monitoring system. Since 1994, 148 selected forest the POPs I (100 pine, 22 spruce, 15 oak and 11 beech ones) have been used also as Second-level Permanent Observation Plots (Second-level Monitoring). Monitoring of forest damage comprises the assessment of defoliation and discolouration of the assimilative apparatus (all plots). Monitoring of soils (148 plots) consists of analysing the total content of such elements as P, K, Ca, Mg, S, Zn, Cu, Mn, Fe, Na, Pb, Al and exchangeable cations. Monitoring of air pollution deposition (148 plots) includes measurements, by the passive method, of SO_2 and NO_2 concentrations as well as chemical composition of atmospheric precipitation (H^+, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, PO_4^{3-}, Al^{3+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{4+}, Pb^{2+}, Na^+, Zn^{2+}). Monitoring data on the health of pine seeds are obtained from 100 plots in coniferous stands, along with entomological monitoring data (insect population densities). The results of annual observations are published in the reports of the Library of Environmental Monitoring (in Polish). Additional information on forest monitoring is available on the following web site:
http://www.gios.gov.pl/monlas/monitoring_lasu.html (in Polish).

Since 2000 UNECE ICP-Vegetation: The subprogramme Heavy Metals in Mosses has been within the framework of the programme ICP-Vegetation. However, collection of moss samples all over the country and determination of element content in mosses have been carried out since 1990 in the framework of international programme coordinated by Sweden (Lund). Collection of moss samples in national parks has been carried out also since 1976 in the framework of the national programme. Department of Ecology, Institute of Botany of the Polish Academy of Sciences in Kraków is responsible for fulfilling these monitoring activities in PL.

UNECE ICP-Materials: Institute of Precision Mechanics, Warsaw, investigates corrosion of tested materials at the station no. 50 Kraków (industrial type of atmosphere).

UNECE ICP Waters: Institute for Meteorology and Water Management, Wroclaw Division monitors concentrations of 44 pollutants in water on 20 sites along rivers and on 248 basic sites 28 water pollutants are being detected. Furthermore, in the framework of approved programmes on 58 border sites water quality is monitored and evaluated with neighbouring countries.

UNECE ICP Modelling and Mapping: The activities of the programme are maintained by the Institute of Environmental Protection, Section of Integrated Modelling, Siemianowice Śl.

UNECE ICP-Integrated Monitoring: Under the Geneva Convention on Long-Range Transboundary Air Pollution, the Integrated Monitoring of Natural Environment (ZMŚP) has been developed in Poland; it is based on the European Integrated Monitoring Programme and realized at 7 basic stations: Wigry, Puszcza Borecka, Storkowo, Koniczynka, Pożary and Święty Krzyż and Szymbark under the scientific guidance of the Adam Mickiewicz University in Poznań. The Institute of Environmental Protection, Wigry National Park, Kampinos National Park, University of Święty Krzyż, Mikołaj Kopernik University in Toruń, Institute of Geography and Spatial Management PAS, do the research. The ZMŚP study objects are the whole river (or lake) catchments, comprising different types of geo-ecosystems, which are representative of the landscape structures of Poland. Studies have been carried out since the mid-1990s and comprise, among others, monitoring of weather and hydrological processes, the results of which are necessary for the assessment of biogeochemical balance of the catchments. Parallel to studies on the abiotic components of the natural environment within the ZMŚP, there were carried out biotic research programmes, using bio-indicators (among others lichens) to estimate changes in the natural environment. To complete chemical analyses of atmospheric air and precipitation, sulphur and heavy metal concentrations were also determined in lichen thalli.

Hungary (HU)

a) Air pollution policy

The network of stations in HU has been measuring local air quality both in larger towns and near local sources of pollution. The Hungarian Air Quality Network manages the operation of the stations (http://www.kvvm.hu/olm/index.php). The network was started to build in the late 1970s in accordance with the International Environmental Agreements (see convention LRTAP). The Hungary signed the Convention on 13 November 1979 and it came into force in 1983. Other agreements for SO_2 were signed in 1985, NO_2 and NO_x in 1989, heavy metals 1998, and other persistent organic pollutants in 2004.

Current networks for monitoring the air quality accomplish the international quality standard (MSZ EN ISO 17025). The information gathered by Hungarian air quality network is available at http://www.airce.info/ and http://www.kvvm.hu/olm/index.php.

Additional information can be obtained at the following pages:
www.adatokertunk.hu
http://emla.hu/englishsite/index.shtml
www.kvvm.hu
http://unfccc.int/resource/docs/natc/hunnc4.pdf.

b) Sources of air pollution and emissions

Hungary joined the European Pollutant Emission Register (EPER), a Europe-wide register of industrial emissions into air and water in 2004. The register includes 87 facilities in Hungary.

c) Stations measuring air quality: Fifty-six automated monitoring stations and 200 temporary (manual operation) sampling points are available in HU. The 56 automated monitoring stations measure concentrations of mainly NO, NO_2, SO_2, CO, O_3, TSP (total suspended particulates), BTEX (benzene-based aromatic hydrocarbons), H_2S, VOC (volatile organic compounds) and a few spots heavy metals (Al, As, Cd, Pb, Cr, Ni, Be, Hg, Mn, Fe, Cu, Zn, Sb, V) in the atmosphere. At 200 stations the concentration of NO_2, SO_2 and settled dust are measured in HU.

The concentrations of NO, NO_2, SO_2, CO, O_3, $PM_{2.5}$, PM_{10} and in particulate matter are monitored in 52 Hungarian cities.

Atmospheric wet-only, bulk or throughfall deposition of major ions, such as SO_4^{2-}, NO_3^-, H^+, F^-, Cl^-, H^+, NH_4^+, K^+, Na^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Fe^{3+}, Al^{3+}, As^{3+} are determined at approximately 5–10 spots.

The analytical results have been gathered in the Hungarian Air Quality Network System Air Quality Information System (OLM, http://www.kvvm.hu/olm/).

Position and distribution of the measuring stations in the map of HU is available at the following addresses:
http://www.kvvm.hu/olm/
http://www.kvvm.hu/olm/index.php.

d) Data of air quality

Primary and evaluated analytical data of ambient air quality are available in the information system. The up-to-date figures of air quality are presented online at http://www.kvvm.hu/olm/ and in a table survey (http://www.airce.info/).

Effective limit values for the protection of health, ecosystems and vegetation accepted in Hungary can be found at: http://www.kvvm.hu.

Tabular yearbooks of analytical results for individual stations and given year are edited since 2005. Details can be found at the following address:
http://www.kvvm.hu/olm/.

e) Monitoring of air pollution effects (ICPs)

HU is included into the International Cooperative Programme on the Assessment and Monitoring of Air Pollution Effects on Forests (ICPs). The programmes ICP-Forests (State Forest Service, Budapest), ICP-Vegetation (Szent István University), ICP-Waters (Budapest University of Technology and Economics), ICP-Modelling and Mapping (Res. Inst. Soil Sci. Agric., Budapest) and Task Force on Health (National Institute of Occupational Health, Budapest) are carried out in HU (http://www.unece.org/env/wge/participation.htm).

Forest health state has been monitored (ICP-Forests) in HU since 1986 through harmonised manuals. The programme ICP-Forests was supported by the EU regulation, and in 1987 a network of monitoring plots was established. In the national network (ICP-Forests/Forest Focus) 1,027 sampling plots of the 4 × 4 km grid have been observed recently (former Level I monitoring). Defoliation and growth parameters of about 24 trees per one plot are monitored, and stand parameters are determined as well as satellite scenes are evaluated (Szepesi 1997, 1998).

3.3 Biomonitoring campaigns in V4

The Visegrad Group countries accomplished several biomonitoring campaigns of bioindication the current atmospheric deposition loads. The most important biomonitoring activities are mentioned in the following survey structured by individual V4 countries.

a) Czech Republic

In 1991 the former Research Institute of Ornamental Gardening, Průhonice, CZ was invited by Scandinavian moss expert to enter the European campaign bioindication of the distribution of current atmospheric deposition loads. The CZ biomonitoring programme was provided by the Laboratory of Trace Elements, which completely arranged collecting and processing of samples, their analyses and evaluation and presentation of the obtained results. Since 1991, staff of this laboratory has carried out all following national and international campaigns in the framework of the ICP-Vegetation programmes. The first European biomonitoring campaigns in 1990/1991 and following in 1995/1996 were co-ordinated by the group of Scandinavian experts in mosses and heavy metals.

The CZ side collected 2 moss species (*Pleurozium schreberi* 82% and *Polytrichum formosum* 18%) at 32 sampling plots situated mainly in Bohemia in 1991. Moss *Scleropodium purum* was collected for an interspecies calibration tests. Ten obligatorily investigated elements (As, Cd, Cr, Cu, Fe, Ni, Pb, Se, V and Zn) were determined in the moss samples using AAS (FP and GTA) techniques. Some of the CZ moss results from this campaign were presented in the national report (Suchara and Sucharová 1994) and all CZ results were included into the evaluation for the whole (Rühling 1994a).

In the second European campaign in 1995/1996 there were collected three moss species *Pleurozium schreberi* (82%), *Scleropodium purum* (8%) and *Hypnum cupressiforme* (10%) at 196 "permanent" plots introduced for the biomonitoring needs in CZ. Thirteen obligatory elements (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mo, Ni, Pb, S, V and Zn) were determined in the moss samples using the ICP-OES instrument. Interspecies calibration tests showed that mosses *Pleurozium schreberi* and *Scleropodium purum* provided very similar results, while *Hypnum cupressiforme* caught was on average about one third higher amounts of all elements in comparison with the remaining species in CZ. Production of the moss species was determined on some plots, and absolute atmospheric deposition loads of the investigated elements ($\mu g.m^{-2}.year^{-1}$) were estimated. Obtained results were published in the CZ national report (Sucharová and Suchara 1998, Sucharová et al. 1999) and the evaluation of the CZ data in the European context is available in the all-European report (Rühling and Steinnes 1998). In parallel, distribution of the long-term accumulated deposition loads of 13 elements in CZ was determined using forest floor humus analyses (Suchara and Sucharová 2000, 2002)

The third European biomonitoring campaign in 2000 was already arranged as the subprogramme "Heavy Metals in Mosses" of the UNECE ICP-Vegetation programme. In the third national/international biomonitoring campaign five moss species *Pleurozium schreberi* 90%, *Scleropodium purum* 6%, *Eurhynchium angustirete* 1.6%, *Brachythecium rutabulum* 1.6% and *B. salebrosum* 0.8% were collected at 250 plots including the 196 plots from the campaign of 1995 in CZ. Fourteen authorized elements (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mo, Ni, Pb, S, V and Zn) and twenty two optionally investigated elements (Ag, Ba, Be, Bi, Ce, Cs, Ga, In, La, Li, Mn, Pr, Rb, Sb, Se, Sn, Sr, Th, Tl, U, Y and N) were determined in the moss using ICP-MS instrument, Hg analyser AMA-254 and distillation of nitrogen (Büchi appliance). For example, the trends of element content in moss on the permanent plots were discussed. Also the effect of altitude, precipitation, land cover, land-use, geomorphology and mother rocks affecting on the sampling plots and element contents in the moss samples was correlated. Obtained results for obligatory investigated elements were presented in the CZ national report (Sucharová and Suchara 2004b), papers (e.g., Sucharová and Suchara 2004c) and in the ICP-Vegetation report (Buse et al. 2003). Results for optionally determined elements will be available in the second part of the CZ national report (print expected in 2007).

In the last European biomonitoring campaign within the framework of UNECE ICP-Vegetation programme 2005/2006 the CZ side provided concentrations of 36 elements in samples of three moss species collected at 288 sampling plots in CZ. The CZ national report has been under preparation. Results of this campaign will be published not earlier than in 2008.

Besides the national/European campaigns several tests of fine scale biomonitoring the atmospheric deposition levels in the surroundings of chosen individual sources of pollution were carried out in CZ (Suchara and Sucharová 2000, 2004, Sucharová et al. 2003, Sucharová and Suchara 2004a, Suchara and Sucharová 2007).

b) Slovak Republic

The Forest Research Institute Zvolen, SK was invited by the Scandinavian moss experts to enter the European campaign of bioindicating the distribution of current atmospheric deposition loads for the first time in 1989. The SK biomonitoring programme was provided by the Forest Research Institute, which completely arranged collecting and processing of samples, their analyses and evaluation and presentation of the obtained results. Since 1990, staff of this laboratory has carried out all following national and international campaigns within the framework of the UNECE ICP-Forest programmes. The accuracy of data was verified by the analysis of standard plant samples and by comparison with the results obtained in 109 laboratories within the IUFRO working group for quality assurance (Hunter, 1994). In 2000 the Joint Institute for Nuclear Research (JINR) in Dubna, Russian Federation, accomplished the chemical analyses of mosses. The first European biomonitoring campaigns on mosses and heavy metals in 1990/1991 and 1995/1996 were co-ordinated by the group of Scandinavian experts.

In 1990, the SK side collected 2 moss species *Pleurozium schreberi* (47%) and *Dicranum* spp. (53%) on 58 forest permanent monitoring plots (PMP) of the national network of monitoring plots (16×16 km) established in the framework of the programme UNECE ICP-Forests (observations Level I). Figures on the determined contents of nine obligatorily investigated elements (Cd, Cr, Cu, Fe, Ni, Pb, S, V and Zn) in the SK regarding moss samples were provided to the Scandinavian moss experts. The element contents were determined using AAS (FP and GTA) techniques. Some of the SK moss results from this campaign were presented in the report (Maňkovská 1997), and the all SK results were included into the all-European evaluation (Rühling 1994a).

In the second European biomonitoring campaign in 1995 there were collected three moss species *Pleurozium schreberi* (38%), *Hylocomium splendens* (8%) and *Dicranum* sp. (42%), on 78 PMP in SK. The moss samples were collected on the permanent plots of the national network used in the international programme UNECE ICP-Forests. Nine obligatorily investigated elements (Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn) were determined using AAS (FP and GTA) techniques. The evaluation of the SK results in the European context is available in the all-European moss monitoring report (Rühling and Steinnes 1998).

In the Slovak national biomonitoring campaigns in 1996 and 1997 there were collected 3 moss species *Pleurozium schreberi* (38%), *Hylocomium splendens* (8%) and *Dicranum* sp. (42%) on 69 PMP in 1996 and 74 PMP in 1997. The monitoring plots were used for the needs of the UNECE ICP-Forests programmes (observations Level I). Ten elements (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn) were determined in the moss samples using the AAS (FP and GTA) techniques. Maňkovská (2000) provided results of these biomonitoring campaigns and their evaluation.

The third European biomonitoring campaign in 2000 was arranged as the subprogramme "Heavy Metals in Mosses" of the UNECE ICP-Vegetation Programme. In the third national/international biomonitoring campaign three moss species *Dicranum* sp. (60%), *Hylocomium splendens* (5%) and *Pleurozium schreberi*

(35%) were collected on 86 permanent monitoring plots serving for the UNECE ICP-Forests Programme. in SK. Forty four elements (Ag, Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Hf, Hg, I, In, K, La, Mg, Mn, Mo, N, Na, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn and Zr) were determined in the moss samples in the Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research (FLNP JINR) in Dubna, Russian Federation using INAA technique. About 0.3 g of each moss specimens were packed in aluminium cups for a long-term irradiation or heat-sealed in polyethylene foil bags for long-term and short-term irradiations in the IBR-2 reactor. The pulsed fast reactor IBR-2 equipped with the fast pneumatic transfer system REGATA and four irradiation channels for the instrumental neutron activation analysis provided activation with thermal, epithermal and fast neutrons. Two channels were cadmium screened for activation with epithermal neutrons (Ostrovnaya et al. 1993, Frontasyeva and Pavlov 2000). The neutron flux density (for thermal or epithermal neutrons) inside the channels was of the order 10^{12} $cm^{-2}.s^{-1}$ (Peresedov 1997). The induced activity could be measured using γ- spectrometers with Ge (Li) ORTEC electronics. The software developed at FLNP JINR, Dubna was used for data processing. An elementary analyser LECO SC 132 was applied to determine concentration of total sulphur contents in moss. An elementary analyser LECO SP 228 was used for the determination of total nitrogen contents. Using an Hg analyser AMA-254 the total Hg contents were determined in the moss samples. Obtained results from this moss monitoring campaign were presented in the papers by Maňkovská et al. (2003), Florek et al. (2007) and in the ICP-Vegetation report (Buse et al. 2003).

In the last European biomonitoring campaign carried out in the framework of UNECE ICP-Vegetation programme 2005/2006 the SK side provided concentrations of 11 elements in samples of three moss species collected on 78 sampling plots in SK. The SK national report is being prepared. Results of this campaign will be not published before 2008.

c) Poland

For the first time, the Institute of Botany of Polish Academy of Science in Kraków was invited to participate in the European environmental monitoring programme using moss species as indicators of air pollution loads in 1990. However, similar monitoring campaigns had been previously carried out mainly in the Polish national parks (Grodzińska 1978, 1990, Berbeka and Godzik 1982, Godzik 1991, Grodzińska et al.1990).

The first European biomonitoring campaign was co-ordinated by the Scandinavian moss experts (1990). The national PL biomonitoring programme was carried out by the Department of Ecology of the Institute of Botany, Polish Academy of Science (IB PAN). Staff of this department arranged completely collecting and processing of samples, chemical analyses and evaluation of the obtained results. There were collected two moss species (*Pleurozium schreberi* and *Hylocomium splendens*) in this campaign. However, due to more rare and irregular occurrence of *Hylocomium splendens* in PL compared to *P. schreberi* the PL results were included only for the latter species into the international report (Rühling 1994a). These moss species were collected on 147 localities in PL during the period from June until September 1990. The samples were taken from glades of coniferous and mixed forests, at least 300 m from main roads, and at least 100 m from any road. Concentrations of eight elements (Cd, Cr, Cu, Fe, Ni, Pb, V, and Zn) were determined employing flame methods of atomic absorption spectrophotometry (spectrophotometer Varian 20BQ).

In the second European programme (1995) the moss *Pleurozium schreberi* was collected on 297 localities in PL. The content of Cd, Cr, Cu, Fe, Ni, Pb, V, and Zn in the moss samples was determined using the AAS Varian 20BQ instrument. The Hg content was estimated using VAP AAS method. According to the formula recommended by Zechmeister (1994) the deposition loads ($\mu g.m^{-2}.year^{-1}$) of 9 heavy metals in the whole country, and particularly in natural and industrial regions, were estimated. Obtained results were presented in the national report (Grodzińska et al. 1997) as well as they were included into the all-European report (Rühling and Steinnes 1998).

In the third European campaign 2000/2001 (arranged as the subprogramme “Heavy Metals in European Mosses” 2000/2001 Survey, UNECE ICP Vegetation) the moss *Pleurozium schreberi* was sampled in PL on 116 plots localized in four areas: two of them belonged to the most polluted, industrial regions (Legnica-Głogów Copper Basin and Upper Silesia region), one was localized in central Poland (moderately polluted area, Warszawa region) and the remaining area was located in north-eastern part of the PL (slightly polluted area). Concentrations of eight elements (Cd, Cr, Cu, Fe, Ni, Pb, V, and Zn) were determined in the moss samples employing flame methods of atomic absorption spectrophotometry (Varian 220FS). The obtained results were included into the ICP-Vegetation report (Buse et al. 2003).

In the last European biomonitoring campaign arranged in the framework of UNCE ICP-Vegetation programme, Moss Survey 2005/2006, the PL side provided concentrations of 8 elements in *Pleurozium schreberi* collected on 271 sampling plots located in 23 national parks. The number of sampling plot in each of national park depended on the size of the park and varied from 4 to 29 plots. These data will be published in 2008 as a separate paper and will be also included into the European report.

d) Hungary

HU joined the International Biomonitoring System in 1994. The Szent Istvan University provided the biomonitoring programme. National campaigns were carried out in 1997, 2000 and 2007. In the course of these campaigns three moss species *Hypnum cupressiforme* (72%), *Brachythecium salebrosum* (8%) and *Brachythecium rutabulum* (20%) were collected on 112 sampling plots in 1997. Eight obligatorily investigated elements (Cd, Cr, Cu, Fe, Ni, Pb, V and Zn) were determined in the moss samples using ICP-AES. Some of the HU moss results from this campaign were presented in the first national report (Ötvös et al 2003).

Besides all-European general evaluations of the biomonitoring results obtained in the national campaigns (Rühling 1994a, Rühling and Steinnes 1998, Buse et al. 2003) some countries, for example Scandinavian countries, published territorial biomonitoring results with much more detailed evaluations and comments (Rühling et al. 1987, 1996).

The national biomonitoring results of some of V4 countries were included into some of central European and western-central European territorial surveys.

Herpin et al. (1996) evaluated metal concentrations in moss samples (806) along west-east industrial and climatic gradient in Europe (the Netherlands, Germany and Poland) obtained in 1995. Very steeply increasing concentrations of elements, mainly of Fe, V and Pb in moss were found in the area from the Netherlands to Poland. Some transboundary transports of metals were indicated.

Markert et al. (1996) compared concentrations of seven metals determined in mosses in Germany, Poland, Slovak and Czech Republic in 1995. Isopleths maps of element distributions in mosses revealed two large hot spots of metals accumulation. The first hot spot appeared in a lignite basin Saxony, where northwestern Bohemia and southwestern Poland are neighbouring. The area of a large coal basin was known to be highly contaminated from local industrial sources of pollution and was called “Black Triangle”. Second large hot spot was situated in the region of borderline of Upper Silesia (southern Poland), northwestern Slovakia and northeastern Moravia. The Ostrava-Katowice region being rich in black coalmines and with concentrated mainly metallurgical industry was named “Black Triangle II” area. In order to better distinguish both areas, the “Black Triangles” was called “Black Triangle I” and “Black Triangle II” in this study. Also ways of mutual transboundary transport of metals were evident in the maps of the distribution of metals in mosses.

The most recent territorial study (Schröder et al. 2007) evaluated figures from biomonitoring campaigns of 2000 in Germany, Italy, Austria, Czech Republic, Slovak Republic and Poland. Multivariate statistics and GIS technique was used for evaluation the national moss analytical results. The most important factors explaining differences in element contents in moss between countries were different moss species analysed and different analytical technique used.

Important partial findings

1. Countries of the Visegrad group had used systems for registration of emitted air pollutants, established networks for monitoring air quality and checking the observance of highest permission limits. After 1990 the national legislations and systems of monitoring ambient air quality are being adjusted to the EU directives.
2. Both the WHO and EU programmes for control of air quality have been engaged in the first line with major air contaminants and the most toxic heavy metals as Cd, Cr, Cu, Hg, Ni, Pb, V and Zn. However, the net of measuring stations is concentrated mainly in highly urbanised and industrialised areas, while rural districts are rather neglected. That may be reason why data of rural background atmospheric deposition loads of toxic metals are lacking. Nevertheless, such information is important to assess critical loads for ecosystems, threat for food chains, decreasing of biodiversity, etc.
3. The moss surveys carried out in V4 determined concentrations of 8 the most toxic elements in mosses on nearly 500 sites, mostly in the rural areas. The accumulation amounts of the metals in mosses very closely correlated with the average atmospheric deposition loads of the relevant elements. Until now the Visegrad Group countries have not gathered and evaluated figures about the distribution of deposition levels of the toxic metal to such great extent. Publishing of this survey may be desirable and usable for environmentalists, civil authorities, hygienists, various experts and broad public as well.

4. EXPERIEMTAL PART

4.1 Aims of the project

The partial findings elicited from the available information about the worldwide, European, territorial and national programmes of the control of ambient air quality indicated that only a few downright toxic metals are monitored by the laws while other metals and elements are due to finance and time limits have not been attention. Nevertheless, some of those ignored elements are toxic or suspicious to be harmful for health or ecosystems. As the concentrations of many elements were determined in mosses collected on about 500 sampling plots of the Visegrad space in 2000, these figures may be the only estimates of atmospheric deposition loads in the Visegrad space and in Central Europe as well. In order to acquire the interest of authorities, environmentalists and public in current situation what concerns air pollution, this report has been compiled with the following crucial aims:

- Find contemporary information about ambient air quality control in Central Europe, Visegrad space and in individual V4 countries
- Evaluate how the figures from biomonitoring, current atmospheric deposition fluxes of 52 elements could extend knowledge on the distribution of atmospheric deposition loads on the territory of the Visegrad group countries
- Gather all available biomonitoring data from the V4 and last campaign 2000 and to make classed post maps (dot maps) and isopleths maps of element concentrations in moss in the Visegrad space
- Comment these maps from the viewpoint of revealing the impact of crucial pollution sources, trajectories of long-range transport of relevant air pollutants, distribution of deposition fluxes in the Visegrad Group, as well as comparison with other countries (if any available data)
- Evaluate contamination loads of the investigated elements and warn against potential harmful effects of pertinently revealed hot spots.

The authors wish the results of this project would contribute to diminishing the unfavourable effects of high atmospheric deposition fluxes and safe, long-term use of the landscape in the Visegrad space.

4.2 Material and methods

The biomonitoring methods have been highly harmonised and standardised since the 1960s. All activities associated with the biomonitoring campaigns in V4 countries observe as strictly as possible the biomonitoring instructions of the Environmental Monitoring and Data Group of the Nordic Countries (Rühling 1994b) renewed by the instructions of the ICP-Vegetation Centre in Bangor. Updated monitoring manual published by the ICP-Vegetation coordination centre for the next biomonitoring survey 2005/2006 (Harmens 2005) is available at the following address:
http://samples-uk.pet-news-review.info/heavy-metals-in-european-mosses-2005-2006-survey-monitoring-ma.

4.2.1 Sampling plots

Sampling plots were situated on open sites where the free atmospheric deposition reached the ground. Plots situated under larger gaps in a tree canopy, at glades or along firebreaks in coniferous forests are the most frequent cases. The area of the sampling plot is recommended 50 × 50 m or larger. The geographical position (World Geodetic System WGS84) of the central part of each sampling plot was registered using GPS receivers. In a few cases the position of the sampling plots centre was determined using special maps of a fine scale and with drawn geographical network.

Due to different landscape and climatic conditions, the selection may differ in individual V4 countries.

a) Czech Republic

The representative moss samples were collected on 250 sampling plots in 2000. The network of "permanent" moss monitoring plots has been developed since 1995. The position of the sampling pots was designed to cover the whole CZ territory in a grid of about 15 × 15 km. However, due to disturbing human activities in forests (wood cutting, timber transport, etc.) and vegetation changes some new plots have to be searched for in order to substitute the damaged plots or add new plots with the aim of elaborating deposition loads in the intended landscape, or in the areas along strong deposition gradients. The typical area of the CZ sampling plot was 50 × 50 m, however, in deteriorated areas or in very dry regions being hostile for coniferous forests the area of plot reached 200 × 200 m or even more.

List of the CZ sampling plots 2000 is available in Table 3. About 155 identical sampling plots were used in the biomonitoring campaigns in 1995 and 2000 to find out atmospheric deposition trends. Data about position stand conditions and location of the sampling marked in a map are available in sampling protocols archived at the Department of Biomonitoring of VÚKOZ.

b) Slovak Republic

The representative moss samples were collected on 86 sampling plots in 2000. The network of "permanent" moss monitoring plots has been developed since 1990. The position of the sampling plot was designed to cover the whole SK territory in a grid at the intersections of 16 × 16 km of Pan–European network used for the UNECE ICP-Forests, Level I Programme.

List of the SK sampling plots 2000 is available in Table 4. About 58 identical sampling plots were used in the biomonitoring campaigns in 1995, 1996, 1997 and 2000 for finding atmospheric deposition trends.

c) Poland

Samples of moss *Pleurozium schreberi* (Brid.) Mittl. were collected from 116 localities in four large areas: two of them were located in heavy polluted areas (one in the Legnica-Głogów Copper Basin - Lower Silesia Province and second in the Upper Silesia Province), third was located in moderately polluted area (central Poland-Mazowsze Province), and fourth in clean area (north-eastern part of PL-Podlasie Province). The moss samples were taken at the distance of at least 300 m from main roads and human settlements, and at least 100 m from smaller roads. The typical area of the sampling plot was 50 × 50 m; however for some plot it reached 250 × 250 m. However, the obtained analytical results for these collected moss samples may be representative for the remaining slightly, moderately and heavily contaminated parts of the country.

List of the sampling plots is available in Table 5. All general information about sampling plots were noted in the field (habitat, type of forest, main vascular plant species, position of plot, etc.) in special sampling protocols archived in the Institute of Botany, Polish Academy of Sciences (IB PAS).

d) Hungary

The HU moss samples were collected on 47 sampling plots in 2000. The position of these sampling plots was designed to cover the whole HU territory in a grid of about 40 × 40 km. Location of the sampling plots respected distance limits (nearest furnace, building, roads, etc.) required by the manual for the international biomonitoring campaign. Typical area of the sampling plot was 50 × 50 m in accordance with the manual for the international biomonitoring programme.

More details of these sampling plots are available in the list in Table 6.

Distribution of the sampling plots in individual countries and in the whole Visegrad space is available in the inserted introductory dot map.

Czech Republic											
Locality code	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**	**Locality code**	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**
1	Brtníky	440	P.s.	505637	142603	**43**	Černčice	530	B.r.	503332	135429
2	Rumburk-Popluží	420	P.s.	505906	143114	**44**	Kletečná	490	S.p.	503411	135900
3	Lípová	420	P.s.	510038	142020	**45**	Dražejov	350	P.s.	503120	143217
4	Chřibská	400	P.s.	505227	142624	**46**	Okna	290	P.s.	503107	144113
5	Raspenava	380	P.s.	505519	150829	**47**	Žehrov	290	P.s.	503117	150700
6	Pertoltice	290	P.s.	505944	150506	**48**	Výsluní	780	P.s.	502828	131318
7	Jindřichovice pod Smrkem	440	P.s.	505720	151313	**49**	Březenec	490	B.r.	502915	132448
8	Bálý Kostel nad Nisou	320	P.s.	505027	145442	**50**	Libotenice	180	P.s.	502912	141305
9	Albrechtice u Frýdlantu	560	P.s.	505146	150245	**51**	Březinka	300	P.s.	502907	144718
10	Maxičky	420	P.s.	504933	141127	**52**	Prachov	440	P.s.	502750	151918
11	Děčín-Bechlejovice	350	S.p.	504540	141401	**53**	Dřevěnice	370	P.s.	502731	152731
12	Bedřichov	680	P.s.	505635	150751	**54**	Bechlín	220	P.s.	502422	142222
13	Petrovice	615	P.s.	504601	135929	**55**	Želízy	250	P.s.	502527	142932
14	Povrly	360	S.p.	504104	140857	**56**	Dlouhá Lhota u Bousova	270	P.s.	502530	150532
15	Přítkov	510	P.s.	504125	134921	**57**	Ohařice	280	P.s.	502639	151537
16	Velká Bukovina	350	P.s.	504348	142538	**58**	Doubravice	400	P.s.	502520	154607
17	Srbská Kamenice	330	P.s.	504915	141930	**59**	Havlovice	420	P.s.	502830	160122
18	Velenice	320	P.s.	504032	143556	**60**	Ondřejov	590	P.s.	502306	130509
19	Čecká. Lípa-Žizníkov	290	P.s.	504032	143556	**61**	Jáchymov	760	P.s.	502243	125629
20	Nový Bor	380	S.p.	504548	143417	**62**	Dobroměřice	240	P.s.	502313	134753
21	Horní Světlá	520	P.s.	505009	143613	**63**	Podhorní Újezd	380	P.s.	502326	153238
22	Křižany	440	P.s.	504432	145340	**64**	Vrchoviny	410	P.s.	502309	160946
23	Rokytnice nad Jizerou	910	P.s.	504321	153001	**65**	Travná	580	P.s.	502212	165627
24	Dolní Kořenov	700	P.s.	504608	152334	**66**	Rokliny	310	P.s.	501945	171050
25	Špindlerův Mlýn	870	P.s.	504205	153422	**67**	Sněžná	680	P.s.	501823	122831
26	Fláje	750	P.s.	504046	133655	**68**	Horní Pochlovice	490	P.s.	500833	123110
27	Lom	300	B.r.	503624	134041	**69**	Černava	650	P.s.	501748	124209
28	Háj u Duchcova	470	B.r.	503841	134205	**70**	Rokle u Kadaně	310	P.s.	502125	131743
29	Stráž pod Ralskem	320	P.s.	504150	145125	**71**	Chrastín	200	P.s.	502213	135919
30	Hodkovice n. M.	460	P.s.	504052	150433	**72**	Deštná v Orlických Horách.	920	P.s.	501734	162323
31	Velká Úpa	900	P.s.	504106	154808	**73**	Tuhaň	180	S.p.	501736	143206
32	Bernartice	850	P.s.	503826	160016	**74**	Otradovice	170	P.s.	501232	144334
33	Bohuslavice nad Úpou	510	P.s.	503330	155914	**75**	Mašťov	390	P.s.	501526	131718
34	Lovečkovice	460	P.s.	503637	141543	**76**	Holedeč	280	P.s.	501618	133457
35	Lbín-Mentaurov	550	P.s.	503434	140841	**77**	Třeboc	500	P.s.	501309	134551
36	Rašovice	280	P.s.	503449	142340	**78**	Bilíchov	430	P.s.	501511	135356
37	Martinice	490	P.s.	503527	153250	**79**	Městec Králové	220	S.p.	501247	151634
38	Vlčice	440	P.s.	503329	154734	**80**	Studce	260	P.s.	501759	150156
39	Dědov	710	P.s.	503428	160912	**81**	Hrádek u Nechanic	290	P.s.	501348	154014
40	Janovičky	560	P.s.	503857	162116	**82**	Malé Záhornice	320	P.s.	501444	160829
41	Boleboř	580	P.s.	503132	132456	**83**	Týniště nad Orlicí	270	P.s.	501132	160343
42	Most	370	S.p.	503026	133612	**84**	Lomy	610	P.s.	501639	161802

Table 3. Names, altitudes and geographical positions of sampling plots in CZ and collected moss species. For abbreviations see the end of this table.

Czech Republic											
Locality code	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**	**Locality code**	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**
85	Říčky	730	P.s.	501205	162844	**129**	Pivnisko	530	P.s.	495010	150835
86	Dětřichov	730	P.s.	501148	171427	**130**	Semanín	430	P.s.	495051	162743
87	Zlaté Hory	810	P.s.	501314	172332	**131**	Strážná	470	P.s.	495348	164127
88	Bohušov	250	P.s.	501418	174159	**132**	Křivá	400	P.s.	495037	171229
89	Aš	420	P.s.	501143	121423	**133**	Ondřejov u Rýmařova	490	P.s.	495435	171700
90	Novosedly	610	P.s.	501731	121040	**134**	Nové Valteřice	580	P.s.	494920	172724
91	Činov	720	P.s.	501159	130041	**135**	Lesní Albrechtice	450	P.s.	494912	175250
92	Vroutek	390	P.s.	501111	132102	**136**	Kerhanice	490	P.s.	495037	173928
93	Bělečko	260	P.s.	500950	155853	**137**	Tísek	360	P.s.	494709	180201
94	Sklené	820	P.s.	500810	165047	**138**	Háj ve Slezsku	310	P.s.	495309	180607
95	Přemyslov	800	P.s.	500649	170356	**139**	Ostrava-Petřvald	290	P.s.	494915	182455
96	Vodná	540	P.s.	500628	125120	**140**	Dobrá	340	P.s.	494045	182621
97	Lužná	390	P.s.	500919	134732	**141**	Lysůvky	305	P.s.	494038	181834
98	Srby	420	P.s.	500907	140146	**142**	Luhov	390	P.s.	494840	130840
99	Slaný	300	P.s.	501301	140447	**143**	Stříbro	450	P.s.	494642	130059
100	Velenka	180	P.s.	500908	145535	**144**	Voznice	410	P.s.	494900	141153
101	Žďárek	560	P.s.	500603	131752	**145**	Vysoký Újezd	460	P.s.	494857	142937
102	Praha-Nebušice	390	P.s.	500609	141918	**146**	Albrechtice	290	P.s.	494712	183029
103	Prameny	820	P.s.	500409	124209	**147**	Lesná	600	P.s.	494553	123248
104	Ostrovec	470	P.s.	500429	132601	**148**	Dolní Plezom	530	P.s.	494617	125046
105	Šedivec	460	P.s.	500338	163113	**149**	Neřežín	450	P.s.	494724	135347
106	Čenkovice	830	P.s.	500627	164232	**150**	Radošovice	420	P.s.	494511	145121
107	Vrbno pod Pradědem	840	P.s.	500518	172010	**151**	Hostovlice	380	P.s.	494743	153202
108	Dolní Žandov	570	P.s.	500148	123152	**152**	Rváčov	560	P.s.	494647	155120
109	Buč	660	P.s.	500121	130421	**153**	Pustá Kamenice	760	P.s.	494556	160749
110	Rozsocha	450	P.s.	500107	162050	**154**	Dobřív	510	P.s.	494349	134120
111	Nové Heřmínovy	500	P.s.	500115	173058	**155**	Trhové Dušníky	510	P.s.	494239	140157
112	Krnov-Mariánské Pole	430	P.s.	500450	174313	**156**	Černice	400	P.s.	494012	132623
113	Lhota u Berouna	420	P.s.	495958	140517	**157**	Nová Víska	370	P.s.	494012	172120
114	Praha-Točná	330	P.s.	495837	142510	**158**	Nýdek	470	P.s.	493953	184720
115	Průhonice	310	P.s.	495910	143248	**159**	Radostín	610	P.s.	493830	155211
116	Jevany	490	P.s.	495731	144715	**160**	Drahošov	500	P.s.	493805	163253
117	Opatovice	370	P.s.	495744	151144	**161**	Mariánské Údolí	390	P.s.	493716	172318
118	Sololusky	310	P.s.	495810	153314	**162**	Boňkov	450	P.s.	493629	174126
119	Černá za Bory	240	P.s.	500143	155049	**163**	Hrabětice	280	P.s.	493608	175314
120	Voleč	280	P.s.	500749	153411	**164**	Myslík	500	S.p.	493650	181535
121	Dvakačovice	260	P.s.	495840	155410	**165**	Míchov	730	P.s.	493551	161021
122	Hostice	450	P.s.	495922	165408	**166**	Jesenec	540	P.s.	493613	165108
123	Chuchelná	280	P.s.	495859	180802	**167**	Náměšť na Hané	340	P.s.	493559	170240
124	Broumov	580	P.s.	495402	123428	**168**	Horní Lomná	530	P.s.	493312	183859
125	Zadní Chodov	610	P.s.	495412	123752	**169**	Morávka	520	P.s.	493528	183222
126	Staré Sedlo	620	P.s.	495655	125749	**170**	Krásná-Visalaje	540	P.s.	493326	182919
127	Podmokly	420	P.s.	495649	134421	**171**	Slatina u Poběžovic	470	P.s.	493256	124853
128	Obora	460	P.s.	495240	132623	**172**	Čečovice	430	P.s.	493418	130243

Table 3. Continued.

Czech Republic											
Locality code	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**	**Locality code**	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**
173	Starý Smolivec	630	P.s.	493223	134555	**212**	Prkošín	550	P.s.	491019	135049
174	Kozárovice	480	P.s.	493229	140733	**213**	Pivkovice	540	P.s.	491009	140459
175	Veletín	670	P.s.	493250	142940	**214**	Horní Lažany	530	P.s.	490636	154736
176	Vilice	540	P.s.	493320	145209	**215**	Brno-Kohoutovice	330	S.p.	491140	163109
177	Košetice	440	P.s.	493420	150539	**216**	Ořechov	240	S.p.	490742	163238
178	Leština	620	P.s.	493346	152455	**217**	Košíky	450	E.a.	491012	172349
179	Bílá	710	P.s.	492625	182525	**218**	Srní	860	P.s.	490508	133000
180	Slatina u Chudenic	530	P.s.	492720	131204	**219**	Solná Lhota	890	P.s.	490127	134701
181	Újezd	560	P.s.	492540	125155	**220**	Kašperské Hory	890	P.s.	490845	133526
182	Plánice	520	P.s.	492429	132654	**221**	Velký Bor	550	P.s.	490432	140716
183	Dušejov	630	P.s.	492612	152440	**222**	Kuklov	670	P.s.	485524	141001
184	Stáj	650	P.s.	492757	154927	**223**	Poněšice	430	P.s.	490535	142850
185	Jemnice	520	P.s.	492546	161037	**224**	Podhájí	490	P.s.	491122	142436
186	Lhota u Lysic	450	P.s.	492742	163119	**225**	Mláka	450	P.s.	490416	145206
187	Boskovice	440	P.s.	492849	164222	**226**	Klášter II	630	P.s.	490145	151200
188	Valašská Bystřice	530	P.s.	492459	180721	**227**	Třebětice	580	P.s.	490255	153001
189	Jezerné	670	P.s.	492253	181616	**228**	Dukovany	350	P.s.	490543	161205
190	Zděchov	530	P.s.	491633	180432	**229**	Maršovice	330	P.s.	490301	162129
191	Vráž	400	P.s.	492403	140849	**230**	Velké Němčice	170	B.s.	485849	163951
192	Myslejovice	390	P.s.	492404	170109	**231**	Zdravá Voda	360	E.a.	490509	165640
193	Jindřichovice	530	P.s.	492320	135159	**232**	Stupava	340	E.a.	490649	171353
194	Chalupy	540	P.s.	492009	130340	**233**	Bohuslavice u Zlína	310	P.s.	490912	173755
195	Slavňovice	460	P.s.	492330	143222	**234**	České Budějovice-Braniš.	410	P.s.	485832	142519
196	Dlouhá Lhota u Tábora	480	P.s.	492120	144908	**235**	Zálesí	460	P.s.	485652	154747
197	Nová Ves	670	P.s.	492019	151000	**236**	Hluboké Mašůvky	350	P.s.	485635	160026
198	Přestavlky	320	S.p.	492343	172932	**237**	Lechovice	160	P.s.	485303	161449
199	Rusava-Ráztoka	450	P.s.	491951	174139	**238**	Ratíškovice	230	S.p.	485506	170810
200	Hrádek u Sušice	610	P.s.	491510	132934	**239**	Bystřice pod Lopeníkem	640	P.s.	485718	174829
201	Hodětín	440	P.s.	491440	143429	**240**	Brumov-Bylnice	430	P.s.	490541	180030
202	Dírná	470	P.s.	491354	145055	**241**	České Žleby	820	P.s.	485409	134840
203	Žirovnice	590	P.s.	491422	151249	**242**	Želinava	905	P.s.	484909	135909
204	Třeštice	610	P.s.	491448	152833	**243**	Mokrý Lom	510	P.s.	485030	143137
205	Věstoňovice	540	P.s.	491629	152317	**244**	Hrdlořezy	470	P.s.	485203	145022
206	Košíkov	520	P.s.	491552	161344	**245**	Drnholec	170	B.s.	485034	162849
207	Drnovice	340	P.s.	491621	165506	**246**	Suchov	400	E.a.	485320	173517
208	Lhota	320	S.p.	491426	170851	**247**	Černá v Pošumaví	780	P.s.	484331	140715
209	Vizovice	520	P.s.	491122	175218	**248**	Valtice	180	S.p.	484533	165017
210	Železná Ruda	930	P.s.	490835	131528	**249**	Ostrovec	640	P.s.	484020	141530
211	Čachrov	820	P.s.	491513	131751	**250**	Malonty	750	P.s.	484057	143557

Table 3. The end. (P.s. = *Pleurozium schreber*i, S.p. = *Scleropodium purum*, E.a. = *Eurhynchium angustrirette*, B.r. = *Brachythecium rutabulum*, B.s. = *Brachythecium salebrosum*).

Slovak Republic											
Locality. code	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**	**Locality. code**	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**
1	Borský Jur	170	P.s.	483742	170553	**44**	Holý vrch	850	H.s.	484656	192936
2	Teplica	185	P.s.	482927	170540	**45**	Poľana	1,260	D.	483806	192831
3	Šajdíkove Humence	210	P.s.	483819	171721	**46**	Píla	515	D.	482919	192902
4	Hradište pod Vrátnou	300	D.	483814	173039	**47**	Imrov kpopec	370	D.	482044	192930
5	Drieňový vrch	300	D.	484637	175651	**48**	Vilanová	800	D.	492050	194243
6	Kostolný vrch	530	D.	483831	175657	**49**	Rovná hoľa	1,285	D.	485537	194156
7	Vršatské Podhradie	620	D.	490413	181021	**50**	Lom nad Rimavicou	690	D.	483803	194423
8	Trenčianske Teplice	450	D.	485532	181001	**51**	Málinec	285	D.	482930	194149
9	Besné	515	P.s.	491230	182226	**52**	Opatová	220	P.s.	482055	194155
10	Visolaje	330	P.s.	490420	182310	**53**	Pohanský vrch	320	P.s.	481242	195414
11	Škrípov	630	P.s.	485539	182308	**54**	Veľká kopa	1,130	D.	491208	195535
12	Skýcov	490	D.	483013	182331	**55**	Východná	775	P.s.	490337	195523
13	Súlov	900	D.	493021	183555	**56**	Veľký bok	1,000	P.s.	485550	195525
14	Turkov	720	D.	492142	183640	**57**	Fabova hoľa	935	P.s.	484621	195459
15	Hričovské Podhradie	460	D.	491235	183612	**58**	Rimavské Zalužany	300	D.	482934	195514
16	M. Lednice	510	P.s.	490400	183551	**59**	Mengušovce	790	D.	490324	200822
17	Dlhá lúka	770	D.	485549	183550	**60**	Kolibisko	1,110	D.	485518	200830
18	Vtáčnik	930	H.s.	483759	183620	**61**	Muránska Huta	885	P.s.	484641	200757
19	Kostivrch	600	P.s.	483002	183549	**62**	Matiašovce	650	P.s.	492049	202116
20	Hronský Beňadik	270	D.	482146	183601	**63**	Slovenská Ves	760	D.	491242	202049
21	Súdovce	235	P.s.	481303	184849	**64**	Jabloň	635	P.s.	485531	202120
22	Dunajov	440	P.s.	492158	184945	**65**	Vyšná Slaná	570	D.	484626	202120
23	Veľká lúka	810	D.	490402	185048	**66**	Litmanová	700	D.	492100	203521
24	Končiar	550	P.s.	482956	185017	**67**	Levočská dolina	715	D.	490404	203437
25	Počúvadlo	565	P.s.	482113	184937	**68**	Teplička	510	D.	485447	203437
26	Rykynčice	220	P.s.	481244	190339	**69**	Henclová	785	D.	484642	203426
27	Vychylovka	650	D.	492123	190300	**70**	Starina	500	P.s.	492103	204749
28	Chleb	820	D.	491228	190251	**71**	Poproč	780	D.	490333	204730
29	Podhradie	540	D.	490432	190251	**72**	Biela skala	455	P.s.	485525	204708
30	Ostredok	1,000	H.s.	485510	190317	**73**	Smolnícka huta	520	P.s.	484645	204719
31	Košiar	710	P.s.	484655	190234	**74**	Bôrka	710	D.	483754	204710
32	Sielnica	615	D.	483832	190314	**75**	Jarovnice	590	D.	490355	210026
33	Dubové	520	D.	482946	190333	**76**	Miklušovce	725	D.	485441	210053
34	Pilsko	860	P.s.	492935	191603	**77**	Zlatá Idka	880	D.	484556	210037
35	Dolné Plachtince	440	P.s.	481257	191550	**78**	Dlhá Lúka	450	D.	491955	211428
36	Lomná	850	D.	492006	191548	**79**	Haniska	250	D.	483749	211350
37	Ružomberok	570	D.	490412	191633	**80**	Dubník	750	D.	485453	212710
38	Liptovská Lúžna	660	P.s.	485536	191542	**81**	Nový Salaš	410	D.	483808	212616
39	Podkon ice	510	P.s.	484734	191635	**82**	Priekopa	183	D.	484536	221902
40	Malé Straciny	235	P.s.	481230	192855	**83**	Čabiny	340	D.	491201	215315
41	Horný Štefanov	1,040	D.	492153	192925	**84**	Pichne	310	D.	490302	220551
42	Chlebnice	920	D.	491213	192930	**85**	Stropkov	280	D.	491213	214003
43	Chabenec	1,250	H.s.	485531	192915	**86**	Ratajovce	220	D.	490334	213940

Table 4. Names, altitudes and geographical positions of sampling plots in SK and collected moss species (P.s. = *Pleurozium schreber*i, S.p. = *Scleropodium purum*, H.s. = *Hylocomium splendens*, D. = *Dicranum* cf. *scoparium*).

Poland											
Locality. code	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**	**Locality. code**	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**
1	Gołdap	172	P.s.	542020	221900	**51**	Marylka	128	P.s.	515945	205402
2	Żytkiejmy	190	P.s.	542000	224000	**52**	Podkowa Leśna	111	P.s.	520705	204805
3	Becejły	203	P.s.	541600	230330	**53**	Julinek	104	P.s.	521615	203620
4	Krzywe	166	P.s.	511100	154500	**54**	Legionów	89	P.s.	522415	205145
5	Monkinie	141	P.s.	540000	230500	**55**	Brody Duże	102	P.s.	522630	200330
6	Hruskie	139	P.s.	534900	230700	**56**	Czerniew	94	P.s.	521520	195230
7	Barany (Ełk)	120	P.s.	534700	222000	**57**	Chociw	160	P.s.	514120	201602
8	Woźnawieś	116	P.s.	534030	224600	**58**	Paszowice	383	P.s.	510100	160400
9	Studzieńczyna	207	P.s.	532845	231845	**59**	Gogołowice	100	P.s.	511700	162000
10	Gugny	123	P.s.	532100	222500	**60**	Wilczków	125	P.s.	511100	162800
11	Knyszyn	139	P.s.	531820	225700	**61**	Rudna	175	P.s.	512900	161100
12	Kruklanki	145	P.s.	540540	215430	**62**	Suszki	237	P.s.	511400	153600
13	Czerwony Dwór	140	P.s.	540740	221120	**63**	Kliczków	185	P.s.	512000	152800
14	Boćwinka	133	P.s.	541320	220850	**64**	Parkoszów	158	P.s.	512500	153300
15	Rutka Tartak	185	P.s.	541850	225810	**65**	Jelenin	150	P.s.	514000	153500
16	Augustów	148	P.s.	535345	230850	**66**	Piotrowice	154	P.s.	513100	154300
17	Stawiski	176	P.s.	532105	221045	**67**	Osiek	138	P.s.	512200	161100
18	Drygały	140	P.s.	534320	220430	**68**	Mochy	83	P.s.	515900	161300
19	Zelki	140	P.s.	535150	220810	**69**	Radomyśl	133	P.s.	515400	161900
20	Barany	216	P.s.	540545	222250	**70**	Śmigiel	128	P.s.	515800	163000
21	Raczki	185	P.s.	535930	224345	**71**	Zdziesławice	90	P.s.	513200	162800
22	Wysokie	131	P.s.	535145	223750	**72**	Grochowice	76	P.s.	514600	155900
23	Ponizie	140	P.s.	534810	225905	**73**	Konotop	81	P.s.	515200	155100
24	Laudańszczyzna	158	P.s.	533545	230730	**74**	Sucha	95	P.s.	515400	153800
25	Czarna Białostocka	152	P.s.	531850	231525	**75**	Mietków	206	P.s.	505900	162700
26	Boczki	136	P.s.	533630	222405	**76**	Błonie	118	P.s.	511100	164100
27	Zabiele	141	P.s.	533350	230030	**77**	Zielona Góra 1	109	P.s.	511100	154500
28	Mikaszówka	127	P.s.	535215	233145	**78**	Zielona Góra 2	141	P.s.	515700	152500
29	Sejny	135	P.s.	540720	232030	**79**	Dębowa Łęka	99	P.s.	515700	153300
30	Goniądz	115	P.s.	532810	223945	**80**	Nowa Sól	74	P.s.	514920	161845
31	Czermno	108	P.s.	522420	194530	**81**	Stary Żagań	114	P.s.	514813	154400
32	Tułowice	78	P.s.	522000	202600	**82**	Kietlów	84	P.s.	514420	152130
33	Palmiry	87	P.s.	522000	205100	**83**	Polkowice	167	P.s.	513700	163400
34	Sękocin	114	P.s.	520530	205230	**84**	Chocianów	176	P.s.	513020	160045
35	Bolimów	101	P.s.	520445	192230	**85**	Wołów	95	P.s.	512500	155100
36	Żyrardów	126	P.s.	520300	202500	**86**	Złotoryja	255	P.s.	512100	163100
37	Karolew	182	P.s.	515430	204400	**87**	Ubocze	347	P.s.	510730	155330
38	Nowe Miasto	137	P.s.	513600	203400	**88**	Lwówek Śląski	267	P.s.	510300	152700
39	Białobrzegi	149	P.s.	513500	205900	**89**	Winowno	317	P.s.	503215	190920
40	Spała	150	P.s.	513200	200800	**90**	Pradła	364	P.s.	503245	193910
41	Baby	210	P.s.	513140	194508	**91**	Lanckorona	267	P.s.	495150	194530
42	Koluszki	213	P.s.	514430	194920	**92**	Pornikiew	365	P.s.	494950	192730
43	Dąbrówka Duża	200	P.s.	514950	194645	**93**	Czernichów	222	P.s.	500010	194020
44	Strzebieszew	171	P.s.	515930	195020	**94**	Miasteczko Śląskie	300	P.s.	502810	185405
45	Bobrowa	182	P.s.	515545	195230	**95**	Brusiek	261	P.s.	503320	184710

Table 5. Names, altitudes and geographical positions of sampling plots in PL and collected moss species. For abbreviations see the end of this table.

Poland											
Locality. code	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**	**Locality. code**	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss species**	**Latitude**	**Longitude**
46	Rogów	190	P.s.	514815	195008	**104**	Sikorka	326	P.s.	502320	191945
47	Zaosie	207	P.s.	513845	195700	**105**	Hutki	317	P.s.	501800	193000
48	Odrzywół	174	P.s.	513125	202640	**106**	Rudziniec	200	P.s.	501600	182300
49	Kaleń	184	P.s.	514720	201840	**107**	Kuźnia Raciborska	252	P.s.	501400	182900
50	Mogielnica	155	P.s.	513840	204540	**108**	Żory	260	P.s.	500430	183050
96	Centawa	227	P.s.	503245	182205	**109**	Landek	270	P.s.	495300	185100
97	Żarki	258	P.s.	500445	191910	**110**	Pludry	231	P.s.	504010	182645
98	Kobiór	267	P.s.	500305	185710	**111**	Dobrodzień	268	P.s.	504405	183130
99	Rogów(Racibórz)	259	P.s.	495930	182215	**112**	Śląskie Herby	263	P.s.	504318	184640
100	Mikołów	257	P.s.	501210	184530	**113**	Boroniów	291	P.s.	504015	184945
101	Bieruń	259	P.s.	500650	190130	**114**	Olsztyn	306	P.s.	504505	191615
102	Porąbka	365	P.s.	494840	191350	**115**	Złoty Potok	364	P.s.	504005	192220
103	Olkusz	426	P.s.	505745	193345	**116**	Lelów	238	P.s.	504510	193820

Table 5. The end. (P.s. = *Pleurozium schreberi*).

Hungary											
Lok. code	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss spec.**	**Latitude**	**Longitude**	**Lok. code**	**Name of the close settlement**	**Altitude m a.s.l.**	**Moss spec.**	**Latitude**	**Longitude**
1	Ajka	334	H.c.	470443	173409	**25**	Miskolc	107	H.c.	480534	205520
2	Alsónémedi	102	H.c.	472024	190815	**26**	Monostorapáti	192	H.c.	465533	173345
3	Baja	107	H.c.	460846	184811	**27**	Nagyatád	137	H.c.	461307	172249
4	Bátaszék	110	H.c.	461142	184109	**28**	Nagybajom	143	H.c.	462421	172813
5	Békéscsaba	84	H.c.	464041	211053	**29**	Nagykőrös	127	H.c.	470337	194309
6	Bölcske	74	H.c.	464309	80940	**30**	Nemesszaló	140	H.c.	471601	171727
7	Budapest	178	H.c.	473022	191438	**31**	Öregcsertő	66	H.c.	463241	190823
8	Csákvár	203	H.c.	472442	182645	**32**	Oroszlány	210	H.c.	473011	182053
9	Csorna	118	H.c.	473808	171630	**33**	Oroszló	208	H.c.	461359	180814
10	Derekegyháza	85	H.c.	463441	202025	**34**	Ózd	214	H.c.	481510	202010
11	Doboz	92	H.c.	464350	211545	**35**	Paks	113	H.c.	463557	184831
12	Dunaújváros	115	H.c.	465707	185153	**36**	Salgótarján	310	H.c.	480408	194926
13	Gödöllő	210	H.c.	473529	192227	**37**	Simontornya	178	H.c.	464443	183202
14	Gyomaendrőd	70	H.c.	465641	205317	**38**	Szarvas	79	H.c.	465215	203556
15	Gyula	88	H.c.	463848	211405	**39**	Százhalombatta	102	H.c.	471830	185437
16	Izsák	70	H.c.	464831	191946	**40**	Szendrőlád	202	H.c.	482012	204432
17	Járdánháza	230	H.c.	480819	201442	**41**	Szolnok	84	H.c.	471223	201147
18	Jászkísér	84	H.c.	472740	201740	**42**	Tárkány	139	H.c.	473618	180137
19	Jósvafő	231	H.c.	482918	203301	**43**	Tatabánya	243	H.c.	473447	182845
20	Kápolna	128	H.c.	474600	201340	**44**	Tiszaújváros	91	H.c.	475243	205930
21	Kocsola	219	H.c.	463147	181228	**45**	Várpalota	167	H.c.	471242	180932
22	Komló	278	H.c.	461158	181804	**46**	Veszprém	307	H.c.	470502	175153
23	Medgyesháza	91	H.c.	463158	205441	**47**	Zalaegerszeg	142	H.c.	465228	165149
24	Mezőnyárád	124	H.c.	475539	203920						

Table 6. Names, altitudes and geographical positions of sampling plots in HU and collected moss species (H.c. = *Hypnum cupressiforme*).

4.2.2 Collection and processing of samples

Following the biomonitoring manual (Rühling 1994b), collection of samples of moss species *Hylocomium splendens*, *Pleurozium schreberi* and *Scleropodium purum* (Frey et al. 2006) was preferred. In deforested or deteriorated landscape other species were allowed to be collected of the order *Hypnum cupressiforme* and then any other pleurocarpous moss species. Because of different climatic and land-use conditions in individual countries sampling of mosses was carried out in a different way. Also different analytical technique was used in the individual V4 countries that needed a little bit different pre-treatment of the moss samples.

a) Czech Republic

Moss samples were collected from the summer to the late autumn 2000. Collection of *Pleurozium schreberi* was preferred, while taking of *Hypnum cupressiforme* was purposely avoided due to findings in the biomonitoring campaign of 1995 that the latter species accumulate in the CZ habitats by about one third higher content of elements than *Pleurozium schreberi*. On the other hand *Pleurozium schreberi* and *Scleropodium purum* give very similar and comparable results in CZ (Sucharová and Suchara 1998). In areas with adverse conditions for the occurrence of preferred mosses, alternative species *Eurhynchium angustirete* and *Brachythecium rutabulum* or *B. salebrosum* were collected at 9 plots (4%). List of the CZ sampling plots is available in Table 1. Distribution of these plots in CZ is illustrated in the introductory dot map.

On each sampling plot seven subsamples of the moss species were collected in a collective sample of total volume of about 8 litres stored in sealed polyethylene bags. The subsamples were collected on sites where moss plants were not affected by throughfall, litter, or contact with small shrubs or grass biomass. Samples were touched and handled exclusively with hands protected by polyethylene bags. Samples were stored in shaded places to avoid condensation of water in bags. Habitat and climatic conditions as well as other details of the conditions of samples collection were recorded in the filled protocols. All these protocols are archived at VÚKOZ (Silva Tarouca Research Institute for Landscape and Ornamental Gardening).

The samples were usually processed in an extra lab room the day after sampling. In exceptional cases, the samples were stored in a cold place for two days maximally. In the laboratory upper green to yellowish segments of moss plants being old 2–2.5 years were analysed. Non-protected hands did not touch the moss samples. The purity of polyethylene gloves and pads of sheets of filter papers were checked frequently. The apical parts of the moss plants of the volume about 3–4 litres from individual moss sample were obtained for chemical analyses. The samples were dried in a dustless environment. Three quarters of each sample were milled in Fritsch mill with titanium rotor and titanium mesh. Teflon coating covered collecting dish of the mill. Particles in powdered samples were smaller or equal to 0.2 mm in diameter. The mill was dissasembled and the parts, which had been in contact with samples, were cleaned, rinsed with de-ionised water, dried and put together again, always between samples. The milled and not milled parts of the moss samples were labelled and archived to the time of analyses.

b) Slovak Republic

The samples of three moss species [*Dicranum* spp. (60%), *Pleurozium schreberi* (35%) and *Hylocomium splendens* (5%)] were collected mainly on the permanent forest monitoring plots (PMP). The collection of samples was performed during the first half of August in 2000. The samples consisted of the last three-years' annual segments, which were exposed to the deposition levels of determined elements for years 1998, 1999 and 2000.

On each sampling plot seven subsamples of the moss species were collected in a collective sample of total volume of about 8 litres stored in paper bags. The subsamples were collected on sites where moss plants were not affected by throughfall, litter, or contact with small shrubs or grass biomass. Habitat and climatic conditions and other details of the conditions of samples collection were recorded in the final report (Bucha et al.2000). The sampling plots are listed in Table 2. Location of sampling plots in SK is available in the inserted map.

c) Poland

Only moss species of *Pleurozium schreberi* was collected on all PL sampling plots in autumn 2000. The sampling plots were situated in southern PL, in the areas most affected by the industrial pollution, in central PL in the area representing moderately loaded parts of the country and in northeastern PL in the cleanest territory of PL. All recommended safe distances of sampling points from potential sources of local pollution were observed in accordance with the instructions of the biomonitoring manual. Typical size of the sampling plot was 50 × 50 m. The list of the sampling plots and some related information is available in Table 3. Location of the plots in PL can be seen in the inserted map.

In laboratory, apical three-year-old segments of moss plants were gathered and air-dried. The dried samples were milled, made homogenous and archived until analyses.

d) Hungary

Moss samples were collected from late summer to the early autumn in 2000. Exclusively moss species *Hypnum cupressiforme* was collected due to its cosmopolitan distribution and common occurrence at different substrates all over the HU. The moss species was frequently used for similar biomonitoring campaigns mainly in the Mediterranean area. List of the sampling plots and their geographical co-ordinates are available in Table 4 and distribution of the sampling plots is in HU is depicted in an inserted map.

On each sampling plot five to ten subsamples of the moss were collected in a collective sample and stored in polyethylene bags. The subsamples were collected at sites where moss plants were not affected by throughfall, litter, and contact with small shrubs or grass biomass. Next day the apical green to greenish-grey parts of moss plants intended for the analysis were picked and dried in an electric dryer under 80^{o} C for 24 hours. The dry moss samples were homogenised and stored.

4.2.3 Determination of elements

a) Czech Republic

About 0.5 g of dry (40° C) homogenous samples were differentially weighed in Teflon PFA pressure-relief type digestion vessels. Two-stage wet digestion procedure was used. The digestion of the samples in nitric acid (Merck suprapure) and hydrogen peroxide (Merck suprapure) was performed in the CEM (MARS 5) assembly. After digestion the samples were diluted to the defined volume 50 ml with de-ionised water. Three weights of each sample were digested at the same time. Each digested sample was measured three times.

Contents of 34 elements, including Cd, Cr, Cu, Fe, Ni, Pb, V and Zn in the samples were determined by means of ICP-MS (Perkin Elmer, Elan 6000) spectrometer. The concentrations of all measured elements in all samples were above the detection limits of the methods used. The detection limits for the methods used were assessed as 3 × standard deviation of digestion blanks for dilution factor f = 100 ml and n = 10. The detection limits of the method for determined 8 toxic elements are presented in Table 7.

Element	**Detection limit (μg.g^{-1})**	**Element**	**Detection limit (μg.g^{-1})**	**Element**	**Detection limit (μg.g^{-1})**	**Element**	**Detection limit (μg.g^{-1})**
Cd	0.0003	**Cr**	0.02	**Fe**	9	**V**	0.002
Pb	0.0005	**Cu**	0.05	**Ni**	0.05	**Zn**	0.2

Table 7. The CZ methods detection limits of digestion blanks, dilution factor = 100.

All internal and external quality assurance rules were kept. Each series of 12 digested and analysed samples included the measurement of a blank and two standard reference materials or of a moss standard laboratory material. Regulation diagrams checked the changes and trends in the course of the analyses. If a blank or if the standard exceeded the regulation limits for any element, then all steps in the process were checked until the reason for the biased analysis was found and removed. The following reference materials were used for the control of the ICP-MS moss analyses: IAEA Lichen 336, IAEA Hay V-10, NIST Pine Needles 1575a, NIST Apple Leaves 1515, international inter-laboratory moss samples M1 M2 and M3 and own archived moss samples (laboratory standards) M64/95P.s. and M68/95P.s. Long-term determinations of certified elements in the standard reference materials were satisfied. The results of recovery for the given elements as well as other additional details are available in the CZ national moss survey 2000 (Sucharová and Suchara 2004b).

b) Slovak Republic

The collected samples of mosses were not rinsed before analysis**.** The samples were dried at the temperature not exceeding 70° C for the period of 24 hours. From each sample about 0.3 g were packed in aluminium cups for a long-term irradiation or heat-sealed in polyethylene foil bags for a long-term and short-term irradiation in the IBR-2 reactor, in Dubna, Russian Federation. The concentrations of 41 elements (including Cd, Cr, Cu, Fe, Ni, Pb, V and Zn) in the samples were determined by means of the pulsed fast reactor IBR-2 in FLNP JINR, equipped with the fast pneumatic transfer system REGATA and four irradiation channels for instrumental neutron activation analysis, provides activation with thermal, epithermal and fast neutrons. Two channels are cadmium screened for activation with epithermal neutrons (Frontasyeva and Pavlov 2000). The neutron flux density (for thermal or epithermal neutrons) inside the channels is of the order 10^{12} cm^{-2}.s^{-1}

(Peresedov 1997). The induced activity can be measured using the γ- spectrometers with Ge (Li) ORTEC electronics. The software developed at FLNP JINR was used for processing the analytical results. The contents of the determined elements were above the detection limit for the method.

Obtained results for the investigated elements were presented in the papers (Maňkovská et al. 2003, Florek et al. 2007) and in the ICP-Vegetation Report (Buse et al. 2003). The accuracy of the data was verified by the analysis of standard plant samples and by comparison with the results obtained in 109 laboratories within the IUFRO working group for quality assurance (Hunter 1994).

c) Poland

The milled, homogenous samples were dried at 65°C. Samples of about 2 g weight were placed into Pyrex tube. The samples were mineralised in 30 ml mixture of concentrated nitric acid (HNO_3, Merck suprapure) and perchloric acid ($HClO_3$, Merck suprapure), in the ratio 4:1. The samples were mineralised using Tecator (Sweden) Kjeldahl digestion system. The obtained digestive was evaporated to about 1 ml and then diluted with de-ionised water to the volume 25 ml. In this solution 8 elements (Cd, Cu, Cr, Fe, Ni, Pb, Zn and V) were determined by the atomic spectrophotometry Varian 220 FS. For every 10 analysed samples one blank and two reference samples were included for the measurement. Concentrations of elements were determined in two standard materials: SRM 1575, SRM 1570a and international inter-laboratory moss samples M2 and M3. Analyses using AAS method were carried out in the laboratory of the Department of Ecology of the Institute of Botany PAS in Kraków.

The detection limits for the each of the analysed element and the analytical procedure and method used are available in the following Table 8.

Element	Detection limit ($\mu g.g^{-1}$)	Element	Detection limit ($\mu g.g^{-1}$)	Element	Detection limit ($\mu g.g^{-1}$)	Element	Detection limit ($\mu g.g^{-1}$)
Cd	0.001	**Cr**	0.1	**Fe**	5	**V**	1
Pb	0.05	**Cu**	0.1	**Ni**	0.2	**Zn**	0.5

Table 8 The PL methods for limits detection.

d) Hungary

Approximately three quarters of each sample were digested in a mixture of HNO_3 and H_2O_2 at 130°C under high pressure in non-stick tubes.

Approximately 0.2 g of each sample was dried in an electric-dryer at 80° C for 24 hours, then three times weighed in different ways and put into three Teflon vessels. Samples were digested in the mixture with ratio 1:1 (65% of HNO_3 (Reanal product) and 30% of H_2O_2 (Reanal product) at 130° C under high pressure in the non-stick vessels. After digestion the samples were diluted with de-ionised (Milli-Q) water to the volume of 10 ml.

Eight elements Cd, Cr, Cu, Fe, Ni, Pb, V and Zn were determined by means of the ICP-AES spectrometer (ICAP 61, Thermo Jarrel Ash, Franklin, MA, USA) at the Department of Chemistry, Corvinus University Budapest. The concentrations of all measured elements in all samples were above the detection limits of the methods. The detection limits for the methods used are available at the SZIU Gödöllő, Institute of Plant and Ecophysiology.

All internal and external quality assurance rules were observed. Each series of 10 digested and analysed samples included a measurement of blank and moss reference material. Regulation diagrams checked the changes and trends in the course of the analyses. The following reference materials were used for the control of the ICP-AES moss analyses: *Pleurozium schreberi* (Finnish Forest Research Institute, Muhos Research Station) No. 506; 507; 508.

4.2.4 Processing of results

Statistical evaluation of moss analytical data (basic statistics, correlation analysis, factor analysis and cluster analysis) was performed using Stat Soft Statistics programme.

Graphical processing of chemical analytical results was done at the Institute for Landscape Ecology in Bratislava. The geographical coordinates of the sampling plots were transformed into the conic map projection LCC (Lambert Conformal Conic). The digital model 2.5D of the topographic base of the Visegrad space territory was adopted from the programme packet ARC GIS, and a terrain model was used from SRTM DEMs. Counting of concentration isopleths in the isopleths maps was performed using the kriging and linear variogram model of the interpolation of the concentration course (Jongman et al. 1996).

The obtained results are presented in the form of classed post maps and isoplet maps. The presentation of processed maps is possible using the programme ARCREADER (ESRI). Graphical results are distributed in the form of hard copies (results for 8 elements determined in the moss samples from all V4) as well as in the electronic form (CD/DVD) including the evaluation of complete results (53 elements).

Processing of text and figures for this report was done using common text programmes of Microsoft Office (Word and Excel).

4.3 Results and discussion

Table 9 provides general information about the obtained results of chemical analyses (basic statistics of analytical data). Further evaluation of the accumulation of investigated elements in mosses in the Visegrad space is included into the comment to individual elements. These comments and maps are ordered alphabetically by chemical symbols for the elements.

	n	Mean	Min.	Max.	S. D.	S. E. M.	Median	Skewness	Kurtosis
Cd – cadmium									
CZ	250	0.284	0.090	2.242	0.207	0.013	0.233	4.671	33.916
SK	86	0.647	0.105	1.486	0.340	0.037	0.592	0.399	-0.454
PL	116	0.684	0.216	7.167	1.000	0.093	0.358	4.323	22.767
HU	47	0.776	0.200	2.300	0.441	0.064	0.700	1.634	3.512
V4	499	0.486	0.090	7.167	0.577	0.026	0.324	6.663	57.698
Cr – chromium									
CZ	250	2.11	0.383	7.66	1.201	0.076	1.88	1.297	2.507
SK	86	8.70	1.100	42.7	7.154	0.771	6.48	2.136	5.821
PL	116	1.18	0.338	10.54	1.088	0.101	0.891	5.935	47.770
HU	47	3.00	0.300	7.60	1.965	0.587	2.50	0.747	-0.676
V4	499	3.11	0.300	42.7	4.106	0.184	1.90	4.414	27.118
Cu – copper									
CZ	250	6.62	3.69	11.7	1.643	1.104	6.52	0.573	0.140
SK	86	9.83	3.92	37.1	4.612	0.497	8.76	3.345	16.360
PL	116	10.7	4.53	39.6	6.941	0.644	8.03	2.408	5.688
HU	47	12.0	4.40	70.0	10.626	1.550	9.60	4.445	21.630
V4	499	8.63	3.69	70.0	5.557	0.249	7.38	5.217	40.224
Fe – iron									
CZ	250	467	176	1859	255.9	16.18	401	2.703	9.106
SK	86	2211	430	13750	2089	225.2	1561	3.043	12.189
PL	116	550	216	4243	444.1	41.23	429	5.573	42.267
HU	47	2065	262	7023	1605.9	234.3	1519	1.386	1.360
V4	499	938	176	13750	1267.8	56.75	494	4.554	30.127
Ni – nickel									
CZ	250	2.09	0.556	10.3	10.294	0.065	1.95	3.117	18.439
SK	86	3.94	0.697	12.6	2.936	0.317	3.21	1.390	1.305
PL	116	1.62	0.724	2.89	0.436	0.040	1.57	0.592	0.297
HU	47	6.15	1.000	23.4	3.837	0.560	5.30	2.141	7.757
V4	499	2.68	0.556	23.4	2.291	0.103	1.98	3.408	17.507
Pb – lead									
CZ	250	8.72	1.81	48.2	4.817	0.305	5.66	4.347	27.591
SK	86	31.7	21.6	104	19.603	2.114	28.1	1.802	3.520
PL	116	13.9	3.94	65.6	10.815	1.004	9.94	2.295	6.240
HU	47	17.1	2.00	57.7	9.918	1.447	14.2	2.538	8.098
V4	499	13.7	1.81	104	13.955	0.625	8.52	2.824	10.638
V – vanadium									
CZ	250	1.66	0.574	5.86	0.685	0.043	1.52	2.309	8.640
SK	86	7.04	1.76	25.9	4.972	0.536	5.53	1.725	3.200
PL	116	6.01	1.92	16.6	2.402	0.224	5.83	1.202	3.096
HU	47	4.44	0.400	32.5	4.949	0.722	3.00	4.306	22.843
V4	499	3.86	0.400	32.5	3.651	0.164	2.42	2.882	13.255
Zn – zinc									
CZ	250	39.0	19.4	149.	16.491	1.043	35.0	3.254	14.777
SK	86	57.3	9.72	159	25.474	2.747	49.9	1.579	3.029
PL	116	61.6	28.4	590	66.500	6.174	41.7	5.536	37.930
HU	47	55.8	24.5	152	24.836	3.623	48.1	1.867	4.459
V4	499	49.0	19.4	590	37.790	1.692	39.6	7.852	94.609

Table 9. Basic statistics for determined variability in content of 8 elements in the moss samples from the Visegrad space. (n = number of samples, S. D. = standard deviation, S. E. M. = standard error of mean).

4.3.1 Cadmium

Symbol	Proton number	Group IUPAC (European)	Oxidative states	Relative atomic weight	Electronegativity (Allred-Rochow)
Cd	**48**	**12 (IIB)**	**II**	**112.4**	**1.46**
	Density (g.cm^{-3})	Melting point (°C)	Boiling point (°C)	Earth crust (mg.kg^{-1})	Human body (mg.kg^{-1})
	8.650	**321.1**	**767**	**0.098-0.150**	**0.700**

a) Sources and effects of the element

Cadmium (Cd) is not much abundant element in the Earth crust. It is typically caverned element with a crustal abundance lower than 0.2 mg.kg^{-1}. However, Cd is concentrated in minerals, for example, greenockite (CdS), which is a common part of polymetallic ores of further chalcophil elements; it is of little importance in other minerals, like cadmoselite (CdSe), monteponite (CdO), otavite ($CdCO_3$) and others. Cd consists of eight naturally occurring isotopes of which ^{114}Cd (29%) and ^{112}Cd (24%) are the most abundant. Furthermore, about 35 radioisotopes are known. Content of Cd tends to increase in the following order of selected rock types: igneous (0.1–0.3) > metamorphic (0.3–1.00) > sedimentary rocks (0.3–11 mg.kg^{-1}). However, content of Cd in the CZ sedimentary rocks is small (0.01–0.3 mg.kg^{-1}), only aleurites (dust sediments) contain Cd at the amounts of about 0.8 mg.kg^{-1} (Beneš 1994). Cd is bound to organic mater of rich raw materials such as crude oils (10–16,000), coal (10–22,000) and peat (370–190,000 mg.kg^{-1}). Increasing content of organic matter in soil causes Cd retention in soils (spodosols 0.07, loess 0.2 and chernozems 0.35 mg.kg^{-1}). For example in CZ, the median arable soil content (cold 2M HNO_3) reaches the value of 0.23 mg.kg^{-1} (MZe 1996). However, content of Cd in soils is under control of reaction (pH), content of humus and Fe and Mn oxides and concentration of phosphates and chlorides.

Natural sources of Cd such as volcanic emissions, transport of wind eroded materials, vegetation fires, sea spray, etc. may release annually about 300 tons of Cd. Cadmium can be obtained as a by-product during extraction of Zn, Pb, Cu from their sulphide ores. Annual anthropogenic sources of Cd may be about 5,500 tons of. Important Cd sources are non-ferrous smelters, coal power plants, incinerators of municipal wastes, car exhausting fumes, eroded urban soil cowers, waste tips, etc. The typical Cd content in street dust is 1–7 mg.kg^{-1}.

Cd is not known to be essential element for any organisms on the Earth. Vegetation contains Cd at the amounts 0.1–2.5 mg.kg^{-1}. As a rule, underground parts accumulate more Cd than aboveground parts. Fortunately, cereal grain contains usually very little Cd. Beneš (1994) performed a survey of metal contents in the CZ agricultural plants. In close to nature beech forest in south Sweden determined Cd contents in beech leaves, leaf litter, forest floor and mushrooms were 0.095, 1.35–2.00, 3.15 and 0.05–14.2 mg.kg^{-1}, respectively (Tyler 2005). Nevertheless, some plants species (e.g., *Thlaspi coerulescens*) can hyper accumulate Cd at amounts exceeding 10 mg.kg^{-1}). *Moehringia trinervia*, a forest floor plant, was reported to accumulate Cd up to about 14 mg.kg^{-1} (Godzik 1992, Kapusta et al. 2006). These hyper-accumulators are tested for the use in phytoremediation of heavily contaminated soils (e.g., Lombi et al. 2001).

Recently Cd was used for production of Ni-Cd batteries, organic cadmium stabilising PVC polymers, photoconductors, special alloys, rubber vulcanite, Cd pigments, herbicides, rodenticides and anticorrosive coating (electroplating) of some components for electronic instruments.

The average yearly background wet deposition (bulk) of Cd in southeastern part of CZ was 0.11 mg.m^{-2}.year^{-1} in 2000 [1] and in the areas affected by industrial pollution 0.2-0.25 mg. m^{-2}.year^{-1} (http://www.chmi.cz/uoco/isko/tab_roc/2000_enh/CZE/kap_22/k_22_3_1_3_html.html).

Cd is very toxic metal, the lethal dose is 250–500 mg. Daily breath intake can be 0.022–0.22 µg, while oral intake is about 10–30 µg. Cigarette smoking and consumption of food in contaminated food chains can increase the intake of Cd dramatically. Acute or chronic exposure to Cd may causes bronchitis, renal damage, disfunctioning of the kidneys, hypertension and bone softening. Kidney damage can be caused even at very low Cd levels of environmental exposure (Järup et al. 1998, Järup 2002). The well-known Itai-Itai bone disease osteomalacia was associated with exposure to Cd as early as the 1950s and 1960s in Japan. Cd causes lung and prostate cancer and it is suspicious for initiating cancer of other organs. A half-life time for Cd in human body is 10–30 years. In plants toxic accumulation of Cd causes many disorders in enzyme activities, metabolism, transpiration, photosynthesis, etc. resulting in production decrease leading to death (Khan and Khan 2006).

Deficiency effects of Cd were not observed.

For more information see, for example, the following addresses:
http://www.gsf.fi/publ/foregsatlas/text/Cd.pdf
http://www.inchem.org/documents/pims/chemical/cadmium.htm
http://www.anellomedicalwriting.com/Jarup_L_Nephrol%20Dial%20Transplant_2002_17_35.pdf
http://www.intox.org/databank/documents/chemical/cadmium/ehc135.htm.

b) Distribution of Cd content in moss in 2000

Content of Cd in mosses in the Visegrad space was found in very wide range 0.09–7.167 µg.g^{-1} (Tab. 9). Distribution of Cd in mosses in individual countries can be seen in inserted classed post map and isoline map.

Individual countries comment the distribution of Cd in moss:

Czech Republic

The current content of Cd in the CZ moss samples ranged from 0.090 to 2.240 µg.g^{-1}. The mean Cd content in moss was 0.287 µg.g^{-1} in CZ in 2000. This is four times higher value than the Cd content in moss reported from the cleanest parts of Europe. Sucharová and Suchara (2004b: 34–35) presented and evaluated the Cd content in mos in CZ in more details.

The inserted maps depict the following regions in CZ with high bio-accumulated levels of Cd in moss:

1. The Ostrava district and its larger surroundings, including the northern part of the Moravskoslezské Beskids in northeastern Moravia is the most important hot spot in CZ.
2. The surroundings of the towns Rokycany and Příbram in southwestern part of central Bohemia.
3. Along the cross border in northern Bohemia and in the Jizerské Mts. and the Krkonoše Mts., mainly around Tanvald.
4. The brown coal basin between Teplice and Chomutov and the adjacent Krušné Mts. in western Bohemia.
5. Southern Moravia with a local hot spot near Kyjov.

The mountain regions of northern Bohemia and Moravia show a local tendency toward higher accumulation of Cd in moss than the lower-lying neighbouring areas. Anyway, the Cd atmospheric deposition loads contaminate heavily the CZ part of the Black triangle II area and the surroundings of Příbram. Distribution of long-term accumulated Cd deposition loads in forest floor and the current distribution of Cd in a 14-km radius around the secondary lead smelter Příbram was determined in a fine map scale in 1999 (Sucharová et al. 1999).

The lowest content of Cd in the moss samples was found in western and southern Bohemia and, surprisingly, also in the lowlands of northern part of Bohemia as well as in southwestern Moravia, where Cd in mosses did not exceed 0.2 µg.g^{-1}.

Slovak Republic

The content of Cd in the SK moss samples ranged from 0.105 to 1.486 µg.g^{-1} and the average content was 0.647 µg.g^{-1}. This is approximately five times higher than the Cd concentration in moss reported from the cleanest parts of Norway. Maňkovská et al. (2003) and Florek et al. (2007) presented and evaluated the Cd concentration in moss in SK in more details.

The inserted maps depict the following regions in SK with high bio-accumulated levels of Cd in moss:

1. Region of Košice - Prešov is the most important hot spot in SK.
2. Region of Pohronie (Žiar basin).
3. Region of Považie, along the cross border in northern Slovakia - mountain forests in Kysuce, Beskids, and Oravská Magura as well as the surroundings of the towns of Považská Bystrica and Prievidza
4. Region of Zemplín, local hot spot near Humenné, Strážske.

The lowest concentration of Cd in the moss samples was found in the Volovské vrchy Mts., and surprisingly, also in the Malé Karpaty, the Veľká Fatra Mts. and the Low Tatra Mts.

The effect of air pollutants in SK is evaluated according to 7 industrial regions (MŽP SR 2002): (1)-region of Bratislava; (2)-region of Považie; (3)-region of Nitra; (4)-region of Pohronie; (5)-region of Lučenec-Gemer-Spiš; (6)–region of Košice–Prešov and (7)–region of Zemplín. We expressed the exceedance of element contents in the SK mosses in comparison with these elements reported from Norway by averages of the coefficients of the relative deposition loads K_F. The obtained values of this coefficient were divided into the following four classes: class 1 – elements are within norm and do not exceed the K_F value 1; class 2 – slight loading (K_F ranges from 1 to 3); class 3 – moderate loading (K_F = 3–5); class 4 – heavy loading ($K_F > 5$) (Maňkovská et al. 2003).

Poland

Cd content in mosses collected in PL in 2000 ranged from 0.216 to 7.167 µg.g^{-1}, reaching on average 0.684 µg.g^{-1}. In three provinces (eastern PL, central PL and Lower Silesia), the average concentrations of Cd were similar, reaching 0.317–0.368 µg.g^{-1}, while in Upper Silesia the average Cd concentration was much higher (1.748 µg.g^{-1}) and the largest variations among particular measuring stations were observed. Table 10 provides basic statistics of Cd content in mosses in the investigated regions of PL.

	Eastern PL	Central PL	Lower Silesia	Upper Silesia
n	30	27	31	28
Mean	0.317	0.368	0.355	1.748
S. D.	0.044	0.060	0.069	1.645
Minimum	0.228	0.241	0.216	0.553
Maximum	0.420	0.494	0.561	7.167

Table 10. Content of Cd in moss *Pleurozium schreberi* ($\mu g.g^{-1}$) in four investigated provinces of PL in 2000. (n = number of samples, S. D. = standard deviation).

The inserted maps show that in the region of Upper Silesia the largest concentrations of Cd were found in mosses collected in the following areas:

1. Surroundings of Miasteczko Śląskie and Olkusz.
2. Central part of Upper Silesia (region of Katowice).
3. Cd concentrations higher than the average were determined in mosses collected in the localities situated to the southeast of Częstochowa (Olsztyn, Złoty Potok, Lelów, Pradła).

The level of Cd contamination of the moss corresponds with the magnitude of Cd emissions in the provinces: the highest emissions were recorded in the province of Upper Silesia, while in the area of Lower Silesia they were about 10 times lower, and in the eastern part of Poland there were no sources of Cd emissions (Table 2).

Hungary

The content of Cd in the HU moss samples ranged from 0.200 to 2.300 $\mu g.g^{-1}$ in 2000. The mean Cd content in moss was 0.776 $\mu g.g^{-1}$ in HU in the same period. This is ten times higher than the Cd content in moss reported from the cleanest parts of Europe and the highest of all Visegrad countries. The inserted maps depict the following regions in HU with high bio-accumulated levels of Cd in moss:

1. Kapolna hot spot represents the highest value with Salgotarjan (near the Slovak Republic) in the northern region of HU.
2. Dunaujvaros and Szazhalombatta in the central region at the river Danube near Budapest.
3. Near Tatabanya and Varpalota in the Dunantul region.
4. Jósvafő in the northern mountains region near the HU/SK borders.
5. Doboz at the border of Romania in the southeastern corner of Hungary.

c) Identification of potential pollution sources

Czech Republic

1. In the Ostrava district and in the nearby industrial region in northeastern Moravia and southern Poland several non-ferrous, steel smelters and engineering works have been operating. Production of batteries and galvanized iron is also concentrated in this region. Very fine aerosols containing Cd are easily moved by wind to the surroundings and adjacent mountainous area; they are effectively washed out from the atmosphere by increased amounts of precipitation.
2. Cd emissions are associated with the operation of metallurgical works near the towns of Rokycany and Příbram. Mainly the secondary lead smelter near Příbram has been known as a major source of Cd emissions in Bohemia for a long time. Since 1998 a much more safe technology has been operating in the smelter.
3. The mountainous area in northern Bohemia between Liberec and Harrachov is known for the long-time operation of local glass works. Cd-based pigments and dust particles eroded from ash and slag heaps around these works contribute to the increased Cd deposition loads in the area.
4. Combustion of enormous amounts of brown coal in power plants concentrated especially in the local coal basin, and the operation of chemical works in this area are important sources of Cd emissions in the brown coal basin in western Bohemia. Increased bioaccumulation of Cd in the moss in the adjacent Krušné Mts. may be caused by easy transportation of fine Cd-bearing aerosols to the mountainous region and their more effective wet deposition there.
5. Sources of Cd in southern Moravia are not known correctly. However, increased Cd contamination of the moss samples is surely associated with high wind erosion and dustiness in the area. Either spreading of particles of some sediments of Carpathian flysch rich in Cd or particles eroded from industrial dumps (dust from a coal power plant, cinder from waste incinerators, etc.) may be blamed.

Better uptake of Cd by moss from wet atmospheric deposition and increased wet deposition in mountains cause higher Cd contents in mountain areas, such as the Krkonoše Mts., the Orlické Mts., the Jeseníky Mts. and the Beskids. Partial correlations showed (Sucharová and Suchara 2004b: 62) that in CZ the increasing altitude significantly decreased Cd content in mosses (r_p = -0.32), while increased precipitations significantly increased the Cd contents in moss in 2000 (r_p = 0.51).

The average values for the sets of moss data of 1995 and 2000 in CZ show a significant decrease of median values by about 27% in 2000 in comparison with 1995. The similar trend showed the CZ moss data for the period 1991–1995. The main reason is restructuring of industry, desulphurisation of power plants and introducing more sophisticated technologies in smelters. For more details see Sucharová and Suchara (1998, 2004b).

Slovak Republic

1. Cd emissions are associated with the operation of ferrous metal industry and production of metallurgical products in the town of Košice. Coal power plants in Košice and Vojany are also located in this region. The coefficient of relative deposition loads K_F reaches values from 9.5 to 11.5.
2. Region of Pohronie - Žiar basin is characterised by the production of aluminium and electricity (thermal power stations are in Žiar nad Hronom and Zemianske Kostoľany) and the production of chemicals and chemical products (Nováky). The coefficients of relative deposition loads K_F are higher than 11.2.
3. In the region of Považie - along the cross border in northern SK (mountain forests in Kysuce, the Beskids, and the Oravská Magura Mts.) neighbouring with the industrial region in northeastern Moravia and in southern PL several - non-ferrous and steel metallurgical and engineering works have been operating there. Very fine aerosols containing Cd are easily moved by wind into the surroundings and adjacent mountainous area, and they may be effectively washed out from the atmosphere by increased amounts of precipitation. The coefficient of relative air pollution K_F ranged from 8.8 to 9.4. Increased content of Cd in moss was also determined around Považská Bystrica (production of basic metals, operation of engineering, machinery and chemical industries and thermal power plant Zemianske Kostoľany). The coefficient of relative deposition loads K_F exceeded 8.
4. In the region of Zemplín Cd emissions are associated with the operation of chemical works near the towns of Humenné and Strážske. In Strážske a military production is located as well.

Better uptake of Cd by moss may be expected from wet atmospheric deposition. Increased wet deposition occurs in mountains and it may cause higher Cd contents in mountains, such as the High Tatra Mts. However, in the SK moss samples the Cd content did not significantly increase with higher altitude of sampling plots (Chapter 4.5). Some contribution of Cd may origin in dust of soil covers fertilised by fertilizers with high Cd content.

The average Cd content in the SK moss samples in 2000 was lower by about 53% in comparison with Cd average content in the moss analysed in SK in 1990. The main reason is a restructuring of industry; desulphurisation of power plants and introducing more sophisticated technologies in smelters. For more details see Maňkovská et al. (1998, 2004).

Poland

1. In the region of Miasteczko Śląskie and Olkusz the mining and metallurgy of non-ferrous metals are the main sources of Cd contamination. In the environs of Olkusz there operate few mines of zinc and lead as well as the biggest Mining and Metallurgy Plant “Bolesław” in Bukowno. Numerous heaps of wastes from the operation of the Zn-Pb metallurgy are probably the crucial sources of Cd in the area.
2. The region of Katowice is the most industrialized area in PL. Numerous non-ferrous metallurgical plants, hard coal power plants, works producing machines for a heavy industry, steel works, machinery production, heaps of mine-spoils and exhausts from vehicles (areas in PL with very high transport density) are the main sources of Cd in this region.
3. Increased Cd content in the moss in the area situated eastern from Częstochowa is associated with emissions from steelworks in Częstochowa.

Hungary

Among the biggest sources of Cd in HU are sewage sludges, production and recycling of batteries, industrial burning of fossil fuels and application of some kind of chemical fertilizer.

1. The highest Cd emission was detected at the border of Bukk Mts. and the Great Plain. Several power stations and non-ferrous, steel, metallurgical and engineering works have been operating (Kapolna) in this area. Lower amounts of Cd emissions were found in Salgotarjan, near the HU/SK borderline. This area (Ozd) was highly industrialized in the last few decades. A steel smelter is an important source of Cd emissions in this area.
2. Cd emissions are associated with the operation of oil refinery and the power station in Szazhalombatta as well as with the operation of metallurgical, chemical and paper industries in Dunaujvaros.

3. The Cd emission in the mountain area in Dunantul is associated with burning of enormous amounts of brown coal in power plants concentrated near Tatabanya. Turf and lignite mining, running of the Aluminium smelter in Inota (close to Varpalota) and operation of the chemical works in Varpalota contribute to the Cd emissions. This area is heavily industrialized as the data shows as well.
4. Very fine aerosols containing Cd are easily moved by wind to the surroundings and adjacent mountain area. The airborne Cd may be effectively washed out from the atmosphere by increased amount of precipitation. It explains the relative high amount of Cd in Josvafo.
5. Sources of Cd in southeastern plain near the Romanian border (Doboz) are not known exactly. Moss samples are exposed to high wind erosion and dustiness in the area.

d) Appraisal of dangerous effects

Cd is very toxic element and even small Cd contaminations of the environment can cause health injury. That is why Cd atmospheric deposition levels should be monitored and taken into account.

Czech Republic

Mainly two hot spots of increased Cd content in mosses should be taken in account, namely the industrial area in northeastern Moravia and the surroundings of the smelter in Příbram. Cd threat is associated with accumulated long-term deposition loads of Cd in soil covers and forest floor humus as well as with surface contaminations caused by current increased deposition fluxes around the Cd sources. However, synergistic effects of accompanying toxic elements may affect at these hot spots. Monitoring the health state and environmental contamination in these areas is desirable.

Slovak Republic

Mainly two hot spots of increased Cd concentration in mosses should be taken in account: the industrial area in eastern Slovakia (Košice region) and the surroundings of the Žiar basin. Cd threat is associated with accumulated long-term deposition loads of Cd in soil covers and in the foliage of forest tree species as well as with the contamination of wildlife. Monitoring of the health state and environmental contamination in these areas is desirable. Determination of Cd content in soil covers in former training areas of Soviet Army in SK (Lešť, Rožňava, Zvolen-Sliač, Ružomberok, Jelšava, Rimavská Sobota, Michalovce, Kežmarok, Vrútky, Nové Zámky) is desirable too.

Poland

Cd poses a big potential threat to the environment in all the three hot spots. This element undergoes bioaccumulation easily. As Cd is highly toxic for humans and animals, the monitoring of environmental pollution, and particularly the contamination of food products should be performed on a regular basis. The former studies on several species of vegetables being grown in allotment gardens in Silesia and Kraków showed that Polish standards pertaining to admissible Cd contents in these food products were considerably exceeded (Marchwińska et al. 1982, Grodzińska et al. 1987, Godzik et al. 1995). The increased Cd concentrations found in the soils of Poland may be in many regions associated with the use of phosphate fertilizers, in which Cd maximum permeable concentrations (NPK) may reach 4 (NPK "Police") up to 40 $\mu g.g^{-1}$ (NPK "Gdańsk") depending on the phosphates used for their production, (Górecki 1990). In the region of Upper Silesia, despite the considerable degradation of the area and intensive industrial activities (mining, metallurgy, urbanization), many areas have been used for agricultural purposes. Food crops produced in these areas can contain the suprastandard concentrations of Cd and should be analysed on a permanent basis.

Hungary

Cd is highly toxic element. In densely settled parts of the Cd hot spots potential harmful effects of the contaminated environmental should be checked, e.g., by epidemiological studies. Anyway, continuing in the campaigns of bio-monitoring the atmospheric deposition loads are desired mainly in the described hot spots.

4.3.2 Chromium

Symbol	Proton number	Group IUPAC (European)	Oxidative states	Relative atomic weight	Electronegativity (Allred-Rochow)
Cr	**24**	**6 (VIA)**	**II; III; VI**	**51.996**	**1.56**
	Density ($g.cm^{-3}$)	Melting point (°C)	Boiling point (°C)	Earth crust ($mg.kg^{-1}$)	Human body ($mg.kg^{-1}$)
	7.14	**1,907**	**2,671**	**90-185**	**0.030**

a) Sources and effects of the element

Chromium (Cr) is relatively abundant crustal element presented in the average concentration of about 120 $mg.kg^{-1}$ in the Earth crust. Chosen characteristics of this metal are given in the introductory table. Naturally occurring Cd consists of three stable isotopes ^{52}Cr (84%), ^{53}Cr (9.5%) and ^{54}Cr (2%), and one radioactive isotope ^{50}Cr (half life time 1.8×10^{17} years). About 19 other radioactive isotopes are known. Cr does not occur in nature in elemental form but it is concentrated in several minerals, of which chromite [$(Mg,Fe)Cr_2O_4$] and crocoite ($PbCrO_4$), the minerals processed for Cr production, have the most practical use. Having similar ionic magnitude as Al^{3+}, Fe^{3+} or Mg^{2+}, the Cr^{3+} may join the elements listed above or substitute them in their compounds.

Natural sources producing approximately 358,000 tons of Cr per year are the weathering of ultrabasic and basic rocks (200–2,000 $mg.kg^{-1}$), ever though; some residual Cr minerals may be very resistant. Cr easily incorporates into the structure of clay minerals or stays in the form of residual minerals. Cr^{3+} moves less than Cr^{6+}, however in general all Cr species can move slowly in the soil matrix. Cr is typical element occurring in soil covers. The Cr content of soil was found to range from 2 to 70 $mg.kg^{-1}$. The average Cr content in CZ chernozems, cambisols and luvisols are reported to be 76, 84, and 117 $mg.kg^{-1}$, respectively (Beneš 1993). Commonly used soil extractants are able to extract only little part (up to 50%, commonly much less) of the total Cr content in the soil. With the exception of atmospheric deposition, Cr can penetrate the soil for example through sewage sludge and fertiliser applications. Soil bacterial activities reduce Cr^{VI} to Cr^{III}. Cr binds moderately to organic matter. Otabbong (1989) gave more details about the chemistry and behaviour of Cr kinds in soils.

Brown coal contains on average 550 mg of Cr per one kg, while in coal ash the Cr content may increase up to 155 $mg.kg^{-1}$. The Cr concentration in crude oil is reported to be about 0.3 $\mu g.l^{-1}$.

Cr is not essential for bacteria, algae, fungi and higher plants. The species Cr^{3+} is essential for animals and humans for sugar metabolism. The Cr^{3+} supports operation of insulin and promotes glucose tolerance. Bowen (1979) determined chromium contents in vegetation from 0.03 to 10 $mg.kg^{-1}$ and Jaysekera (1993) has determined Cr concentrations in forest tree species between 0.44 and 1.37 $mg.kg^{-1}$. Maňkovská (1996) found the average Cr contents in foliage of beech (*Fagus sylvatica*) 1.1–2.9, oak (*Quercus robur*) 0.8–1.1, spruce (*Picea abies*) 0.7–1.0, pine (*Pinus sylvestris*) 0.6–0.4 and fir (*Abies alba*) 0.6–0.8 $mg.kg^{-1}$ in SK. Exogenous Cr was present on 1.6% of the surface of analysed leaves. In southern Sweden in close to nature beech forest the determined Cr contents in beech leaves, leaf litter, forest floor humus and mushrooms were 0.32–0345, 0.6–1.06, 2.02 and 0.24–0.70 $mg.kg^{-1}$, respectively (Tyler 2005).

Cr deficiency causes diabetes. Cr is toxic for plants in the form of $Cr(OH)_3$, CrO_4^{2-}, Cr^{+6} in the concentrations in soil solution above 1 $mg.l^{-1}$. Cr^{3+} is bound mostly to cell walls, whereas Cr^{6+} ends up in cell liquids. Some plant species, for example, *Leptospermum scoparium and Pimelia suteria* can accumulate Cr at higher amounts. Markert (1992) estimated total chromium content in world plant biomass at 2.762×10^6 t.

Cr is needed to produce special resistant alloys and it is used in Cr electroplating of metallic parts, production of anticorrosive paints, glass pigments, compounds for leather processing, photography and chemical industry, etc. Anthropogenic sources of Cr are the combustion of fossil fuels, the processing of Cr based ores, metallurgical, chemical and leather industries. Human activities cause the release of about 94,000 tons of Cr per year.

In London the current annual average content of Cr in the air is about 8 $\mu g.m^{-3}$. The concentration of Cr in the urban and the rural atmosphere in the CZ was 6.7 and 3.8 $ng.m^{-3}$, respectively. The average atmospheric deposition of Cr is assessed to be around 40 $g.ha^{-1}.year^{-1}$ in CZ.

Cr is toxic and carcinogenic element. In general, Cr^{+3} compounds are approximately 1,000 times less toxic than Cr^{+6} compounds. Cr is blamed for inducing allergies, chromosome damages, lung cancer, mutagenesis (chromosome damages), etc. Because of carcinogenic effects of Cr no concentration limit in the environment can be recommended as safe. High concentration of Cr in soil can reduce root growth of plants, disturb H^+-K^+ root exchange, phosphorus and other nutrient uptake, etc.

Deficiency of Cr^{3+} in humans may cause increasing of blood cholesterol and pressure, problems with sugar metabolism, fatigue, increase of accumulation of plaque in the aorta, anxiety, impaired physical growth in the youngs, slower healing time after surgery or injury, atherosclerosis, decreased glucose tolerance, and possibly decreased fertility and longevity.

Additional information can be obtained, for example, at the following addresses:
http://www.gsf.fi/publ/foregsatlas/text/Cr.pdf
http://www.epa.gov/ttn/atw/hlthef/chromium.html
http://www.inchem.org/documents/ehc/ehc/ehc61.htm.

b) Distribution of Cr content in moss in 2000

Content of Cr in the Visegrad space was found to be 0.30–42.7 $\mu g.g^{-1}$. Basic statistics for obtained Cr contents in mosses are available in Table 9.

Distribution of Cr in mosses in the Visegrad countries is depicted in the inserted classed post map and isopleth map. Situation in individual V4 countries is shortly commented as follows:

Czech Republic

Basic statistics describing the variability in the Cr content in the CZ moss samples are available in Table 9. Moss plants accumulated Cr between 0.38 and 7.66 $\mu g.g^{-1}$ in CZ in 2000. The mean content of Cr in moss was found to be 2.23 $\mu g.g^{-1}$. This average Cr content in moss in CZ is nearly four times higher than the reported Cr content in moss from the cleanest parts of Europe.

The following areas of marked accumulation of Cr in moss can be recognised in the inserted maps:

1. Near the town of Rožnov pod Radhoštěm, in eastern Moravia.
2. Along the CZ/SK border eastern from Strážnice, in southeastern Moravia.
3. In the brown coal basin in western Bohemia, with a local hot spot near Chomutov.
4. Small local areas near, e.g., Příbram, Kutná Hora, Brno, and in intensively exploited agricultural lowlands.

In contrast, the lowest Cr contents in the moss samples were found in large areas in southern and southwestern Bohemia. Only on about 50% of the CZ territory Cr contents in moss were lower than 2 $\mu g.g^{-1}$.

Slovak Republic

Basic statistics describing the variability in the Cr concentration in the SK moss samples are available in Table 9. Moss plants accumulated Cr between 1.1 and 42.7 $\mu g.g^{-1}$ in SK in 2000. The average content of Cr in moss was found to be 8.7 $\mu g.g^{-1}$. This average Cr content in moss in SK is nearly six times higher than the reported Cr content in moss from the cleanest parts of Europe.

The following areas of marked accumulation of Cr in moss can be recognised in the inserted maps:

1. Region of Košice – Prešov in southeastern Slovakia.
2. Region of Zemplín (Humenné, Stropkov, Svidník) northeastern SK and along the border SK/PL.
3 Along the CZ/SK border western from Brezová, Myjava, Stará Turá, Trenčín in western Slovakia.
4. Region Lučenec – Gemer-Spiš, with a local hot spot near Lubeník – Jelšava.
5. Small local areas near, e.g., the town of Detva in Central Slovakia, Liptovský Mikuláš, Považská Bystrica, and in intensively exploited agricultural lowlands.

In contrast, the lowest Cr contents in the moss samples were found in large areas in Northern and Central Slovakia (the Strážovské vrchy Mts., the Spišská Magura Mts., the Low Tatra Mts., the Volovské and Levočské vrchy Mts.)

Distribution of determined Cr content in the foliage of forest tree species (Maňkovská 1996) supports findings of the moss campaign. Cr contents in leaves exceeded 2 $mg.kg^{-1}$ in industrial areas of Central and Eastern Slovakia. The highest total Cr contents in leaves of *Fagus sylvatica* were determined in southern part of the Low Tatra Mts. and in Žiar Basin, as well as in the leaves of *Quercus robur* in Horná Nitra basin.

Poland

The contents of Cr in mosses from PL ranged from 0.338 to 10.54 $\mu g.g^{-1}$. The least differences among localities in Cr concentrations were found in the eastern part of PL and in Lower Silesia (Table 11). Slightly higher contents and greater variations among sampling sites were noted in central PL. Much higher contents of Cr, 10 times higher than the average for PL, were found close the village of Żarki near Częstochowa. The concentrations of Cr were also higher than the average value for PL also in about ten-twenty localities in Upper Silesia.

	Eastern PL	Central PL	Lower Silesia	Upper Silesia
n	30	27	31	28
Mean	0.75	1.00	0.84	2.18
S. D.	0.280	0.361	0.345	1.819
Minimum	0.371	0.637	0.338	0.779
Maximum	1.52	2.40	1.70	10.54

Table 11. Content of Cr in moss *Pleurozium schreberi* (µg.g^{-1}) in four investigated provinces of PL in 2000. (n = number of samples, S. D. = standard deviation).

As shown in the inserted maps, the highest Cr contents (more than 2 µg.g^{-1}) were found in the Silesian province and in the adjacent western part of the province of Małopolska, what is consistent with the magnitude of emissions generated by huge industrial plants located in Silesia. In the years 1998–2000 these emissions amounted about 4,000 kg.year^{-1} and were much higher than in the remaining investigated areas (Table 2). The highest contents of Cr were found in the following areas:

1. Environs of the village of Żarki (southeast from Częstochowa).
2. Environs of Olkusz (Olkusz, Sikorka, Hutki).
3. Central part of Silesia (environs of Katowice, villages of Żory, Mikołów, and Bieruń).
4. Area situated to the west from Kraków (towards Upper Silesia), villages of Czernichów and Lanckorona.

Hungary

Moss plants accumulated Cr between 0.300 and 7.600 µg.g^{-1} in HU in 2000. The mean content of Cr in moss was found to be 3.00 µg.g^{-1}. This mean Cr content in moss is more than four times higher than the reported Cr content in moss from the cleanest parts of Europe.

The following areas of marked accumulation of Cr in moss can be recognised in the inserted maps:

1. Oroszlany (the highest value) and Tatabanya and Varpalota.
2. Csorna, Dunaujvaros and Szazhalombatta along the river of Danube.
3. Miskolc in the northeastern region.
4. Budapest in central parts.
5. Josvafo along the HU/SK.

c) Identification of potential pollution sources

Czech Republic

Cr can be categorised as a typical terrigenous element. In addition to metallurgical and engineering industrial Cr sources, deposition of soil dust and coal ash can be considered as potential contributors to Cr deposition in CZ. We believe, that the Cr content in moss can be substantially controlled by long-term soil moisture decreasing wind erosion of soil (or yearly precipitation frequency and precipitation amounts) as an important explanatory factor. During long-term dry periods a heavy soiling of moss by sediment soil particles carrying Cr appears and it may increase the values of the results obtained in the bio-monitoring campaigns. However simple bivariate correlation showed, that the Cr content in moss is not significantly dependent on biennial precipitation and partial correlation showed even significant and possitive effect of the biennial precipitation amounts (r_p = 0.18), (Sucharová and Suchara 2004b: 62).

The following sources may have led to an increased accumulation of Cr in moss in the above listed parts of CZ:

1. The reason for the high Cr content in the moss near Rožnov pod Radhoštěm is not quite clear. Some local industrial sources of potential Cr emissions operate in the area, e.g., production of electrotechnical components. Alternatively, the sampling plot may have been accidentally soiled or dusted in the past.
2. The local high accumulation of Cr in the moss along the CZ/SK border near Strážnice may be associated with the operation of nearby Slovak industrial sources in Myjava and Stará Turá (metallurgical and chromium-plated products).
3. The brown coal basin in western Bohemia and its surroundings suffer from high deposition loads of industrial ash and ground dust, including aerosol particles associated with the operation of numerous power plants accumulated in the area.
4. Small areas near some towns are affected by high atmospheric deposition loads originating in the operation of a smelter (Příbram), wind erosion of heaps of industrial wastes and slag heaps situated near former polymetallic mines and smelters (Kutná Hora, Příbram), dust from industrial zones of cities and waste incinerators (Brno, České Budějovice). In addition, deposition of eroded soil particles in large-scale agriculturally utilised areas (lowlands) contributes to the local atmospheric Cr deposition levels, mainly during dry and windy seasons.

The average Cr content in moss in 2000 insignificantly increased in comparison with the Cr average in 1995. The highest increase was found in heavily agriculturally exploited lowland. On CZ territory relatively dry year in 2000 might cause higher dustiness and increased atmospheric Cr deposition levels in these areas.

Slovak Republic

Cr is used as an alloying element in metallurgy. Relatively enhanced concentrations of Cr were found in the surrounding of magnesite works (Lubeník – Jelšava). Deposition of soil dust and coal ash can be considered potential contributor to Cr deposition in SK. The following sources might have led to the increased accumulation of Cr in moss in the above listed parts of SK:

1. Region of Košice – Prešov in southeastern SK. Cr pollutants are associated with the manufacture of metal industry and thermal power plants in Košice and Vojany. The coefficient of relative deposition loads K_F was counted from 9.4 to 17.1.
2. Region of Zemplín in northeastern SK. The highest contents of Cr were found near Humenné, Snina, Stropkov, Svidník - areas influenced by production of chemicals, wood pulp and paper products, and in Strážske production for army. The coefficient of relative deposition loads K_F reached values from 9.4 to 18.2.
3. Along the CZ/SK border western from Brezová Myjava, Stará Turá and Trenčín where metallurgical plants operate, that use chromium-plating widely. The coefficient of relative deposition loads K_F was found from 10.9 to 16.4.
4. Region Lučenec- Gemer-Spiš, with a local hot spot near magnesite works (Lubeník – Jelšava) The K_F coefficient reached 9.4 in this area.
5. Small local areas e.g., in Central Slovakia near the town of Detva, Podbrezová, and Hriňová (engineering industry and production for army). The coefficient of relative deposition loads K_F reached 28.5. In Liptovský Mikuláš leather is processed and in Považská Bystrica metallurgical works using chromium-plating technology operates. Local hot spots were also found in the surroundings of the town of Svit and Ružomberok with chemical and pulp industry. High contents of Cr in moss appeared near ferro-alloys works in Orava, near Martin (production of machinery) and in intensively exploited agricultural lowlands.

Poland

1. It is difficult to explain the increased contents of Cr in the environs of the village of Żarki. It is probably connected with emissions originating in Częstochowa (steel production), which is situated at a distance of some ten-twenty kilometres from Żarki. The increased concentration of Cr may also result from the use of fertilizers and crop protection chemicals (the affected plots are situated in a typical agricultural-forest area).
2. In the area situated to the east from Olkusz, the higher concentrations of Cr in moss may be associated with emissions generated by the “Bolesław” Mining and Metallurgy Plant in Bukowno (processing of zinc and lead ores). Transportation of dust from post-flotation waste heaps from that plant can be blamed as well. The western environs of Olkusz are affected by emissions from the “Katowice” Metallurgy Plant in Dąbrowa Górnicza-Strzemieszyce Południowe.
3. In the central part of Upper Silesia, the sources of Cr are numerous, namely smaller and larger metallurgical plants. For example, motor and power industries and plants producing machines and metal appliances operate in this area.
4. Cr contamination of the area situated to the east from Silesia (western periphery of the Małopolska province) is caused by the operation of chemical plants in Alwernia, producing mainly phosphorus and chromium-based products ("Alwernia S.A.”).

Hungary

Cr is widely used in metallurgical and leather industries and as catalyst in chemical industry.

1. The locally highest Cr concentration was found in Oroszlany, near Tatabanya town, which is situated in lignite mining area. High deposition loads of industrial ash and ground dust, including aerosol particles is associated with the operation of numerous power plants causing the pollution in this area. Operation of the chemical industry in Tatabanya region contributes to the increased Cr deposition as well.
2. The reason for the high Cr content in the moss near the river of Danube (Csorna, Dunaujvaros and Szazhalombatta from south to north) is unequivocal if we consider the operation of the steel industry in Dunaujvaros and chemical plants in Szazhalombatta.
3. Miskolc is a leader in running the steel, chemical and engineering industries. Many smelters can be found in this area.
4. The same is valid for Budapest as for Miskolc.

5. The reason of the increased Cr content in moss in Josvafo is not clear. Deposition of eroded soil particles or transport of fine Cr-bearing aerosols from other regions may be the reason.

d) Appraisal of dangerous effects

Czech Republic

Bio-indicated increased deposition loads of Cr in the hot spots are caused mainly by soil particles. They represent relatively small health danger. Suitable hygiene and washing of raw fruits and vegetable may decrease satisfactorily potential harmful effects of environmental contamination in the Cr hot spots. However, around industrial sources synergistic effect of increased contamination by other elements, mainly Ni should be expected. In the surroundings of the smelter Příbram there are many toxic metals and radioactive elements. In this case permanent monitoring of the environmental contamination and health effects is desired.

Slovak Republic

Mainly two hot spots of increased Cr concentration in mosses should be taken in account: the industrial area in eastern Slovakia (Košice region) and Zemplín region, in the northeastern Slovakia. Cr threat is associated with accumulated long-term deposition loads of Cr in soil covers and foliage of forest tree species. Monitoring of Cr around plants producing products for army is arguable. In the surroundings of the smelter Detva and Hriňová simultaneous synergistic effects of many toxic metals and radioactive elements should be expected.

The average Cr values for the 1990 and 2000 sets of SK moss data show a decrease of average values by about 67% in 2000 in comparison with 1990. The main reason is a restructuring of the industry; desulphurisation of power plants and introducing more sophisticated technologies in smelters. For more details see Maňkovská at al. (1998, 2004).

Poland

In PL there is no serious risk of contamination of the environment by Cr. However, as a result of the local inputs of this element to the atmosphere, soil and water, Cr can be included in the biogeochemical cycles, which may be dangerous for man. The storage of blast-furnace slag, taking place in Upper Silesia, may cause locally an increase of Cr concentrations in the environment (upper soil layers, ground water). Cr is highly mobile despite the reduction of Cr^{+6} to Cr^{+3}, and hence it can pose a health risk for the inhabitants of the region. In heavy metals-loaded Upper Silesia Cr together with other elements may have synergistic effect.

Hungary

The bio-indicated atmospheric deposition loads in the hot spots do not seem extremely dangerous. Due to contamination mainly by dust particles, common hygiene at the most contaminated sites may be a sufficient remedy.

4.3.3 Copper

Symbol	Proton number	Group IUPAC (European)	Oxidative states	Relative atomic weight	Electronegativity (Allred-Rochow)
Cu	**29**	**11 (IB)**	**I; II**	**63.546**	**1.75**
	Density ($g.cm^{-3}$)	Melting point (°C)	Boiling point (°C)	Earth crust ($mg.kg^{-1}$)	Human body ($mg.kg^{-1}$)
	8.920	**1,085**	**2,927**	**19-75**	**1.00**

a) Sources and effects of the element

Basic properties of copper (Cu) are presented in the introductory table. Elements with similar properties as Cu are classified into the group of chalcophile elements. With the exception of rare fine copper, several Cu minerals, e.g., chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), cupritte (Cu_2O), azurite ([$Cu_3(CO_3)_2(OH)_2$], malachite [$Cu_2(CO_3)(OH)_2$], etc. can be found in nature and used for Cu production. The average crustal content of Cu is about 60 $mg.kg^{-1}$. In nature Cu appears in two stable isotopes: ^{63}Cu (69%) and ^{65}Cu (31%). More than thirty Cu radioisotopes are known. ^{64}Cu is used for cancer diagnosis and treatment. The respective contents of Cu in seawater and in stream waters are 0.003 and 0.003 $mg.l^{-1}$. For example, brown coal contains on average about 190 $mg.kg^{-1}$ of Cu, while coal ash only about 35 $mg.kg^{-1}$ (Chreneková and Poláček 1987).

Natural production of Cu is about 20,000 tons per year. The source of Cu is weathering of usually Cu-sulphide microglobules being present in parent rocks. Cu sulphate produced easily penetrates environmental matrices. Little mobile Cu complex compounds can arise in accordance with the environmental pH values and concentration of presented ions.

Cu content in soils was found to range from 2–100 $mg.kg^{-1}$ and the average soil Cu concentration may be about 25 $mg.kg^{-1}$. The average Cu content in chernozems, cambisols, and luvisols in CZ are 17.6, 18.0, and 18.0 $mg.kg^{-1}$, respectively, while the average Cu content in arable horizons is 2.06 $mg.kg^{-1}$ (Beneš 1993). Cu tends to accumulate in humus. However, in northern Europe the Cu contents in humus are frequently less than 5 $mg.kg^{-1}$, while in Western and Central Europe exceed 15 $mg.kg^{-1}$.

Copper is essential element for bacteria, algae, fungi, higher plants and animals. It is part of many metalloenzymes, redox protein plastocyanin, blood pigments of some animals, etc. Most frequent Cu contents in plant tissues are determined between 1–20 $mg.kg^{-1}$. Relatively low concentrations of Cu can be found in the grains of cereals (1–15 $mg.kg^{-1}$), contrasting with the relatively high concentrations found in perennial plants, e.g. grass (2–40 $mg.kg^{-1}$). About 70% of total Cu in plants is bound to chlorophylls. Bublinec (1990) put Cu content in leaves of coniferous and deciduous trees at 2–12 and 6–14 $mg.kg^{-1}$, respectively. Innes (1995) stated respective contents of Cu in spruce (*Picea abies*) and pine (*Pinus sylvestris*) two-year-old needles 2.8–27.5 $mg.kg^{-1}$ and 3–11.5 $mg.kg^{-1}$. In SK average Cu contents in the foliage of forest tree species were found as follows: beech (*Fagus sylvatica*) 10.0±6.1, oak (*Quercus robur*) 9.3±13.6, spruce (*Picea abies*) 5.1±4.8, pine (*Pinus sylvestris*) 8.7±12.4 and fir (*Abies alba*) 8.2±7.1 $mg.kg^{-1}$. Exogenous copper was detected in 0.4% of stomata of the analysed foliage of forest tree species (Maňkovská 1996).

However, some plant species can accumulate Cu at high amounts (*Aeolanthus biformifolius, Becium homblei, Cryptosepalum maraviense, Elsholtzia haichowensis, Gypsophila patrinii, Lychnis alpina, Polycarpaea spirostylis, Silene dioica, Silene vulgaris, Veronica glaberrima*). Markert (1992) estimated total copper content in world plant biomass at 1.841×10^7 t.

Cu is needed for the production of Cu sheets, electric wires, kettles, and classical alloys with Sn (bronze), Zn (brass) or special hard alloys (P, Be). Some Cu compounds are used as glass pigments, in electroplating, paints, etc. In the CZ, some Cu-based fungicides may be used for the protection of potatoes or grapevine plantations.

Anthropogenic Cu sources producing about 265,000 tons of Cu per year are Cu smelting and electroplating works, Cu alloy foundries, works producing Cu based pigments, coal combustion, Cu pesticide spreading, etc.

In the 1990s the Cu content in the air in London was 0.25 $\mu g.m^{-3}$. The average atmospheric Cu deposition in CZ was at the end of the 1980s about 50 $g.ha^{-1}.year^{-1}$, the average wet Cu deposition in CZ (1994) was 38.8 $g.ha^{-1}.year^{-1}$.

However, a high input of Cu into biota may act toxically. Increased intake of Cu may cause gastrointestinal distress, nausea, vomiting, abdominal pain, liver damage, coughing, pulmonary fibrosis, etc. Minimal hazardous limit for oral Cu uptake is 0.01$mg.kg^{-1}.day^{-1}$. Carcinogenicity of Cu was not confirmed reliably.

Dissolved Cu concentrations in soil solution exceeding 0.5–8 $mg.l^{-1}$ are toxic for plants. Cu can be accumulated in chloroplasts and decrease the intensity of photosynthesis. Metabolic disturbance and growth inhibition are the most common reactions of Cu sensitive plants. Fernandes and Henriques (1991) provided more details of the effects of Cu in plants.

It was found that Cu deficiency increased the susceptibility of lipoproteins to peroxidation in rats and increased oxidative DNA damage in lymphocytes in culture. Some cardiovascular disorders are associated with Cu deficiency. In plants the Cu deficiency causes pile yellowing of young leaves, retardation of stem elongation, and decrease of yields.

Further details are available, for example, at the following addresses:
http://www.gsf.fi/publ/foregsatlas/text/Cu.pdf
http://www.atsdr.cdc.gov/toxprofiles/tp132-c2.pdf
http://www.saanendoah.com/cudefsoil.html
http://www.merck.com/mmpe/sec01/ch005/ch005c.html.

b) Distribution of Cu content in moss in 2000

Content of Cu in mosses in the Visegrad space was found within the range 3.7–70.0 µg.g^{-1} (Table 9). Distribution of Cu in moss in individual countries is depicted in inserted classed post map and isopleth map.

Czech Republic

The variability in Cu content in moss in the CZ moss samples is described by parameters of basic statistics in Table 9. The total copper accumulated in moss fluctuated within the range 3.7–11.7 µg.g^{-1}. Mean content of Cu was 6.6 µg.g^{-1}. Average Cu content in moss in CZ is about 1.5 times higher than the typical Cu content in moss in the least contaminated parts of Europe.

The following relevant hot spots of high Cu accumulation in moss were found in CZ:

1. The brown coal basin in western Bohemia and the adjacent parts of the Krušné Mts.
2. Agricultural land in southern Moravia, especially near Kyjov.
3. Locally at a small spot near Náchod, in northern Bohemia.
4. Moderately increased bioaccumulation was found in the Ostrava district (northern Moravia), in the northern border mountains (the Krkonoše Mts., the Orlické Mts., the Jeseníky Mts.), and in the Bílé Karpaty Mts. (in eastern Moravia).

Moss samples from large areas in southern and western Bohemia as well as southwestern Moravia contained the least amounts of Cu in 2000. Only on about one half of the CZ territory the moss samples contained Cu at amounts smaller than 6 µg.g^{-1}. Sucharová and Suchara (2004b: 40–41) provided more details about Cu distribution in moss in CZ in 2000.

Slovak Republic

The variability in Cu content in the SK moss samples is described by parameters of basic statistics in Table 9. The total Cu accumulated in moss fluctuated within 3.9–37.1 µg.g^{-1} and the average content of Cu was 9.8 µg.g^{-1}. The average Cu content in SK was about 1.9 times higher than the typical Cu content in moss in the least contaminated parts of Europe.

The following relevant hot spots of high Cu accumulation in moss were found in SK:

1. Region Lučenec: Gemer-Spiš, with a local hot spot near Krompachy.
2. Region of Košice: Prešov.
3. Region of Považie: Martin, Žilina.

Moss samples from large areas in the Low Tatra Mts., the High Tatra Mts., the Veporské Mts., the Levočské Mts. and the Tríbeč Mts. contained the least amounts of Cu in 2000. Maňkovská et al. (2003) and Florek et al. (2007) provided more details about Cu distribution in moss in SK in 2000.

The map of Cu concentrations in the leaves of forest tree species in the geochemical atlas (Maňkovská 1996) showed that Cu content in leaves exceeded 5 µg.g^{-1} on the two-thirds of the SK territory. In the leaves of Fagus sylvatica Cu contents over 10 mg.kg^{-1} were found in central Spiš and in southern part of the Low Tatra Mts., in the needles of Picea abies in the Western Tatra Mts. and in the leaves of remaining species (*Quercus rubur, Pinus sylvestris* and *Abies alba*). The highest concentrations of Cu were found in central Spiš.

Poland

The lowest concentrations of Cu were recorded in the eastern part of PL (average concentration was there 4.53 µg.g^{-1}) and slightly more copper was accumulated by *Pleurozium schreberi* collected in the central part of PL and in the region of Upper Silesia. In both regions the concentrations of Cu varied a lot among sampling sites. The highest concentrations of Cu, twice or three times higher than the average for PL, were found in Lower Silesia (Table 12).

	Eastern PL	Central PL	Lower Silesia	Upper Silesia
n	30	27	31	28
Mean	6.59	7.85	17.93	9.86
S. D.	1.111	2.043	9.783	2.420
Minimum	4.53	5.86	6.95	6.03
Maximum	9.10	16.17	39.64	15.54

Table 12. Content of Cu in moss *Pleurozium schreberi* ($\mu g.g^{-1}$) in four investigated provinces of PL in 2000. (n = number of samples, S.D. = standard deviation).

According to the inserted maps the highest contents of Cu in moss were found in the following areas:

1. Legnica-Głogów Copper District: a dozen of moss sampling sites.
2. Environs of Olkusz: Olkusz, Sikorka, Hutki.
3. Environs of Miasteczko Śląskie.

Hungary

The total Cu accumulated in moss fluctuated within 4.40–70.0 $\mu g.g^{-1}$ and average content of Cu was 12.0 $\mu g.g^{-1}$ in 2000 Average Cu content in moss in HU is about three times higher than the typical Cu content in moss in the least contaminated parts of Europe.

The following hot spots of high Cu accumulation in moss have been found in HU:

1. The agricultural lowlands in Csorna, Izsak and near Paks.
2. Szazhalombatta and Dunaujvaros near the river of Danube.
3. In the middle part of northern HU around Budapest.

c) Identification of potential pollution sources

Czech Republic

Although Cu is locally accumulated in some types of rock, e.g., carboniferous, undisrupted soil covers in these types of bedrock are not, in general, recognised as a crucial source of Cu for atmospheric deposition in CZ. Nevertheless, some contribution of Cu from eroded soil particles that contained Cu (Cu-based antifungal sprays used in potato, hop, grapevine plantations) should be considered, mainly in lowlands and dry years.

Areas of marked Cu accumulation in moss can be explained by the following impacts:

1. Combustion of brown coal in power plants and industrial furnaces concentrated in the coal basin, the release of more coarse particles during extraction and erosion of material in heaps of overburdens and of ash fields.
2. High deposition loads of Cu in exclusively agricultural land may be associated with the long-term application of Cu-based protective sprays used in vineyards and fields (southern Moravia) and by deposition of eroded soil particles. However, the typical (ash free) contents of Cu in forest floor humus in the area were 20–40 $\mu g.g^{-1}$, without any marked increase near Kyjov (Sucharová et al. 2002).
3. The local increased content of Cu in moss near Náchod, which was not recognised in 1995, cannot be explained satisfactorily. It might be caused by a short-term effect of some local pollution source, or by accidental contamination of the sampling plot. However, stone-coal power plant and several heating plants combusting local coal extracted from local Cu rich carboniferous rock are operating in the area.
4. Increased bio-accumulation of Cu in moss from the Ostrava district can be explained by the deposition of industrial dust from the metallurgical and engineering works, extraction and industrial combustion of stone coal in the local power and heating plants and combustion of municipal wastes in incinerators. The mountain areas along the Czech/Polish borders may be influenced by increased background Cu deposition loads due to long-distance transport of Cu-bearing aerosols that originated in Cu smelting and processing in the industrial areas in southern PL. A local increase in Cu content in the moss at the CZ/SK border near Strážnice may be a consequence of the operation of the nearby Slovak metallurgical works in the Nové Mesto nad Váhom district.

The altitude and precipitation sum are important factors, which significantly controlled Cu contents in the CZ moss samples in 2000. The altitude of sampling plots significantly decreased (r_p = -0.38) and the biennially precipitation sums significantly increased (r_p =-0.39) Cu contents in mosses in CZ (Sucharová and Suchara 2004b: 62).

Slovak Republic

Metallurgical industry including processing of non-ferrous metals (75%), and smelters belong to the main pollution sources of Cu. Distribution of deposition loads of some other metals (Zn, Ag, Sb, Pb) shows very similar pattern in SK.

1. Region Lučenec: Gemer-Spiš, with a local hot spot near Gelnica, and Krompachy. The coefficient of relative atmospheric deposition load K_F ranged from 3.7 to 7.1.
2. Region of Košice is the most important hot spot in SK. The area has been under the effect of metallurgical industry.
3. Increased bio-accumulation of Cu in moss in Považie region (Martin, Žilina, Nové Mesto nad Váhom) can be explained by the deposition of industrial dust from the metallurgical and engineering works, extraction and industrial combustion of stone coal in the local power and heating plants as well as combustion of municipal wastes in incinerators. The coefficient of relative atmospheric deposition load K_F reaches the value of about 3.

The average Cu values for the 1990 and 2000 sets of the SK moss data show a decrease in average values by about 52% in 2000 in comparison with 1990. The main reason is restructuring of industry and introduction of more sophisticated technologies in smelters. For more details see Maňkovská (1997), Maňkovská et al. (2003).

Poland

1. The largest concentrations of Cu found in the mosses collected in the region of Lower Silesia are easy to explain. Mining and processing of copper is the crucial source of contamination of that area. The copper production of the Legnica-Głogów Copper District constitutes about 10% of the world resources of Cu (estimated at 2.3 billion tons). The Copper Mining and Metallurgy Company (KGHM "Polska Miedź S.A.") mines and processing copper ores in several localities (Lubin, Rudna, Orsk, Legnica, Polkowice and Głogów).
2. In the region of Olkusz higher concentrations of Cu are connected with emissions generated by The "Bolesław" Mining and Metallurgy Plant in Bukowno (processing of zinc and lead ores) and steel metallurgy (The Katowice S.A. Steel Works in Dąbrowa Górnicza).
3. The processing of zinc and lead ores in Miasteczko Śląskie is responsible for the increased concentrations of Cu in that area. Dusts transported by wind from waste heaps containing copper can be also the potential source of environmental contamination by this element.

Hungary

Local effects of agriculture or industry could mainly explain the detected increased Cu contents in moss.

1. Higher deposition of Cu in Csorna, Izsak and Paks may be associated with the long-term application of plant protective Cu-based agents.
2. The metal industry in Dunaujvaros and the chemical-factory in Szazhalombatta can be blamed for the local Cu pollution.
3. The increased Cu content in mosses in Budapest can be explained by a long-term deposition of dust from the local metallurgical and electronic industries.

d) Appraisal of dangerous effects

The bio-indicated Cu concentrations in the hot spots in the Visegrad space represent relatively low environmental hazard. However, synergistic effects of other metals appearing in these hot spots should be considered.

Czech Republic

Contamination levels of the environment in the hot spots are relatively low. Nevertheless, in the close vicinity of pollution sources (non-ferrous smelters) or after application of Cu-based fungicides and fertilizers the Cu income can increase substantially. Regular monitoring of contamination loads in food chains and the environment as well as screening of the health of residents should be desired in such cases.

Slovak Republic

The Cu contamination level of the environment in the hot spots is relatively low. Nevertheless, in the close vicinity of pollution sources (non-ferrous smelters Gelnica, Krompachy) some monitoring of the current contamination levels is recommended.

Poland

In general, copper poses no risk to the environment in PL, except for the region of Lower Silesia, where the suprastandard concentrations of Cu in soils (Kabata-Pendias 2001) can result in the increased concentrations of that metal in cultivated plants (particularly root crops/vegetables); the same, the intake of Cu by human organisms may be greater. Due to the permanent input of Cu to the environment (intense production of the KGHM Polska Miedź S.A.), this element should be monitored on a regular basis in Lower Silesia.

Hungary

The bio-indicated deposition loads of Cu in the hot spots are relatively small. Keeping basic hygienic rules can be a sufficient prophylactic measure.

4.3.4 Iron

Symbol	Proton number	Group IUPAC (European)	Oxidative states	Relative atomic weight	Electronegativity (Allred-Rochow)
Fe	**26**	**8 (VIIIA)**	**II; III**	**55.845**	**1.62**
	Density ($g.cm^{-3}$)	Melting point (°C)	Boiling point (°C)	Earth crust ($mg.kg^{-1}$)	Human body ($mg.kg^{-1}$)
	7.874	**1,538**	**2,861**	**50,000-71,000**	**60.0**

a) Sources and effects of the element

Iron (Fe) is relatively abundant, typical crustal element (62,000 $mg.kg^{-1}$) on the Earth. Chosen properties of pure iron are stated in the introductory table. Four naturally occurring isotopes include three stable isotopes (^{56}Fe 92%, ^{57}Fe 2.11%, ^{58}Fe 0.2%) and one radioactive ^{54}Fe (5.8%) with a long half-life time 3.1×10^{22} years. About other 30 radioisotopes are known, the most stable is ^{60}Fe (life-time 1.5×10^{6} years). Occurrence of Fe is connected with deposits of Fe ores or minerals like haematite or bloodstone (Fe_2O_3), limonite/goethite [FeO(OH)], siderite ($FeCO_3$), pyrite (FeS_2) and others. Seawater contains surprisingly low amounts of Fe (0.003 $mg.l^{-1}$). Stream waters contain 0.67 mg of Fe per litre. Brown coal may contain on average about 57,000 $mg.kg^{-1}$ of Fe (arsenopyrite), while coal ash can concentrate Fe up to 92,000 $mg.kg^{-1}$.

Natural emission source of Fe (27,775,300 tons per year) is weathering of Fe-based minerals contained mainly in igneous basic rocks (3–10% of Fe). The mobility of Fe is influenced by the current redox potential, pH values, phosphorus concentration, microbial activities, etc. Ferrous (Fe^{2+}) compounds are much more soluble and available to biota than ferric (Fe^{+3}) ones. Fe can penetrate the soil profile in the form of organic bound Fe (fulvates) and complex compounds. Soil contains 2–5.5% of Fe; average value reaches about 3.5% (35,000 $mg.kg^{-1}$). Beneš (1993) reported that Fe content in chernozems, cambisols and luvisols was 2.6, 2.7, and 3.7%, respectively. However, plants cannot accept about 99% of Fe due to the fixation of Fe in oxides, clay minerals, humic complexes, etc. In the pH range of 4.0–7.0, humic-Fe, Fe-mugineic and Fe-citrate complexes account for more than 95% of Fe in the soil solution.

It is essential element for plants and animals. However, hardly 1% from the omnipresent Fe can be potentially received by biota from the environment. That is why Fe behaves as a microelement in biota bodies. Fe is part of cytochromes, ferredoxine, some enzymes, and it is necessary for chlorophyll and haem syntheses, etc. The natural content of Fe in plants is within 40–500 $mg.kg^{-1}$, grains of cereals contain 20–120 $mg.kg^{-1}$, and perennial grass species 50–450 $mg.kg^{-1}$. Innes (1995) determined Fe content in two-year-old needles of *Picea abies* and *Pinus sylvestris* within the range 40–169 and 77–373 $mg.kg^{-1}$, respectively. In larch (*Larix decidua*) needles in CZ average Fe content of 63 $mg.kg^{-1}$ was found (Materna 1989). Kaupenjohan et al. 1989 stated typical Fe content in larch needles at 50 $mg.kg^{-1}$. Average iron contents in foliage of individual forest tree species found in SK were as follows (in $mg.kg^{-1}$): beech (*Fagus sylvatica*) 216±1635, oak (*Quercus robur*) 131±79, spruce (*Picea abies*) 123±370, pine (*Pinus sylvestris*) 146±111, and fir (*Abies alba*) 246±1059. Exogenous iron was present in 94.4% of stomata (Maňkovská 1996). In close to nature beech forest in southern Sweden Fe contents in beech leaves, leaf litter, forest floor humus and mushrooms were stated at 70–80, 110–310, 770 and 19–74 $mg.kg^{-1}$, respectively (Tyler 2005).

Fe accumulates in ferruginous bacteria, lichen *Acarospora smaragdula*, haemoglobin and fish liver. Total Fe content in the world plant biomass was estimated at 2.76×10^{8} t (Markert 1992).

Since the Iron Age people have explored Fe abundantly for producing steel, cast iron, sheets, wires, rails, Fe tools, building parts, instruments, machines, etc. Special kinds of steel are prepared when some additives (Ni, Cr, Mo, W, Co, etc.) are used. Fe salts and complexes are used in the chemical and glass industries, analytical chemistry, water processing, magnetic tapes production, etc.

Anthropogenic sources of Fe (10,700,000 tons per year) are melting and steel works, ferrous metallurgy, industrial furnaces, ash and slag deponia, grounding rocks, suspension of soil particles, rusted or abraded anthropogenic iron objects, etc. In airborne solid particles Fe is associated with coarse particles of about 4 μm in diameter (e.g., Milford and Davidson 1985). The average yearly background wet deposition (bulk) Fe in southeastern part of CZ was 0.06 $g.m^{-2}.year^{-1}$ in 2000.
(http://www.chmi.cz/uoco/isko/tab_roc/2000_enh/CZE/kap_22/k_22_3_1_3_html.html).

An excess of Fe can be toxic for biota. Fe intake of 20–30 $mg.kg^{-1}.day^{-1}$ or less can cause intoxication and dose above 60 $mg.kg^{-1}.day^{-1}$ is usually lethal. The intoxication signs may be gastrointestinal distress, vomiting, diarrhoea, anorexia, irritation of mucosal tissues, etc. Mitochondrial dysfunctions can cause injuries of liver, heart, kidneys, lungs and other tissues.

Dissolved Fe compounds in soil solution in concentration 10–200 $mg.l^{-1}$ are strongly toxic to plants as Fe is concentrated in chloroplasts, the plants become dark green, and photosynthesis and growth are depressed. Bublinec (1990) stated that maximal permissible Fe content in leaves of coniferous and deciduous forest trees are 70–300 and 200–2,000 mg.kg^{-1}. High atmospheric Fe deposition can be linked with the harmful effects of dust sediment on plant surfaces. For example, a dustcoat may cause the overheating of plant leaves or may block gases exchange through stomata. Application of solutions containing Fe^{+2} is a reliable way of killing mosses in lawns.

Iron deficiency is a leading cause of anaemia, affecting over one-half billion people worldwide. In plants Fe deficiency causes intervenial iron chlorosis resulting in decreasing of biomass production.

For more details see, for example, the following addresses:
http://www.gsf.fi/publ/foregsatlas/text/Fe.pdf
http://www.epa.gov/ecotox/ecossl/pdf/eco-ssl_iron.pdf
http://en.wikipedia.org/wiki/Iron_deficiency_(medicine)
http://www.uni-saarland.de/fak8/botanik/publikationen/2003-03.pdf.

b) Distribution of Fe content in moss in 2000

Content of Fe in mosses in the Visegrad space was found within very wide range of 176–13,750 µg.g^{-1} (Table 9).

Position of sites with increased accumulation of Fe in mosses in individual countries can be seen in inserted classed post map and isopleth map.

Czech Republic

The content of Fe in the CZ moss samples ranged from 176 to 1,859 µg.g^{-1} and the mean was 467 µg.g^{-1} in 2000 (Table 9). These figures indicate that Fe content in moss in CZ is about twice higher than Fe content in moss at the least affected sites in Europe.

The following sites with highly accumulated Fe in moss can be recognised in the inserted maps:

1. The Ostrava district, in northern Moravia.
2. Highly agrarian southern Moravia, between Kroměříž and Mikulov.
3. The brown coal basin in western Bohemia.

The high Fe content in moss was detected in southern Moravia, in the CZ side of the Black Triangle II area and increased Fe content in moss was found in the CZ side of the Black Triangle I area. The lowest Fe contents in moss samples were found in south and southwestern Bohemia along the CZ/D borderline. On about 75% of the CZ territory Fe content in moss did not exceed 500 µg.g^{-1}.

Slovak Republic

The content of Fe in the SK moss samples ranged from 430 to 13,750 µg.g^{-1} and the average was 2,210µg.g^{-1} in 2000 (Table 9). These figures indicate that Fe concentration in moss in SK is about five times higher than Fe concentration in moss at the least affected sites in Europe.

The following sites with highly accumulated Fe in moss can be recognised in the inserted maps:

1. Region of Lučenec: Gemer-Spiš (central Spiš).
2. Region of Košice: Prešov, (Steel works Košice).
3. Region of Zemplín: Snina-Stropkov northeastern Slovakia.
4. Along the CZ/SK border: Brezová, Myjava, Stará Turá, Trenčín in southwestern Slovakia.
5. Small local areas, e.g., near the town of Detva in Central SK, Liptovský Mikuláš, Považská Bystrica, Martin, Ružomberok, Žiar, Zvolen and in intensively exploited agricultural lowlands.

The lowest Fe contents in moss samples were found in the Central SK (the Low Tatra Mts., the Strážovské and Levočské Mts).

The geochemical atlas of Slovakia (Maňkovská 1996) shows that the total Fe contents in the leaves of forest trees exceeded 200 µg.g^{-1} on two-thirds of the SK territory. High Fe contents are clearly bound to industrial areas. The highest Fe concentrations in *Fagus sylvatica* were determined in southern parts of the Low Tatra Mts. and in industrial area around Košice, while *Abies alba* showed the highest values in the Žiar basin and central Spiš, and *Pinus sylvestris* in central Spiš as well.

Poland

The average content of Fe found in mosses from PL was 550 µg.g^{-1}. Fe contents determined in mosses collected in central Poland and Lower Silesia were similar, and ranged from 261 to 871 and from 216 to 703 µg.g^{-1}, respectively (Table 13). Slightly higher average concentration of Fe was found in the eastern part of PL (168.5 µg.g^{-1}). Fe contents amounting more than 1,000 µg.g^{-1} were found only in 9 localities in the region of Upper Silesia. The average and maximum concentrations of Fe occurring in mosses from PL were much lower than in Slovakia and Hungary, but similar to those found in the Czech Republic.

	Eastern PL	Central PL	Lower Silesia	Upper Silesia
n	30	27	31	28
Mean	442	468	351	966
S. D.	168.5	126.5	114.4	731.1
Minimum	249	261	216	392
Maximum	911	871	703	4 243

Table 13. Content of Fe in moss *Pleurozium schreberi* ($\mu g.g^{-1}$) in four investigated provinces of PL in 2000. (n = number of samples, S. D. = standard deviation).

According to the inserted maps, the largest concentrations of Fe were recorded in the following areas:

1. Environs of Olkusz: Sikorka, Olkusz, Hutki.
2. Region of Miasteczko Śląskie.
3. Environs of Żarki near Częstochowa.
4. Region of Żory.

Hungary

The content of Fe in the moss samples ranged from 262 to 7,023 $\mu g.g^{-1}$ and the average was 2,065 $\mu g.g^{-1}$ in 2000 (Table 9). These figures indicate that Fe content in moss in HU is much higher than Fe content in moss at the least affected sites in Europe.

The following sites with highly accumulated Fe in moss can be recognised in the inserted maps:

1. Csorna Dunaujvaros and Szazhalombatta in the central region along the Danube river.
2. The brown coal basin in Oroszlany and Tatabanya, and the lignite and turf mines in Varpalota.
3. Josvafo and Salgotarjan in northern HU near the HU/SK borders.
4. Oroszlo in the Mecsek Mts. in southern HU.

c) Identification of potential pollution sources

Czech Republic

Besides emissions from the metallurgical and engineering industries, iron species are naturally abundant in compounds of rock and soil material. High accumulation of Fe in the areas listed above can be explained by the operation of the following pollution sources:

1. Operation of local metallurgical and engineering plants, including industrial furnaces combusting coal or coke, and by the erosion of surface materials from large-scale land reclamation, industrial waste dumps, ash and slag deposits.
2. Wind erosion and deposition of particles from soil covers contribute to the increased Fe atmospheric deposition in agrarian southern Moravia. Extraction of lignite, reclamation of the former lignite pits and the operation of a lignite power plant increase the atmospheric Fe deposition in this area.
3. The high accumulation of Fe in moss in the coal basin in western Bohemia is caused by the operation of power plants concentrated in this area. Extraction and transport of brown coal contribute to the increased deposition of soil cover particles.

The average content of Fe in moss in 2000 decreased by about 12%, while the median did not change in comparison with respective data of 1995. However, the difference of average contents of Fe in moss for 1995 and 2000 were not significant. The increasing altitude of sampling plots decreased significantly the Fe content in moss (r_p = -0.38) while the increasing biennial precipitation sums increased significantly Fe contents in moss (r_p = 0.21) in CZ in 2000. For more details see Sucharová and Suchara (2004b: 62).

Slovak Republic

Iron is considerably higher in Slovakia than in neighbouring countries (Austria, Czech Republic and Poland). Besides emissions from the metallurgical and engineering industries, iron species are naturally abundant in compounds of rock and soil material. High accumulation of Fe in the areas listed above can be explained by the operation of the following pollution sources:

1. Operation of metallurgical plants including industrial furnaces combusting coal or coke in central Spiš (Krompachy, Nižná Slaná, Rudňany, Gelnica) and erosion of surface materials from large-scale land reclamation, industrial waste dumps, ash and slag deposits.
2. Along the CZ/SK border in Brezová, Myjava, Stará Turá, Trenčín in southwestern Slovakia - operation of metallurgical industry and industrial combustion of coal.
3. Small local areas, e.g., near the town of Košice, Detva in Central SK, Liptovský Mikuláš, Považská Bystrica, Martin, Ružomberok, Žiar, Zvolen and in intensively exploited agricultural lowlands. Combined effects of emissions from metallurgical industry and eroded soil particles from arable soil.

The average content of Fe in moss in 2000 exceeded by about 12% the average Fe content in moss obtained in 1990. For more details, see Maňkovská et al. (2003) and Florek et al. (2007). Long-term atmospheric deposition loads of Fe have contaminated substantially soil covers (Čurlík and Šefčík 2002); forest trees (Maňkovská and Bucha 2002).

Poland

All areas of the increased concentrations of Fe in mosses have been under the influence of emissions from metallurgic industry.

1. Environs of Olkusz and Hutki are affected by the operation of non-ferrous metallurgy and plants of steel metallurgy ("Katowice S.A. Steelworks") operate near Sikorka.
2. The surroundings of Miasteczko Śląskie have been under the effect of emissions from non-ferrous metallurgy.
3. Żarki region has ben affected by the operation of steel works closely to Częstochowa.
4. In the region of Żory there are accumulated numerous iron and steel metallurgic plants, located in Silesia.

Hungary

1. The highest concentrations of Fe in moss in the central region of HU are caused by the operation of power plants concentrated in this area.
2. Extraction and transport of brown coal contribute to the increased deposition of soil cover particles. Many smelters can be found in this area as well.
3. The deposition of Fe in the area of Josvafo (National Forest Reserve) may be explained by a long-term deposition of industrial pollutants transported to the area from more remote industrial areas. There have not been operated any important sources of Fe at this site.
4. Effects of the operation of close metallurgical and engineering plants (Pecs and Komlo).

d) Appraisal of dangerous effects

The bio-indicated levels of Fe contamination in the hot spots are assumed to consist of little soluble and little toxic forms of Fe. Washing off industrial and soil dust can decrease substantially oral intake of Fe. However, synergistic effects of other toxic elements presented in industrial dust should be taken into account. Inhalation of industrial and soil dust may cause some respiratory diseases, immunity damage, etc.

Czech Republic

Fe deposition loads in hot spots present small health risk. Since 1990 the bio-indicated deposition loads have decreased. Only local harmful effects can be expected in a close vicinity of multi-element sources of air pollution (steel works).

Slovak Republic

Fe deposition loads in hot spots present health risk. Since 1990 the bio-indicated deposition loads have increased. Local harmful effects can be expected in a close vicinity of multi-element sources of air pollution (central Spiš and Košice steel work).

Poland

The magnitude of Fe deposition in the hot spots shows small health risk. Only local harmful effects can be expected in the vicinity of the main Fe sources (steel works), where Fe can have a synergistic action with other elements.

Hungary

The increased deposition of dust particles containing Fe is the crucial cause of the hot spot. Since oxidised Fe is only little toxic, none or hygienic precaution can be recommended.

4.3.5 Nickel

Symbol	Proton number	Group IUPAC (European)	Oxidative states	Relative atomic weight	Electronegativity (Allred-Rochow)
Ni	**28**	**10 (VIIIA)**	**II; III**	**58.093**	**1.75**
	Density ($g.cm^{-3}$)	Melting point (°C)	Boiling point (°C)	Earth crust ($mg.kg^{-1}$)	Human body ($mg.kg^{-1}$)
	8.908	**1455**	**2,913**	**51-105**	**0.10**

a) Sources and effects of the element

Nickel (Ni) is relatively abundant element on the Earth. It is naturally occurring in five stable isotopes ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni and ^{64}Ni, most abundant is ^{58}Ni and ^{60}Ni participating by 68% and 26%, respectively. About 18 radioisotopes have been proved. ^{59}Ni is a long-lived cosmogenic radionuclide with a half-life of 76,000 years. Nickel occurs in several ores and minerals such as chloantite or nickelskuttedudite [(Ni,Co)As_3-x], millerite (NiS), ullmannite or kallilite (NiSbS), garnierite or genthite (hydrous nickel silicates), etc. Frequently, Fe exchanges part of Ni in minerals and vice versa, Ni easily exchanges iron in Fe minerals. The average crustal concentration of Ni is about 90 $mg.kg^{-1}$. Seawater and stream waters contain about 0.002 and 0.0003 mg Ni in a litre. The Ni content in soils ranges widely from 1–350 $\mu g.g^{-1}$ in accordance with the parent rock. Beneš (1993) reported that the average Ni content in chernozems, cambisols and luvisols were 32.0, 35.0 and 74.0 $mg.kg^{-1}$, and the total Ni content on average was 40.0 $mg.kg^{-1}$. However, soils at serpentines or soils near smelters can contain 1,000–5,000 $mg.kg^{-1}$ (e.g., Chardot et al. 2007). The main natural source of Ni (28,300 tons per year) is the weathering of parent rocks. The highest content of Ni is in ultrabasic igneous rocks (about 1,500 $mg.kg^{-1}$), the lowest in carbonate rocks (about 5 $mg.kg^{-1}$). Released Ni can be bound on soil organic matter, Fe/Mn oxides, and clay minerals. Dissolved in water and soil solution, Ni can be transported over a long distance.

Ni is biogenous essential element needed by animals and at least some groups of plants and probably algae and bacteria. As hostage of Ni decreases animal growth, causes anaemia and some enzyme dysfunctioning. In the 1990s Ni was found to be required for activation of enzymes ureases, at least in legumes and several temperate cereal crops. Essentiality of Ni to higher plants was accepted about 2000.The content of Ni in plants is in the range of 0.4–5.0 $\mu g.g^{-1}$ (Bowen 1979, Markert 1992). The grains of cereals contain 0.1–2.0 $\mu g.g^{-1}$, and perennial grass species 0.15–2.5 $\mu g.g^{-1}$. Average nickel content in foliage of individual tree species in SK was found (Maňkovská 1996) (in $\mu g.g^{-1}$) as follows: beech (*Fagus sylvatica*) 3.9±3.4, oak (*Quercus robur*) 4.3±3.1, spruce (*Picea abies*) 2.6± 2.5, pine (P*inus sylvestris*) 3.1±3.4 and fir (*Abies alba)* 3.8±2.4. Exogenic nickel was detected in 6.8% of stomata of analysed leaves.

Ni does not tend to be accumulated in most of plant species, however, more and more Ni plant hyper-accumulators have been found, e.g., *Alyssum bertolonii, A. murale, A. lesbiacum, A. goesingense, Berkheya coddii, Bornmuellera tymphaea, Euphorbia helenae, Iberis intermedia, Leptoplax amarginata, Leucocroton linearifolius, Plyllanthus orbicularis, Senecio coronatus, Thlaspi caerulescens*, and others, etc. (Reeves et al. 1981). Total nickel content in world plant biomass was estimated at 2.76×10^6 t (Markert 1992).

Ni and its compounds are needed for ferrous alloys, electroplating, magnets, chemicals, pigments, alkaline batteries, electrotechnics, etc. No wonder that in 1995 the world consumption of refined Ni reached a record 972,400 metric tons.

Anthropogenic emission Ni sources (98,000 tons per year) include works producing and processing Ni alloys, electroplating tools, Cd-Ni batteries, Ni-catalysers etc. Burning of fossil fuels releases relatively smaller quantity of Ni. For example,

average Ni content in coal can be about 25 $mg.kg^{-1}$, in coal ash about 50 $mg.kg^{-1}$, and in crude oils 0.20–76.0 $mg.kg^{-1}$. Urban air may contain about 10–20 ng Ni per m^3 compared with about 0.5–5.0 $ng.m^{-3}$ in the rural air. The mean concentration of Ni in the urban and rural atmosphere in the CZ in the 1990s was reported to be as high as 132 and 71 $ng.m^{-3}$, respectively. The mean yearly background wet deposition (bulk) of Ni in southeastern part of CZ was 1.12 $mg.m^{-2}.year^{-1}$ in 2000.
(http://www.chmi.cz/uoco/isko/tab_roc/2000_enh/CZE/kap_22/k_22_3_1_3_html.html).

Due to carcinogenity of Ni no safe limit of Ni content can be introduced in the environment. Lengthy exposure of to Ni may case for example lung cancer, allergies, renal tubular dysfunctions, and dermatitis in humans. Delayed embryonic development and lesion of spermatogenesis due to a Ni exposition were observed as well. Compared to the relatively small toxicity of inorganic Ni-compounds, the carbonyl of Ni is extraordinarily poisonous. It might also arise when a cigarette is burning (1–3 µg of Ni per cigarette), because the most serious health effects occur when nickel is inhaled. However, about 10% of women and 2% of men in the population are highly sensitive to Ni (coins, jewellery, clothing fasteners, handles etc.) tough direct contact (nickel dermatitis). The risk for cancer of the respiratory tract is increased when the atmospheric concentration of soluble nickel exceeds 1 $mg.m^{-3}$ and that of insoluble derivatives exceeds 10 $mg.m^{-3}$.

A Ni income above 100 $\mu g.g^{-1}$ can be harmful or toxic for most plants. Ni may inhibit root growth, activate oxidative stress defence enzymes and decrease production (Brown et al. 1987). Soil cation exchange capacity is the best predictor of growth inhibition of plants (Rooney et al. 2007).

Deficiency of Ni can be hardly recognized. Hormone imbalances, deterioration of thyroid-adrenal function, prolactin regulation, growth and pigmentation, decreased hematocrit, increased blood cholesterol and fatigue may be symptoms of Ni deficiency.

The Ni deficiency in plants may appear more frequent and disrupts ureide catabolism (accumulation amino acids in leaves).

For more details look at:
http://www.gsf.fi/publ/foregsatlas/text/Ni.pdf
http://www.nal.usda.gov/wqic/Bibliographies/hypera.html
http://www.inchem.org/documents/ehc/ehc/ehc108.htm.

b) Distribution of Ni content in moss in 2000

Content of Ni in mosses in the Visegrad space was found within wide range of 0.556–23.4 $\mu g.g^{-1}$ in 2000. Chosen parameters of basic statistics for measured sets of Ni determinations are gathered in Table 9.

Distribution of Ni content in moss in individual countries can be seen in inserted classed post map and isopleth map. The following sites of increased Ni accumulation in mosses are depicted in these maps:

Czech Republic

Content of Ni in CZ ranged between 0.56 and 10.3 $\mu g.g^{-1}$, average values were about 2.18 $\mu g.g^{-1}$ (Table 9). Typical values of Ni content in moss in areas with the lowest deposition loads in Europe (Scandinavia, e.g.) are about 1.8 $\mu g.g^{-1}$ (Reimann et al. 2001), which is 60% of the average CZ values.

The inserted colour maps show the following hot spots on the CZ territory:

1. Brown coal basin and the nearby Krušné Mts. in western Bohemia.
2. An isolated small hot spot near Moravský Krumlov, in southern Moravia.
3. Southern and southeastern Moravia, between Vyškov and Blatnice.
4. Local area near Valašské Meziříčí, in northeastern Moravia.

The larger area of increased accumulation of Ni in moss are southern Moravia and the Black Triangle I area. Moss in northern Bohemia and eastern Moravia accumulated more Ni than in southern Bohemia and eastern Moravia. The lowest Ni contents in moss were found in southern, southwestern and southeastern Bohemia and partly in northern Bohemia and in northwestern and southwestern Moravia. Total area of these sites is about 40% of the CZ territory and typical content of Ni in moss in these areas was less than 2 $\mu g.g^{-1}$.

Slovak Republic

Concentration of Ni in SK ranged between 0.70 and 12.6 $\mu g.g^{-1}$, average values were about 3.94 $\mu g.g^{-1}$ (Table 9). Typical values of Ni concentration in moss in areas with the lowest deposition loads in Europe (Norway.) are about 1.6 $\mu g.g^{-1}$, which is 27% of the average SK values. The inserted colour maps show the following hot spots in the SK territory:

1. Region of Lučenec: Gemer-Spiš is the most important hot spot in SK.
2. Region of Považie along the cross border in southwestern Slovakia and the surroundings of the towns Martin and Ružomberok.
3. Region of Pohronie and military training area Lešť.
4. Region of Zemplín and local hot spots near Bardejov, Stropkov, Humenné, Strážske.

The lowest content of Ni in the moss samples was found in northern part of the Low Tatra Mts., the High Tatra Mts., Malé Karpaty Mts., Tríbeč Mts. and in Levočské Mts.

Associated with industrial areas and mountain forests, Ni contents in the leaves of forest tree species in SK above 2 $\mu g.g^{-1}$ occurred in northwestern, southern and eastern SK. The highest total Ni content in the leaves of *Fagus sylvatica* was found in the mountain forests of Kysuce Mts., the Beskids and in southern part of the Low Tatra Mts., and in all industrial areas except for the Horná Nitra basin and the military training area Lešť. In leaves of *Quercus robur, Pinus sylvestris* and *Abies alba* in all studied industrial areas and in *Picea abies* needles in mountain forests, in central Spiš and in Košice metropolitan area (Maňkovská 1996).

Poland

Among the V4 countries, Poland shows the lowest Ni concentrations in mosses. The average concentration of Ni was 1.62 $\mu g.g^{-1}$ in *Pleurozium schreberi* from PL. As compared with other analysed elements in mosses, Ni concentrations showed the least variation among particular sampling sites. The lowest average concentration of Ni was found in mosses from the eastern part of PL (1.34 $\mu g.g^{-1}$), similar values were found in the central part of PL and Lower Silesia (1.68 and 1.67 μg.g^{-1}, respectively). Slightly higher values were recorded in mosses from the region of Upper Silesia (1.81 μg.g^{-1} on the average).

	Eastern PL	Central PL	Lower Silesia	Upper Silesia
n	30	27	31	28
Mean	1.34	1.68	1.67	1.81
S. D.	0.331	0.333	0.480	0.446
Minimum	0.724	1.070	0.776	1.134
Maximum	2.07	2.24	2.89	2.84

Table14. Content of Ni in moss *Pleurozium schreberi* (μg.g^{-1}) in four investigated provinces of PL in 2000. (n = number of samples, S. D. = standard deviation).

Areas where mosses contained Ni at the amount exceeding 2 μg.g^{-1} are listed below:

1. Environs of Warsaw: Palmiry, Bolimów, Podkowa Leśna, Legionowo.
2. Environs of Rudna: Radomyśl, Zielona Góra, Polkowice, Ubocze in Lower Silesia.
3. Environs of Mikołów: Olkusz, Żory, Landek in the region of Upper Silesia.

The highest emissions of Ni from heavy industry were bioindicated in the Mazovia province. The moss samples contained in this area 3-4 times more Ni than mosses from the Silesia province (Table 14).

c) Identification of potential pollution sources

Czech Republic

Nickel-bearing pollutants are released from metallurgical and engineering plants. As a terrigenous element, Ni is present in soil particles eroded from some soil covers. Ni content in moss may reflect both level of industrial Ni deposition levels and level of soiling of analysed samples. The following reasons can be mentioned for increased accumulation of Ni in moss in the areas listed above:

1. Abundant dust and ash deposition from the operation of local power plants and sedimentation of soil particles released during extraction of coal in the coal basin. Operation of remaining metallurgical and engineering plants.
2. The reason for the locally increased Ni in moss near Moravský Krumlov is not clear. The moss contained low levels of Ni at this monitoring plot in 1995. Either short-term effects of the operation of local engineering plants, the operations of an airport or rather soiling of the sampling plot by eroded soil covers originating from local outbursts of syenites and serpentinites may be the reason.
3. The territory of southern Moravia suffers from high soil erosion and abundant deposition of eroded particles from local soil covers. Deposition of industrial aerosol particles from metallurgical and engineering works is expected to the east of Vyškov. In the cross border area near Blatnice the impact of aerosols from the metallurgical industry in the adjacent Slovak industrial districts of Myjava and Stará Turá (Ni-, Cr-plated products) may be manifested in this area.
4. The pollution source of Ni near Valašské Meziříčí has not been definitely identified. Some effects of the former or current operation of some industrial plant, e.g., production compounds for electrical appliances, may be the cause.

As for the most elements, Ni accumulation in moss significantly and negatively correlated with altitude of the sampling plots (r_p = -0.26) and significantly and positively with the biennial precipitation sums (r_p = 0.15). In more details the results were commented in the CZ national report (Sucharová and Suchara 2004b: 48–49 and 62).

Slovak Republic

The median value for the Ni contents in the SK mosses (3.2 μg.g^{-1}) is higher than in neighbouring countries (1.26–2.06 μg.g^{-1}). High correlation with Al, Sc, Ti, V, Fe and Co contents was found. The In general high Ni level in SK mainly reflects the geochemistry of the area (Košická basin and around the old mining districts). However, more than 60% of Ni in the anthropogenic emissions originates from burning of fossil fuels. High amounts of emitted Ni can be found near plants producing Ni-based products and in the surroundings of coal power plants and around old deposits of metallurgical slugs. The most important sites with high Ni accumulation in moss follow:

1. Region of Lučenec, Gemer, Spiš (Krompachy, Rudňany, Nižná Slaná, Gelnica, Fiľakovo, Rimavská Sobota, Kokava) is influenced by operation of metallurgical industry, production and processing of non-ferrous ores with running of operation of local municipal fireplaces; power stations; manufacture of machinery and equipment.

2. Industrialised region of Považie in western SK is affected mainly by combustion of coal in local metallurgical and engineering works, instrument industry, glass in heating and power plants. In the region of Nitra, main source of NO_x is coal power plant in Zemianske Kostoľany.
3. Non-ferrous ores and smelters, old mining districts in Žiar nad Hronom, Banská Štiavnica, Podbrezová and military training area in Lešť.
4. Manufacture of basic metals and fabricated metal product, chemical products near Bardejov, Stropkov, Humenné, Strážske. The area may be affected by Ni pollution originating in the close PL emission sources.

In 2000 mean concentration of Ni in moss increased by about 79% in comparison with the respective data from 1990. In more details the results were commented in Maňkovská et al. (2003) and Florek et al. (2007).

Poland

1. The increased concentrations of Ni in mosses collected in central PL are most probably connected with contamination caused by emissions from electrical and electronic works, metallurgical works (steel products, Lucchini Steel Works in Warsaw) and emissions from hard coal power plants, as well as emissions from the largest petroleum refinery in PL located in Płock.
2. Ni contamination of the area of Lower Silesia is connected with emissions originating from copper metallurgy (KGHM "Polska Miedź S.A.”), emissions produced by burning of lignite in the region of Turoszów (Black Triangle). The increased Ni contamination may be also associated with the transport of dust from numerous rock processing plants (e.g. serpentine marble with a high Ni content).
3. The increased concentrations of Ni in mosses samples originating from Upper Silesia are connected with the operation of numerous iron metallurgy works, electroplating plants, as well as hard coal-burning power plants.

d) Appraisal of dangerous effects

Ni is carcinogenic elements deserving special observation and monitoring.

Czech Republic

Even in hot spots the environmental Ni contents are relatively small. However, if any dustiness from industrial sources is expected, health risks and remedies should be introduced because inhalation of Ni compound may be carcinogenic. Effect of deposition loads of soil particles in southern Moravia can be diminished through washing hands and raw vegetables.

Slovak Republic

Ni is considered for hazardous element. In the hot spots the environmental Ni contaminations are important. If any dustiness from industrial sources is expected any remedies should be introduced because inhalation of Ni compound may be carcinogenic. Weathering and erosion of Ni-based wastes or ores can release and transport Ni to a long distance.

Poland

The environmental concentration of Ni is relatively small in the hot spots in PL. However, in the areas where the Ni content is high in the air, this element can cause or increase an allergic reaction.

4.3.6 Lead

Symbol	Proton number	Group IUPAC (European)	Oxidative states	Relative atomic weight	Electronegativity (Allred-Rochow)
Pb	**82**	**14 (IVB)**	**II; IV**	**207.200**	**1.55**
	Density ($g.cm^{-3}$)	Melting point (°C)	Boiling point (°C)	Earth crust ($mg.kg^{-1}$)	Human body ($mg.kg^{-1}$)
	11.34	**327.46**	**1,749**	**8-15**	**1.70**

a) Sources and effects of the element

Lead (Pb) is chalcophile and litophile element, whose properties are stated in the introductory table. Naturally occurring Pb consists of four stable isotopes, isotope ^{204}Pb (1.4 %) and three stable final products of U, Ac and Th radioactive decay series ^{206}Pb (24.1%), ^{207}Pb (22.1%) and ^{208}Pb (52.4%). About 27 other radioactive Pb isotopes have been proved. Pb can be found in more than 200 ores and minerals, for example, in galena (PbS), cerussite ($PbCO_3$), anglesite ($PbSO_4$), crocoite ($PbCrO_4$), pyromorphite [$Pb_5(PO_4)_3Cl$], etc. Pb joins other minerals in which Pb may exchange with an element of similar ion diameter (e.g., K, Ca, Ba, Sr). The average crustal Pb content is about 13 $\mu g.g^{-1}$. The average Pb content of soil is assessed to be about 40 $\mu g.g^{-1}$. The Pb content in chernozems, cambisols and luvisols is reported to be 29.0, 36.0, and 38.0 $\mu g.g^{-1}$, respectively (Beneš 1993). Median of the Pb content (2M HNO_3) in arable soils in the CZ is 16.6 $\mu g.g^{-1}$ (MZe 1996). Pb is counted among the least mobile metals in the environment. Relative Pb stability of Pb compounds is in the following order: inorganic Pb (II) > organoPb (IV) > inorganic Pb (IV) > organoPb (II). Pb cations are easily absorbed to clay minerals, organic matter, Fe/Mn oxides and precipitated in phosphates, carbonates, sulphates, sulphides, etc.

Pb is not necessary element either for plants or animals. The natural Pb content in plants is in the range of 0.2–5.0 $mg.kg^{-1}$, small amount of Pb is concentrated in cereal grains (0.1–1.0 $\mu g.g^{-1}$), and higher content of Pb can be found in perennial plants (0.5–15 $\mu g.g^{-1}$). Average Pb contents in foliage of individual forest tree species in SK (Maňkovská 1996) were as follows (in $\mu g.g^{-1}$): beech (*Fagus.sylvatica*) 3.7±11.6, oak (*Quercus robur*) 1.8±3.9, spruce (*Picea abies*) 1.7±2.7, pine (*Pinus sylvestris*) 3.7±4.5 and fir (*Abies alba*) 2.6±3.1. Exogenous Pb has not been detected in stomata of the analysed foliage (Maňkovská 1996). However, some plants, such as *Amorpha canescens, Minuartia verna* and the lichen *Stereocaulan pileatum* were found out to accumulate Pb at higher amounts. Pb content in world plant biomass was estimated at 1.841×10^6 t (Markert 1992).

The natural source of Pb (4,000–6,000 tons per year) is the weathering of Pb-based minerals from parent rocks. The Pb content decreases from acidic (20 $\mu g.g^{-1}$) to ultrabasic (5 $\mu g.g^{-1}$) ignite rocks and from clay sediments (20 $\mu g.g^{-1}$) to sandstone and limestone (5 $\mu g.g^{-1}$) rocks. Pb isotopes also arise during the disintegration of unstable elements such as U, Th, in the soil, water and air. Pb may be also released by bio-methylation. It is believed that the virgin atmosphere, which is not influenced by human activities, may contain less than 0.04 ng of Pb in m^3. Pb may be also released into the atmosphere during large vegetation fires and volcanic activities.

Pb has been used in production of auto-batteries, alkyl-Pb petrol additives, alloys, anticorrosive dyes and pigments, cable sheathing, PVC stabilisers, ammunition, anti-friction substances, X-ray protective shields, crystal glass, etc. Yearly Pb production is about 4.3×10^6 tons. More than one third of the Pb produced comes from the recycling of Pb waste materials.

Anthropogenic sources of Pb (400,000 $t.year^{-1}$) are works producing, recycling and utilising Pb, producers of batteries, Pb-based pigments, crystal glass and ceramics, etc. Less Pb is released by fossil fuels and waste incineration. Pb may be introduced into soils by irrigation, fertilisation, and sewage sludge application. About 227 tons of Pb was released by the combustion of leaded petrol (0.15 mg of alkyl lead per litre) in the CZ in 1995. However, since 2000 any distribution of leaded petrol has ceased in CZ. The burning of coal is an important Pb source because about 20 mg of Pb is released through combustion of one kg of coal. Coal ash, for example, contains about 2 $mg.kg^{-1}$ of Pb. In the urban air, Pb is associated with fine particles formerly originating mainly in car exhaust.

The mean yearly background wet deposition (bulk) of Pb in southeastern part of CZ was 2 $mg.m^{-2}.year^{-1}$ in 2000, while in areas affected by industrial pollution 3–3.5 $mg.m^{-2}.year^{-1}$ (http://www.chmi.cz/uoco/isko/tab_roc/2000_enh/CZE/kap_22/k_22_3_1_3_html.html).

However, higher income of Pb is toxic for both plants and animals. Concentrations of Pb ($PbCO_3$) in soil solution of 3–20 $mg.l^{-1}$ were phytotoxic. In contaminated environment Pb is gathered in plant roots (90% of Pb content). Aboveground plant parts store about 10% of the internalised Pb. However, the surface of aboveground plant parts is contaminated by Pb deposit. Pb is located in plant cell membranes, nuclei, chloroplasts, and mitochondria. The activity of many enzymes is affected.

Pb penetrates the human body via inhalation, ingestion and the skin. Absorbed Pb travels through the blood stream, brain, and kidney and into bones where it is stored for a long time. Pb affects the peripheral and central nervous systems, blood cells and metabolism of vitamin D, calcium and iron. Pb may cause reproductive difficulties, carcinogenic effects, renal insufficiency, hypertension, etc. The tolerable Pb daily intake is set at 430 μg for adult humans, i.e., Pb daily uptake about 43 μg.

Not any effects of Pb deficiency are known.

Additional information can be found, for example at the following addresses:
http://www.gsf.fi/publ/foregsatlas/text/Pb.pdf
http://www.inchem.org/documents/ehc/ehc/ehc85.htm
http://www.phyles.ge.cnr.it/htmling/toxicityoflead.html
http://www.emedicine.com/MED/topic1269.htm.

b) Distribution of Pb content in moss in 2000

Content of Pb in moss samples in the Visegrad space reached 1.81–104 $\mu g.g^{-1}$ in 2000. Table 9 gives other parameters of basic statistics for Pb determination.

Distribution of Pb in moss in the V4 countries is depicted in inserted classed post map and isopleth map. The following hot spots of increased Pb accumulation in moss can be seen:

Czech Republic

Pb content in moss ranged between 1.81 and 42.8 $\mu g.g^{-1}$ in CZ. Mean Pb content was found to be 6.75 $\mu g.g^{-1}$. Moss samples in anthropogenically least influenced European areas contain less than 2.5 $\mu gPb.g^{-1}$ (Reimann et al. 2001), i.e., 2.5 times less than the average Pb contents in CZ.

The inserted maps show the following hot spots:

1. Příbram and Rokycany districts, in the southwestern part of central Bohemia.
2. Ostrava district and the nearby the Moravskoslezské Beskids, in northeastern Moravia.
3. Cross border mountain areas in the northern part of CZ, in the Orlické Mts., the Rychlebské Mts. and the Jeseníky Mts.
4. Locally in the Krkonoše Mts., in northern Bohemia.

The most important areas of increased Pb deposition levels is the CZ part of the Black Triangle II area and the surroundings of the secondary lead smelter Příbram. However, introduction of the sophisticated technology in the lead smelter in 1998/1999 should decrease the emitted amounts of metals in future. The fine scale bioindication of long-term and current deposition loads of Pb in a 14-km radius around the smelter in Příbram was carried out in 1999 (Sucharová et al. 1999). In contrast, very low Pb accumulation in moss was found in western and southern Bohemia and in southwestern Moravia, and surprisingly, in some parts of central Bohemia. On about 90% of the CZ territory the Pb contents in moss did not exceed 10 $\mu g.g^{-1}$. The accumulation of Pb in moss correlated significantly and negatively with the altitude (r_p = 0.23) and positively with the biennial precipitation sums (r_p = 0.41). For more details see Sucharová and Suchara 2004b).

Slovak Republic

The Pb concentration in moss ranged between 21.6 and 104 $\mu g.g^{-1}$ in SK. The mean Pb concentration was found to be 31.7 $\mu g.g^{-1}$ (Table 9). Moss samples in anthropogenically least influenced European areas contain less than 2.5 $\mu g.g^{-1}$, i.e., 12.7 times less than the average Pb concentration in SK. The inserted maps show the following hot spots:

1. The region of Lučenec-Gemer-Spiš: Krompachy town, the Spišsko-gemerské rudohorie Mts., the Volovské vrchy Mts., Košice Málinec, Lučenec and Hnúšťa.
2. Zemplín: Michalovce, Vranov.
3. The region of Považie: Moravskoslezské Beskids, in the northwestern Slovak parts of Beskids.
4. Banská Štiavnica and Banská Bystrica towns and their surroundings.

In contrast, very low Pb accumulation in moss was found in Javorníky Mts., Strážovské vrchy, Mts., Malé Karpaty Mts., Tríbeč Mts. and in northern part of the Low Tatra Mts.

The distribution of Pb content in the leaves of forest tree species in the SK forests was found to be similar to the distribution of Pb in mosses. The map of Pb content in the leaves of tree species showed (Maňkovská 1996) that the Pb contents exceeded 5$\mu g.g^{-1}$ in industrial areas in central and eastern SK. Higher Pb contents were determined in leaves of *Fagus sylvatica* in central Spiš, *Quercus robur* in Žiar and Horná Nitra basins, and in *Pinus sylvestris* in central Spiš.

Poland

The average content of Pb found in mosses collected in Poland was 13.9 $\mu g.g^{-1}$. At particular sampling sites Pb concentrations ranged from 3.94 to 65.6 $\mu g.g^{-1}$. The average Pb contents greatly varied in the four regions of PL where moss samples were collected. The lowest concentrations were found in the eastern part of PL (6.4 $\mu g.g^{-1}$ on the average); they were higher in the central part of PL (9.1 $\mu g.g^{-1}$ on the average) and next in

Lower Silesia (15.4 µg.g^{-1}). The largest contents of Pb were recorded for mosses collected in the region of Upper Silesia (25 µg.g^{-1}on the average).

	Eastern PL	Central PL	Lower Silesia	Upper Silesia
n	30	27	31	28
Mean	6.4	9.1	15.4	25.0
S. D.	1.884	1.657	10.896	12.013
Minimum	3.94	6.49	6.72	11.41
Maximum	13.3	12.6	55.5	65.6

Table 15. Content of Pb in moss *Pleurozium schreberi* (µg.g^{-1}) in four investigated provinces of PL in 2000. (n = number of samples, S. D. = standard deviation).

According to the inserted maps, the areas of increased Pb concentrations (more than 20 µg.g^{-1}) are as follows:

1. Environs of Wilczkowo, Rudna, Zielona Góra, Nowa Sól, Kietlów and Polkowice in Lower Silesia.
2. Environs of Miasteczko Śląskie and Olkusz.
3. Area situated to the east of Częstochowa (Olsztyn, Żarki, Pradła).
4. Central part of Upper Silesia (Mikołów, Bieruń).

In PL, the highest emissions of Pb from industrial works were noted mainly in the area of Upper Silesia. They exceeded considerably (5–10 times) emissions of Pb in Lower Silesia. Pb emissions in central PL are much lower (about 10 times as low as in Lower Silesia). As in the eastern part of PL no heavy industry is located, Pb emissions have not been registered (Table 15).

Hungary

Pb content in moss ranged between 2.00 and 57.7 µg.g^{-1}. Mean Pb content was found to be 17.1 µg.g^{-1}. However, moss samples in anthropogenically least influenced European areas contain typically less than 2.5 µg.g^{-1}, which is 6 times less than the average Pb contents in HU.

The inserted maps showed the following hot spots:

1. High Pb contents were measured in northeastern HU (Miskolc) and in Balatonfelvidek (near Monostorapati), and in Veszprem and Ajka too.
2. In the central regions Szazhalombatta, Alsonemedi and Dunaujvaros.
3. In the Mecsek Mts. (southern HU), Komlo and along the east part of Danube (Bataszek).
4. Tiszaujvaros in northeastern HU.

c) Identification of potential pollution sources

Czech Republic

Common CZ pollution sources of Pb are aerosols originating in the metallurgical, engineering and glass industries, emissions from combustion of fossil fuels, municipal incinerators and exhaust fumes.

High content of Pb in moss in the areas listed above can be explained by the operation of following Pb emission sources:

1. Operation of secondary lead smelter in Příbram and a foundry near Rokycany.
2. Industrial dust from metallurgical and engineering works, production of batteries, and aerosols from industrial coal furnaces. The Moravskoslezské Beskids Mts. suffer from import of Pb- bearing aerosols from the Ostrava district and increased wet Pb deposition in the mountain environment.
3. The bioindicated increased Pb deposition loads in the Orlické Mts. and the Jeseníky Mts. may be the effect of increased background Pb deposition loads originating in the industrial region of northeastern Bohemia and on the southern edge of the Polish industrial regions. Pb has a general tendency to be deposited intensively in mountain areas in CZ.
4. Locally increased Pb contents in moss from the Krkonoše Mts. may reflect the operation of local glass works in western part of the mountains and the effects of marginal deposition of Pb from outlying pollution sources from the Czech and Polish parts of the brown coal basin (Polish coal power plant Turów).

Partial correlation of Pb contents in moss and the altitude of sampling plots and biennial precipitation showed significant and negative effect of the altitude (r_p = -0.23) and significant and possitive effect of the biennial precipitation (r_p = 0.41) on the Pb accumulation in moss in CZ. The obtained results, comparisons with other countries and trends of Pb deposition were commented in the national report in more details (Sucharová and Suchara 2004b).

Slovak Republic

Common SK pollution sources of Pb are aerosols originating in the metallurgical, engineering and glass industries, emissions from combustion of fossil fuels, municipal incinerators and exhaust fumes. The distribution of Pb foliage concentration in the SK forests was found to be similar to the distribution of Pb in mosses (Maňkovská 1996). High content of Pb in moss in the areas listed above can be explained by the operation of the following Pb emission sources:

1. Increased concentrations of Pb are related to long-term operation of former smelters and ore processing facilities in Spišská Nová Ves, Krompachy, Nižná Slaná, Rudňany, Gelnica, Spišsko-Gemerské Rudohorie Mts., Volovské vrchy Mts., glass-ceramic production (Málinec, Lučenec), and manufacture of chemicals (Hnúšťa).
2. Processing of basic metals, production of chemicals, fertilizers and military orders (Michalovce, Strážske, Vranov right to the SK/HU borderline, Užhorod basin).
3. Old contamination loads and production of batteries in Banská Štiavnica.
4. Industrial dust from metallurgical and engineering works, production of batteries, and aerosols from industrial coal furnaces and the effects of marginal deposition of Pb from outlying pollution sources from the Czech and Polish parts of the Beskids in northwestern Slovakia.

The average values for the 1990 and 2000 sets of SK moss data show a decrease in mean values by about 48% in 2000 in comparison with 1990. The main reason is restructuring of industry, ceased production and distribution of leaded petrol, desulphurization of power plants and introducing of more sophisticated technologies in smelters. The obtained results, comparisons with other countries and trends of Pb deposition were commented in more details (Maňkovská et al. 2003 and Florek et al. 2007).

Poland

1. High Pb content in mosses from Lower Silesia is connected with emissions originating in non-ferrous metallurgy and foundry work (mainly copper), as well as burning hard coal and lignite. Dusts emitted by some ceramic plants ("Krzysztof", "Wałbrzych", "Książ") may also contribute to the increased Pb deposition levels.
2. Much higher concentrations of Pb noted in the environs of Miasteczko Śląskie and Olkusz can be associated with the operation of metallurgic works (non-ferrous metals, mainly zinc and lead).
3. Higher level of Pb in the area situated to the east of Częstochowa is connected with the emissions from steelworks located in that town.
4. High concentrations of Pb found in mosses collected in the central part of Upper Silesia are the result of emissions generated by numerous metallurgical plants, foundries and coal power plants in this area.

Hungary

1. Industrial dust from metallurgical, building and engineering works and glass plant in Balaton-felvidek. Operation of heavy industry in Miskolc.
2. Operation of petrol chemistry and oil refinery along Danube.
3. Effects of brown coal basin and production of china.
4. Local running of oil chemistry.

Distribution of leaded petrol has been ceased in HU. The remarkable decreasing of Pb contents in moss has been found all over the HU territory.

d) Appraisal of dangerous effects

Despite relative Pb toxicity the bioindicated deposition loads of Pb in central Europe are decreasing. Except for a few hot spots the environmental contamination levels are not extraordinary dangerous. However, due to the old contaminated loads at some sites, proper monitoring of contamination status is desirable.

Czech Republic

The current bioindicated deposition loads of Pb are relatively small except for 2–3 localities. In spite of decreased current deposition loads of Pb in the surroundings of Příbram, the western Krkonoše Mts. and western parts of the Beskids near Ostrava, very high accumulated long-term deposition loads of Pb are expected near the industrial sources of pollution (smelters, production of batteries and glass works). Income of Pb in plants, berries, mushrooms, local games, etc. from soil covers and forest floor humus should be monitored. Just the hidden contamination of humus may be a health risk for the local residents.

Slovak Republic

The current bioindicated deposition loads of Pb may be dangerous at four sites. In spite of decreased current deposition loads of Pb in the surroundings of central Spiš, eastern part of Zemplín region, Banská Štiavnica and northwestern parts of Beskids (near the industrial sources of pollution in CZ and PL.

Poland

Except for the areas being under the influence of non-ferrous metals and iron metallurgy and large coal-burning power plants (mainly Lower and Upper Silesia), a threat to the environment posed by Pb is small in PL. In polluted areas all environmental components (soils, water, air, plants and animals) contain the increased amounts of Pb. In these regions, children are particularly vulnerable because they gain this metal easier than adults.

Hungary

Pb is under considerable interest of toxicologists. That is why health screening and continuous biomonitoring are desired in Pb hot spots. Nevertheless, the atmospheric deposition loads of Pb are getting low in the whole Europe. An abidance of the common hygienic rules could protect residential in the hot spots against possible harmful Pb effects.

4.3.7 Vanadium

Symbol	Proton number	Group IUPAC (European)	Oxidative states	Relative atomic weight	Electronegativity (Allred-Rochow)
V	**23**	**5 (VA)**	**II; III; IV; V**	**50.942**	**1.45**
	Density ($g.cm^{-3}$)	Melting point (°C)	Boiling point (°C)	Earth crust ($mg.kg^{-1}$)	Human body ($mg.kg^{-1}$)
	6.000	**1,890**	**3,380**	**135-230**	**0.03**

a) Sources and effects of the element

Vanadium (V) does not appear in pure form in nature. It can be found in about 65 different minerals among which carnotite $[K_2(UO_2)_2(VO_4)_2.\ H_2O]$, roscoelite $[K(V,Al,Mg)2AlSi_3O_{10}(OH)_2]$, vanadinite $[Pb_5(VO_4)3Cl]$, and patronite (VS_4) are important sources of the metal. Naturally occurring V consists of two isotopes ^{50}V (0.2%) and ^{51}V (99.2%), the former is slightly radioactive (half-life 1.5×10^{15} years). Basic igneous rocks contain more than 200 $mgV.kg^{-1}$; asphalt even more than 400-500 $mg.kg^{-1}$. On the contrary limestones contain hardly 20 $µg.g^{-1}$ (Beneš and Pabiánová 1987). Natural sources of V (65,000 $t.year^{-1}$) are the weathering of V minerals in parent rocks, volcanic activities, fires of organic matter, showers of meteorites, etc. V^{+3} can be oxidised into mobile V^{+4} and V^{+5}, and concentrated and precipitated in secondary minerals. The V content in the CZ chernozems, curtisols and luvisols are on average 73.0, 87.0, and 100 $mg.kg^{-1}$ (Beneš 1993). Mean total V content in European soil covers is about 60 $µg.g^{-1}$. Aqua regia can extract about one half of this amount. Sea and stream waters contain about 0.001 mg of V in litre. In the environment is V relative very mobile.

V is essential in the control of some enzyme systems (e.g., ATPases) in many animal species or V nitrogenases in soil microorganisms. Some sea animals, ascidians, e.g., *Ascidia gemmata*, use the coloured V-protein in blood for the oxygen transport. Although the necessity of V was not confirmed for humans sometimes a dose of about 0.1 mg V per day is recommended for an adult human. Vanadium has not been demonstrated to be essential for vascular plants some bacteria and fungi. However, low V doses may stimulate growth and yields, higher doses are toxic (Kaplan et al. 1990). Grains of cereals contain 7–50 $µg.g^{-1}$, while perennial grasses can contain V in the range of 150–2,000 $µg.g^{-1}$. Tyler (2005) stated in a beech forest in southern Sweden V contents in beech leaves, leaf litter, forest floor and mushrooms 90–100, 460–1,900, 4,300 and 6–150 $µg.g^{-1}$. Arithmetic mean of total V content in foliage of forest tree species in SK was found 0.8±2.7 $µg.g^{-1}$ (Maňkovská 1996). The average V contents in leaves of the forest tree species were as follow (in $µg.g^{-1}$): beech (*Fagus sylvatica*) 0.7±2.2, oak (*Quercus robur*) 0.4±1.1, spruce (*Picea abies*) 0.9±3.2 pine (*Pinus sylvestris*) 1.0±2.1 and fir (*Abies alba*) 1.0±4.4. Exogenous vanadium has been present in 16.1% of stomata of analysed leaves. However, some organisms, such as fly agaric *Amanita muscaria* or North American astragalus species *Astragalus confertiflorus* can accumulate V at higher amounts. V content in world plant biomass was estimated (Markert 1992) at 9.2×10^4 t.

V is used in the production of high-strength steels, full alloy steels, Al, Ti-alloys, catalysts, high speed tools, ceramics and glass pigments, electronics, batteries, printing inks, super conducting magnets. Anthropogenic sources of V (210,000 $t.year^{-1}$) are V steel and alloys producers and processors, producers of reinforcing bars, jet engines and high speed tools, electronics, ceramics and glass works, some producers in chemistry, etc. However, the most important source of V is the burning of crude oils, coal, bitumen, wasted boiler soot, etc. Coal and coal ash contain about 120 and 270 µg V per g respectively.

The rural atmosphere contains 0.001–3 ng of V per m^3, the urban industrial atmosphere 7–200 $ng.m^{-3}$. V is associated with solid particles of very small aerodynamic diameter, which may persist in the atmosphere for a long time. Wet atmospheric deposition of V in the CZ may range (the end of the 1990s) from 5–35 $g.ha^{-1}.year^{-1}$.

Exposure to large amounts of V and its compounds mainly through inhalation is toxic. V dust irritates the lungs, skin, and eyes. Inhalation exposures to 35 $mg.m^{-3}$ of vanadium are considered immediately dangerous to life and health. The maximum safe concentration of V in the atmosphere is recommended to be 1 $µg.m^{-3}$. Vanadium compounds are poorly absorbed through the gastrointestinal system. The toxicity of V increases with the oxidation stages of the element, for example, pentavalent $VOSO_4$ has been reported to be more than 5 times as toxic as trivalent V_2O_3. V causes diarrhoea and vomiting. The lethal dose of V LD_{50} for rats has been determined as 0.8 $mmol.kg^{-1}$. Environmental Protection Agency (EPA) has not classified vanadium as to its human carcinogenecity. No increase in tumours was noted in long-term animal studies.

Deficiencies of vanadium are unknown in humans. In rats, chickens and goats, a variety of inconsistent deficiency symptoms have been seen but only under conditions of synthetic diets with all vanadium excluded.

Signs include reduced growth, poor bone development, impaired reproductive capacity and, in chickens, poor feather development. Small doses of V rather stimulated growth of experimental plants.

More information can be found, for example, at the following addresses:
http://www.gsf.fi/publ/foregsatlas/text/V.pdf
http://www.epa.gov/ecotox/ecossl/pdf/eco-ssl_vanadium.pdf
http://www.nature.nps.gov/hazardssafety/toxic/vanadium.pdf
http://www.inchem.org/documents/ehc/ehc/ehc81.htm.

b) Distribution of V content in moss in 2000

Content of V in mosses in the Visegrad space was found in the large range from 0.40 to 32.5 $\mu g.g^{-1}$. Table 9 gives additional figures of basic statistics for the V analytical data.

Inserted classed post map and isopleth map depict the distribution of V in mosses in the V4 countries. Comments to these maps follow:

Czech Republic

The moss analyses found that the V content in moss was in the range of 0.57–5.86 $\mu g.g^{-1}$. In the anthropologically least influenced parts of Europe the V content in moss is below 1.1 $\mu g.g^{-1}$ (e.g., Reimann 2001), which is more than 60% lower than the determined average V content in moss in CZ.

The following areas of high V accumulation in moss are documented in the inserted maps:

1. The brown coal basin, with the local hot spots near Kadaň and Most and in the adjacent Krušné Mts. in western Bohemia.
2. Southern Moravia, with the highest V accumulation in moss in Kyjov district.
3. The western part of central Bohemia, with local maximum of V accumulation in moss near Mělník.

A modest increase of V content in moss can be seen in Pardubice district (northeastern Bohemia), Frýdlant district (northern Bohemia), and near the towns of Frýdek Místek and Zlín (northeastern and eastern Moravia). In general, only two main areas of increased V content in moss (southern Moravia and the CZ part of the former Black Triangle I area) should be discussed in details. Large areas of low accumulation of V in moss are situated in south and southwestern Bohemia and in smaller areas elsewhere. Surprisingly, no V hot spot was found in the CZ part of the Black Triangle II area. On about 80% of the CZ area the V content in moss did not exceed 2 86 $\mu g.g^{-1}$. In more details the analytical results are commented in the national CZ moss report (Sucharová and Suchara 2004b: 54–55).

Slovak Republic

The moss analyses found that the V content in moss was in the range of 1.8–25.9 $\mu g.g^{-1}$. In the anthropologically least influenced parts of Europe (Norway) the V concentration in moss is below 2 $\mu g.g^{-1}$ which is by more than 28% lower than the determined average V concentration in moss in SK.

The following areas of high V accumulation in moss are documented in the inserted maps:

1. Southeastern SK (Region of Zemplín and Košice, along the border SK/UA with adjacent region of Užhorod) is the most important hot spot in SK.
2. Along the CZ/SK border western from Brezová, Myjava, Stará Turá centre of production of basic metal, metal products, machinery and equipments in southwestern Slovakia.
3. Large areas of low accumulation of V in moss are situated in central Slovakia: near Martin (region of Považie); near the towns of Svit; Podbrezová (region of Pohronie); southern SK: in the Veľký Krtíš district and Šahy district, in vicinity of magnesite plants in Lubeník, Jelšava, in central Spiš and northeastern SK (Stropkov).

The lowest concentration of V in the moss samples was found in a north part of the Low Tatra Mts. and the High Tatra Mts., Strážovské and the Levočské Mts. In more details the analytical results are commented in the paper (Maňkovská et al. 2003; Florek et al. 2007).

Also the map of V content in leaves of forest tree species in SK (Maňkovská 1996) showed increased V concentrations in several locations in central and eastern SK. The total V contents exceeding 0.8 $\mu g.g^{-1}$ in needles of *Picea abies* were found in the vicinity of magnesite plants in Lubeník and Jelšava, in central Spiš and the High Tatra Mts., and in leaves of *Fagus sylvatica*, *Pinus sylvestris* and *Abies alba* near magnesite plants in Lubeník and Jelšava as well as in central Spiš.

Poland

The level of V shows little variation in mosses from PL; the average concentration of this element was 6.01 $\mu g.g^{-1}$, ranging from 1.92 to 16.6 $\mu g.g^{-1}$ (Table 9). The typical V contents in moss in four investigated provinces in PL are available in Table 16. Among the V4 countries PL showed the lowest V contents in mosses. In the eastern part of PL the content of V exceeded 10 $\mu g.g^{-1}$ only at one locality, in central PL concentrations of that order were not found, in Lower Silesia such contents were found at two localities only and in Upper Silesia, at 5 localities.

	Eastern PL	Central PL	Lower Silesia	Upper Silesia
n	30	27	31	28
Mean	5.02	5.86	5.88	7.35
S. D.	1.902	1.260	2.360	3.136
Minimum	1.92	3.44	2.01	3.01
Maximum	10.18	8.48	10.82	16.63

Table 16. Content of V in moss *Pleurozium schreberi* ($\mu g.g^{-1}$) in four investigated provinces of PL in 2000. (n = number of samples, S.D. = standard deviation).

According to the attached maps, the following areas are characterized by the concentration of V higher than 10 $\mu g.g^{-1}$:

1. Environs of the village of Studzieńczyna in eastern PL.
2. Environs of Wilczkowo and Kliczkowo in Lower Silesia.
3. Żarki, Sikorka, Kuźnia Raciborska, Pludry and Boroniów in Upper Silesia.

Hungary

The moss analyses found that the V content in moss was in the range of 0.40–32.50 $\mu g.g^{-1}$. The mean V content was found to be 4.44 $\mu g.g^{-1}$. The following areas of high V accumulation in moss are documented in the inserted maps:

1. In the central HU, along the river of Danube were revealed two hot spots Dunaujvaros and Szazhalombatta, and a hot spot near Budapest with the lower accumulated amounts of V in moss.
2. In the western part of HU near Varpalota and Oroszlany.
3. Southern HU in intensively agriculturally used lowland in the region Duna-Tisza Koze, Csorna.

c) Identification of potential pollution sources

Czech Republic

Soot particles released during combustion of fossil fuels, industrial dust from metallurgical and engineering works and eroded soil particles from some types of soil covers are In general recognised to be the basic sources of V pollution in CZ. The operation of the following pollution sources can explain the high V accumulation in moss in the above listed hot spots:

1. The brown coal basin is known to be very dusty due to the operation of power plants, the extraction and transport of brown coal, and the operation of several engineering and chemical plants, including an oil refinery.
2. Agrarian southern Moravia suffers from strong wind erosion of arable soil and reclaimed areas after extraction of local lignite. Drilling and operation of oil wells may have increased, e.g., Ni and V deposition loads in the area through increased deposition of soil particles contaminated by crude oil. However, the inserted colour map documenting the fine-scale distribution of V in epixylar *Hypnum cupressiforme* moss in the area (Sucharová et al. 2003) does not show increased V accumulation in moss at sites with the most concentrated oil wells, in the area near Hodonín and Ždánice. Neither nickel nor other element accumulation levels in moss corresponded with the concentration of oil wells in southern Moravia. However, local former extraction of lignite and the operation of a lignite power plant in eastern part of the area contributed through a wind erosion of soil particles and power plant ash to the increased V deposition bioindicated in this district.
3. The western part of central Bohemia is influenced by industrial combustion of fossil fuels in industrial plants, cement and lime kilns, the operation of metallurgical and engineering works and, finally, by activities associated with the operation of the local coal power plant near Mělník and heating plants and waste incinerators near the towns.

The increased V content in moss in Pardubice district in northeastern Bohemia is caused by industrial combustion of fossil fuels in local works and in local Chvaletice coal power plant.

The operation of the Polish power plant in Bogatynia increases V deposition in Frýdlant district and in the Jizerské Mts. in northern Bohemia. Industrial burning of coal and the operation of metallurgical and engineering plants processing stainless steels in these towns can satisfactorily explain the greater accumulation of V in moss near Frýdek Místek, Třinec and Zlín.

The correlation analyses of the V moss analytical results showed that V content in moss was significantly and negatively correlated with the altitude of the sampling plots (r_p = -0.28) and positively correlated with the precipitation amounts (r_p = 0.14).

Slovak Republic

Soot particles released during combustion of fossil fuels and oil combustion, in manufacture of basic metals and fabricated metal product, industrial dust from metallurgical and engineering works and eroded soil particles from some types of soil covers are In general recognised to be the basic sources of V pollution in SK. The operation of the following pollution sources can explain the high V accumulation in moss in the above listed hot spots:

1. Southeastern SK: Region of Zemplín and Košice – border SK/UA (region of Užhorod). Pollutants are associated with the manufacture of metal industry and fabricated metal products in the town of Košice; and operation of the thermal power plants in Košice and Vojany. The coefficients of relative atmospheric deposition load K_F are from 5 to 13. The high concentrations of V were found out at the following affected areas: Michalovce and Trebišov (production of chemicals, wood pulp and paper products and military orders (Strážske); northeastern SK near Stropkov (production of basic metals and metal products). The share of agricultural activities on V emissions in the area is not known. The coefficient of relative atmospheric deposition load K_F is maximally 13 in this area.
2. Along the CZ/SK border western from Brezová, Myjava, Stará Turá, manufacture of basic metal products and fabricated metal products, machinery and equipments in southwestern SK. The coefficients of relative atmospheric deposition load K_F reached values from 8 to 15.2.
3. Large areas of low accumulation of V in moss are situated in central SK: near Martin (region of Považie); near the town Svit (manufacture of chemicals and operation of fibre glass industry); region of Pohronie (Podbrezová – running of metal industry; the plant Petrochema in Dubová - processing of heavy oil); southern SK: in the Veľký Krtíš district and Šahy district – operation of magnesite plants in Lubeník and Jelšava, and in central Spiš -industrial activity metallurgy, nonferrous ores and processing factories.

Poland

1-2. The increased concentrations of V noted in the eastern part of PL and in Lower Silesia can be explained by the operation of electronic, glass-making and ceramic works.

3. In the region of Upper Silesia the increased V level is most probably connected with the tool industry because vanadium is used as an additive to harden metal alloys.

Hungary

1. Operation of an oil refinery in Szazhazhalombatta and metallurgical industry in Dunaujvaros.
2. Effects of running of petrol chemistry in Varpalota, mining activities and industrial combustion of lignite Oroszlany.
3. This lowland with oil fields is mainly agriculturally utilised. However, drilling and operation of oil wells may have increased nickel, vanadium and partly lead deposition loads in the area through increased deposition of soil particles contaminated by crude oil.

d) Appraisal of dangerous effects

Czech Republic

The environmental contamination by V seems to be little dangerous in the current hot spots. However, hot spots with a combination of increased soil and industrial dustiness near deposits of power plant ash and furnace slugs are recommended to be monitored for environmental contamination levels of V and potential health effects. However, in such hot spots a synergic operation of V with other toxic metals and risky elements should be considered. Evaluation of harmful effects of individual elements is difficult in such cases.

Slovak Republic

Mainly two hot spots of increased V concentration in mosses should be taken in account: the industrial area in southeast of SK (Region of Košice and Zemplín) and the CZ/SK border to the west from Brezová.

Poland

The present V level poses a low risk to the environment. However, as the burning of fossil fuels (above all, of petroleum) is the main source of V contamination, one can expect overloading of the environment with vanadium and aggravation of the effects of its synergic action with other metals.

Hungary

Vanadium is counted among highly dangerous elements. Mainly deposition of V bound on depositing particles is most abundant in the hot spots. The bioindicated contamination levels are not extreme high. Washing of hands and raw agricultural products can be a sufficient precaution

4.3.8 Zinc

Symbol	Proton number	Group IUPAC (European)	Oxidative states	Relative atomic weight	Electronegativity (Allred-Rochow)
Zn	**30**	**12 (IIB)**	**II**	**65.38**	**1.66**
	Density ($g.cm^{-3}$)	Melting point (°C)	Boiling point (°C)	Earth crust ($mg.kg^{-1}$)	Human body ($mg.kg^{-1}$)
	7.14	**419.53**	**907**	**73-80**	**33.0**

a) Sources and effects of the element

Chosen characteristics of zinc (Zn) are presented in the introductory table. Naturally occurring Zn consists of five stable isotopes, from which most abundant are ^{64}Zn (49%), ^{66}Zn (28%) and ^{68}Zn (19%). About 21 radioisotopes of Zn are known. Zn does not occur in pure form but it is abundantly present in many minerals, such as sphalerite [(Zn,Fe)S], goslarite ($ZnSO_4.7H_2O$), smithsonite ($ZnCO_3$), hemimorphite [($Zn_4Si_2O_7(OH)_2$)], zincite [(Zn,Mn)O], adamite [$Zn_2(AsSO_4)OH$], willemite (Zn_2SiO_4) and others. In lattices of silicates Zn can replace iron and magnesium Igneous basic rocks contain Zn in the range of 80–120 $mg.kg^{-1}$, while acid rocks contain 20–60 $mg.kg^{-1}$. In sedimentary calcareous rocks is Zn contained at small amount of about 10–30 $mg.kg^{-1}$. The sea and stream waters contain 0.005 $mg.l^{-1}$ and 0.01 $mg.l^{-1}$, respectively. Beneš (1993) reported that the average Zn content in chernozems, cambisols, and luvisols are 96.0; 74.0; and 64.0$mg.kg^{-1}$, respectively in the CZ. The median of Zn content in CZ arable soil is 16.6 $mg.kg^{-1}$ (MZe 1996). Soil organic matter, clay minerals and Fe/Mn/Al oxides easily bind Zn. Natural sources of Zn (35,800 tons per year) include the weathering of minerals in parent rocks, volcanic activities and large vegetation fires.

Zn is essential microelement. More than 200 metalloenzymes included in metabolism of proteins, lipids and carbohydrates require Zn in order to operate properly. Zinc is the structural component of a wide variety of proteins, neuropeptides, hormone receptors and polynucleotides. It is needed for synthesis of DNA, transcription of RNA, regulating gene expression keeping membrane integrity, operation of immune system, for bone and teeth mineralization, etc. The U.S. Recommended Daily Allowance of Zn is 12 $mg.day^{-1}$ for a woman and 15 $mg.day^{-1}$ for a man. Zn is essential for wound healing, digestion, reproduction, kidney and skin functioning, etc. In plants Zn is needed for activity of enzymes, synthesis of chlorophyll, in operation of dehydrogenases, protein degradation and formation of growth agents, etc.

The average Zn content in plants appears to range from 10–100 $mg.kg^{-1}$, grains of cereals have 5–40 $mg.kg^{-1}$, vegetative parts of perennial plants up to 100 $mg.kg^{-1}$. Bublinec (1990) stated that permissible Zn values for conifers are 15–80 $\mu g.g^{-1}$ and for deciduous species 20–80 $\mu g.g^{-1}$. Innes (1995) determined 2–55 $\mu g.g^{-1}$ Zn in two-year-old needles of Picea *abies* and 2–68 $mg.kg^{-1}$ Zn in *Pinus sylvestris*. Tyler (2005) found the respective Zn content in beech leaves, leaf litter, forest floor humus and mushrooms of unpolluted beech forest in southern Sweden 26–30, 36–70, 47 and 36–240 $mg.kg^{-1}$. The average zinc content in foliage of individual tree species in SK forests was found as follow (in $\mu g.g^{-1}$): beech (*Fagus sylvatica*) 41±46, oak (*Quercus robur*) 26±22, spruce (*Picea abies*) 42± 21, pine (*Pinus sylvestris*) 58±44 and fir (*Abies alba*) 57±38. Exogenous Zn was detected in 2.6% of stomata of analysed leaves (Maňkovská 1996).

However, some plants species, e.g., *Arabidopsis halleri*, *Conyza canadensis*, *Helianthus tuberosus*, *Minuartia verna*, *Polygonum lapathifolium*, *Silene vulgaris*, *Solanum nigrum*, *Thlaspi alpestre*, *Viola calaminaria* and others can accumulate Zn at high amounts without observable symptoms of damage (Zhao et al. 2000, Cui et al. 2007). For Zn receiving were observed the highest transfer coefficient for system soil-plant. Total Zn content in world plant biomass was estimated at 9.2×10^7 t (Markert 1992).

Zn is being used for protection against corrosion, in the construction of buildings, in brass and bronze production, and Al, Mg alloys, batteries, etc. Zn compounds are needed for tire and rubber-goods production, pharmaceutical and cosmetics preparations, fertilisers, pigments, rhodenticides (zinc phosphide), etc. The world total Zn production was about 7,241,000 metric tons (2000), and the metal consumption in the CZ was 11,000 metric tons.

Anthropogenic Zn sources are works melting Zn ores, recycling Zn wastes, electroplating works, some chemical plants, etc. Zn is emitted in the atmosphere by burning coal in power stations and industrial furnaces and waste incinerators. Zn is presented in coal at the amount of 200–1,000 $mg.kg^{-1}$, while coal ash has about 60 mg of Zn per kg. In cities, Zn is eroded and washed off from the roofs, gutters, railings, etc. and contaminates drain water and sewage sludge proportionally to the city size. Particles of rubber released by the abrasion of car tires contain Zn as well. Fertilisers and sewage sludge application may introduce Zn into soils.

The mean yearly background wet deposition (bulk) of Zn in southeastern part of CZ was 18 mg.m^{-2}.year^{-1} in 2000, while in industrial areas 200–300 mg.m^{-2}.year^{-1}.
(http://www.chmi.cz/uoco/isko/tab_roc/2000_enh/CZE/kap_22/k_22_3_1_3_html.html).

Zn toxicity for humans appears after the inhalation of Zn dust causing a fever for several days or lung oedema. Alimentary poisoning causes for example vomiting, epigastria pain, diarrhoea and the disfunctioning of the pancreatic gland. Zn may support the growth of cancerous tumours. Chronic toxicity may cause a copper deficiency. The element's toxic symptoms include disturbed sexual development, impaired skin and greying hair. Rare Zn toxicity in plants may appear when the Zn content in dry weighted biomass exceeds 500 µg.g^{-1}. High concentrations of Zn may inhibit Ca, Mg, P input and decrease the yield of plants (Berry and Wallace 1989).

In animals and humans, zinc deficiency results in rapid and marked atrophy of the thymus caused in an immune deficiency. Zn deficiency in the dog, cats and birds most commonly occurs as a skin ailment (zinc responsive dermatitis). Deficiencies of Zn in plants causes the production of abnormally small leaves with necrotic margins, disorders in polymerisation of nuclide acids, disorders of membrane permeability, etc. (e.g., Lindsay 1972). Deficiency of zinc inhibits growth, causes pale-green coloration of older leaves and disturbs fructification.

Additional information can be found at the following addresses:
http://www.gsf.fi/publ/foregsatlas/text/Zn.pdf
http://web1.msue.msu.edu/msue/imp/modf1/05209706.html
http://www.frankmckinnon.com/zinc_compounds.htm
http://www.merck.com/mmpe/print/sec01/ch005/ch005j.html.

b) Distribution of Zn content in moss in 2000

Content of Zn in mosses in the Visegrad space was found in the wide range of 9.70–590 µg.g^{-1}. Table 9 gathers basic statistics for analytical results from individual countries.

Distribution of Zn content in mosses in individual countries is depicted in colour classed post map and isopleth map. The following sites of increased Zn accumulation in moss can be seen:

Czech Republic

The content of Zn in moss in CZ ranged between 19.4 and 149 µg.g^{-1}, while the mean value was 39 µg.g^{-1}. Moss from areas little affected through atmospheric deposition loads of Zn typically contains less than 25 µg.g^{-1}.

The inserted maps depict the following Zn hot spots:

1. The surroundings of the town of Příbram in southwestern part of central Bohemia.
2. Brown coal basin and the neighbouring of the Krušné Mts., with local hot spots near Teplice and Chomutov in western Bohemia.
3. The industrial part of the northeastern Moravia, with a local hot spot near Frýdek Místek.
4. Several isolated sampling plots scattered mainly in northern Bohemia and in central Moravia.

Relatively low Zn deposition loads were bioindicated throughout the remaining parts of CZ. On about 85% of the CZ territory the Zn content in moss did not exceed 50 µg.g^{-1}. A new definition of the content classes for Zn are being introduced in the European monitoring programme because Zn contents in moss in Europe has been dramatically diminished recently and the current classification classes do not enable to recognize distribution of Zn in moss for common Zn contents.

In more details the Zn distribution in moss in CZ is discussed in the national moss survey 2000 (Sucharová and Suchara 2004b: 56–57).

Slovak Republic

The concentration of Zn in moss in SK ranged between 9.7 and 159 µg.g^{-1}, while the mean value was 57 µg.g^{-1} (Table 9). Moss from areas little affected through atmospheric deposition loads (Norway) of Zn typically contains less than 36 µg.g^{-1}.

The inserted maps depict the following Zn hot spots:

1. The surroundings of the town of Podbrezová in central part of Slovakia (region Pohronie) and region Lučenec, Gemer, Spiš and region Košice.
2. The industrial part of the northeastern Slovakia with a local hot spot near Trstená (SK/PL border).
3. Several isolated sampling plots scattered mainly in western SK (Púchov, Myjava, Martin, Považská Bystrica, Piešťany and Nováky).

The lowest content of Zn in moss samples was found in the Levočské and Strážovské Mts., the Vtáčnik Mts. and surprisingly, also in the Krupinská Plain. In more details the Zn distribution in moss in SK is discussed in the paper (Maňkovská et al. 2003 and Florek et al. 2007).

The moss results are supported by the results of determination of Zn content in leaves of woody species in the SK forests (Maňkovská 1996). In leaves of forest tree species Zn content exceeded 45 µg.g^{-1} in one half of the SK territory. However, still higher concentrations were detected in needles of *Picea abies* in Horná Nitra and

Žiar basin, in the Lubeník-Jelšava area and in a southern part of the Low Tatra Mts. as well as in leaves of oak *Quercus robur, Fagus sylvatica, Pinus sylvestris* and *Abies alba* in central Spiš.

Poland

The average content of Zn found in mosses collected in PL was 61.6 $\mu g.g^{-1}$, which is similar to values noted in other V4 countries. The range of Zn concentrations were rather wide, amounting to 28.4–590 $\mu g.g^{-1}$. The lowest average Zn concentration was found in mosses originating from the eastern part of PL (36.4 $\mu g.g^{-1}$). In central PL and Lower Silesia the respective average concentrations were slightly higher and similar, 44.8 and 44.3 $\mu g.g^{-1}$. In the region of Upper Silesia the content of Zn in moss was thrice higher (124.0 $\mu g.g^{-1}$) in comparison to the previous regions (Table 17).

	Eastern PL	Central PL	Lower Silesia	Upper Silesia
n	30	27	31	28
Mean	36.4	44.8	44.3	124.0
S. D.	6.188	33.073	9.286	110.764
Minimum	28.4	30.3	29.0	45.1
Maximum	57.5	208.1	72.2	589.9

Table 17. Content of Zn in moss *Pleurozium schreberi* ($\mu g.g^{-1}$) in four investigated provinces of PL in 2000. (n = number of samples, S. D. = standard deviation).

In accordance with the inserted maps the following areas of the highest Zn concentration in mosses are listed:

1. Region of Miasteczko Śląskie.
2. Environs of Olkusz.
3. Central part of Upper Silesia.

Hungary

The Zn content of moss in HU ranged between 24.5 and 152 $\mu g.g^{-1}$, while the mean value was 55.8 $\mu g.g^{-1}$. Moss from areas little affected through atmospheric deposition loads of Zn in northern Scandinavia typically contains less than 25 $\mu g.g^{-1}$.

The inserted maps depict the following Zn hot spots:

1. The southeastern part of the mountains in northern HU (Miskolc, Ozd, Salgotarjan).
2. In the central part of HU near Budapest, Szazhalombatta and Dunaujvaros and Alsonemedi.
3. Tatabanya and Varpalota in the Dunantul mountains.
4. Izsak and Csorna in the Duna-Tisza Koze lowland.
5. Oroszlo in the southern HU (the Mecsek Mts.).

c) Identification of potential pollution sources

Czech Republic

Zn and its compounds can be released easily into the environment, where they are very mobile. However, the crucial Zn pollution sources in CZ that affected the hot spots said above can be reliably identified:

1. The local Zn hot spot in Příbram was surely caused by the operation of the local secondary lead smelter, which also produces non-ferrous alloys.
2. Brown coal basin in western Bohemia suffers from abundant aerosol deposition originating in the operation of local power plants, coal burning in industrial and heating plants, municipal wastes in incinerators, chemical and engineering works. Zn-bearing aerosols are released in built-up areas from galvanised sheets, and also by cars.
3. Northeastern Moravia has been under the influence of abundant dust deposition from the metallurgical and engineering works concentrated in this area, industrial burners, and incinerators combusting municipal wastes. High density of built-up area increases the Zn content in local atmospheric deposition in the area.
4. Small areas affected by high local Zn deposition level may be influenced by increased dustiness from local heating stations (central Moravia), activities associated with a large building site, dustiness from heaps near former steel works and engineering centres (e.g., Kladno and Liberec). They may be due to increased exposure to atmospheric deposition in geomorphologically exposed sites, such as the Červenovodské Saddle mountain saddle.

The important sites of the current accumulation of Zn in moss is the CZ part of the Black Triangle II and Black Triangle I areas and the surroundings of the secondary lead smelter in Příbram. Correlation analysis of the analytical data showed that the Zn content in moss correlated significantly and negatively with the altitude of the sampling plots (r_p = -0.25) and significantly and positively with the precipitation amount (r_p = 0.33).

Slovak Republic

Zn and its compounds can easily be released into the environment, where they are very mobile. In the foliage of forest tree species Zn concentration exceeded 45 $\mu g.g^{-1}$ in one half of the SK territory. However, still higher concentrations were detected in Horná Nitra and Žiar basin, in the Lubeník-Jelšava, area and in southern part of the Low Tatra Mts. as well as in central Spiš (Maňkovská 1996). However, the crucial Zn pollution sources in SK that affected the hot spots said above can be reliably identified:

1. The local Zn hot spot in Podbrezová was surely caused by the operation of the production of basic metals and metal products (region Pohronie – southern part) and the hot spot went on into southern part of this region Lučenec, Gemer, Spiš (production of other non-metallic alloys and products) and towards the region Košice (operation of steel works and engineering centres).
1. The industrial part of the northeastern SK with a local hot spot near Trstená (manufacture of electrical and optical equipments) and in the vicinity of the SK/PL border. The latter site may be affected by deposition of Zn originated in close Polish emission sources.
2. Several isolated sampling plots scattered mainly in western SK (the local hot spot near Púchov is caused by an operation of rubber industry, near Myjava, Martin, Považská Bystrica and Nováky operates chemical industry)

The average values of Zn contents in moss in the 1990 and 2000 in SK show a decrease in mean by about 67% in 2000 in comparison with 1990. The main reason is a restructuring of industry, and introduction of sophisticated technologies in smelters. For more details see Maňkovská (1997) and Maňkovská at al (2003).

Poland

1-3. In all three areas listed above, the main reason of increased Zn accumulation in mosses was industrial emissions originating mainly from the metallurgy processing zinc and lead, as well as emissions generated by numerous coal power plants. The distribution pattern of Zn contents in mosses corresponds well with the spatial pattern of Zn emissions in Poland (Table 2).

Hungary

Zn is widely used in both the steel and non-ferrous metallurgy and in production of corrosion resistant compounds and Zn electroplated wheels for a car industry. Substantial Zn amounts are detectable in cement and chemical fertilizers, too.

1. The metallurgical, build and engineering industries operating in northeastern HU may cause the elevated Zn content in the moss samples.
2. In central HU there are located metallurgical and engineering works and oil and coal burning heating plants. Oil refinery and petrol chemistry operate there as well. The high building density in this area increases the Zn content in local atmospheric deposition.
3. Coal burning in industrial and heating plants affects the Dunantul region. Metallurgical plants operate in Varpalota.
4. Locally increased Zn contents in moss from the lowland may reflect the usage of chemical fertilizers in agricultural plantations.
5. Small areas affected by high local Zn deposition level may be influenced by increased dustiness from local heating stations (Pecs) and engineering works.

d) Appraisal of dangerous effects

Czech Republic

The bioindicated environmental loads of Zn do not present high health danger in the Zn hot spot except in Příbram. The latter site suffers from high deposition loads of other heavy metals from the smelter and elements released from utilised stones from former uranium pits. High deposition loads and synergic effects of many toxic and harmful elements are expected in this hot spot. The current environmental and health monitoring is highly recommended.

Slovak Republic

The contamination by Zn is usually related to operation of the nonferrous and ferrous metals industries (~ 60%). Secondary main source of Zn emissions is combustion of coal and oil. Relative considerable input of Zn was observed to soil covers in the hot spots. The bioindicated environmental loads of Zn do not present high health danger in the SK hot spots except for Podbrezová in southern part of Pohronie, southern part of the region Lučenec, Gemer, Spiš and southern part of the region Košice.

Poland

Except for the area being under the direct influence of emissions from the metallurgical industry (mainly Upper Silesia and the area situated eastern), this metal does not pose the environmental risk in PL. An excess of zinc in organisms is considered as one of the causes of cancer. In addition, in areas heavily contaminated by metals, such as Lower and Upper Silesia, it may pose a threat resulting from synergic reactions with other elements. Therefore, the monitoring of Zn should be performed in these areas on a regular basis.

Hungary

Zn is highly mobile in the environment. The substantial cause of the hot spots is increased deposition loads of industrial and soil dust. Jeopardy of intoxication through the environmental contamination in the hot spots is small. Keeping of common hygienic rules can be recommended as a sufficient prophylactic step.

4.4 Correlation and cluster analyses

a) Correlation analysis

Simple correlation matrix for the contents of 8 elements determined in the moss samples in all countries is presented in Table 18. The correlation analysis shows the following results:

Czech Republic

In the CZ moss samples the contents of all 8 elements are significantly and positively correlated at the level $p = 0.01$. However, the correlations are rather weak ($r < 0.50$) or medium ($r = 0.50–0.75$). Closer correlation, explaining the relationships in more than 55% ($r \geq 0.75$) was found only for the contents of Cr-Ni and Fe-V. All these elements are emitted from works of metallurgical industry and from furnaces combusting fossil fuels. On the other hand all these elements are litophile. It is hardly to decide, if the CZ moss samples are influenced more abundantly by the atmospheric deposition of industrial sources of pollution or by deposition of soil dust, and in what proportions these two factors affect together.

Slovak Republic

Significant correlation in the contents of 8 elements in the SK moss samples was not found for the following combinations pairs of elements: Cr-Cd, Cr-Zn, Fe-Zn, Ni-Pb, Ni-Zn, Pb-V and V-Zn. For remaining combinations of the element contents there were found significant and positive correlations. At the level $p \leq 0.5$ there was found the correlation for the contents of Cd-Fe, Cd-V, Cr-Cu, Cr-Pb, Cr-Ni, Cu-V and Fe-Pb. However, these correlations were usually weak or medium. Closer correlation ($r \geq 0.75$) was found for the contents of Cr-Ni and Ni-V. Cr-Fe and Fe-V correlation was little bit lower. The correlations for the elements contents in moss in SK were similar to the correlations found for the CZ moss samples.

Poland

In the moss samples from PL there was not found any significant correlation between the contents of the following pairs of elements: Cd-Cu, Cd-Ni, Cr-Cu, Cu-Fe, Cu-Ni, Cu-V, Ni-Pb, Ni-V and Ni-Zn. Significant correlation between Cd and V contents was found only at the level $p = 0.05$. For remaining 17 combinations of elements pairs there were found significant and positive correlations. However, these correlations were rather weak or medium except for Cd-Zn ($r = 0.82$).

Hungary

Contents of elements in the HU moss samples did not show significant correlations for element combination pairs: Cd-Cu, Cu-Pb, Cu-Ni, Cu-Pb, Cu-V, Fe-Pb, Ni-Zn, Pb-V, Pb-Zn. In five combination pairs the contents of elements correlated only at the level $p = 0.05$ (Cd-Ni, Cr-Cu, Cu-Fe, Fe-Ni, Pb-Zn). Only twelve combinations of elements contents showed significant and positive correlations. Relative close correlations were found between Cr-Ni ($r = 0.89$) and Ni-V ($r = 0.81$) contents, while for the remaining elements contents the correlation was weak or medium. Closely correlated elements belong to typical litophile elements. That may indicate that the moss samples had been affected rather by soil dust than the deposition of pollutants originated in some industrial sources of pollution.

All V4 countries

Content of all 8 elements for the total set of 499 moss samples showed significant ($p < 0.01$) and positive correlation for all combination pairs of elements contents. Relatively close correlation ($r > 0.75$) was found for Cd-Zn and Cu-Fe contents in the moss samples. However, the total results are affected mainly by the elements contents in the CZ moss samples, for which significant correlations were found for all elements contents, and the CZ samples represent 50% of all samples of the V4. That is the reason the correlations mentioned above might be misleading. The relationships in elements contents in moss must be interpreted for individual countries independently.

b) Cluster analysis

The results of cluster analysis for elements contents in the moss samples from the individual countries and for all samples of the V4 countries are presented in Figures 1–3. Correlation coefficients (r) were used as distance measures of similarity in the elements contents variability and the Ward´s method was used as an amalgamation rule to gather elements according to similar content variability.

Czech Republic

Figure 1 (on the left) shows the results of cluster analyses of elements contents for 8 toxic elements in the CZ moss samples. The figure shows four couples of elements representing four individual clusters of two elements. The most similar variability in the moss samples was found for V and Zn contens. Very similar values showed the contents of Ni and Cr. Less similar was the content of Pb and Cd, and Zn and Cu contents were not similar. No wonder that these four couples of elements reached the highest correlation coefficients (see Table 18). Two pairs of elements have a tendency to be gathered in a larger cluster (Ni, Cr, Zn, Cu) indicating very similar variability of these elements in the moss samples. V and Fe join this cluster. It has more different variability in the moss samples. However, the most different variability in content showed Pb and Cd. It is difficult to interpret properly the reasons of such behaviour of given elements. The latter (Pb and Cd) are typical chalcophile elements emitted mainly from non-ferrous smelters in CZ. However, in the remaining cluster are combined both the typical chalcophile elements emitted mainly from smelters (Zn, Cu) and typical litophile elements (Cr, Fe, Ni, V) mostly associated in CZ with wind erosion and spreading of soil particles.

Slovak Republic

In Figure 1 (on the right) the results of the cluster analysis divided the element content variability in SK in two distinct clusters. The elements Ni, Fe and V and Cr forming a cluster are very similar in variability of their contents in the moss samples. The remaining elements Pb, Cu and Zn and Cd were gathered in a second cluster. In case of the SK moss samples, it is evident, that the typical litophile elements joined in the first cluster are associated mainly on soil particles and their contents in moss may rather reflect soil dustiness than effect of industrial emission. In contrary contents of the elements from the second group of chalcophile elements may be rather associated with metallurgical emissions than other sources.

Poland

Figure 2 on the left depicts the result of cluster analysis for element contents in the moss collected in PL. Two groups (clusters) of elements can be seen in the tree diagram. The contents of Zn and Cd are most closely correlated and Pb and Fe are joined with them. All these elements join a relatively compact group of elements. Their content in the PL moss can be caused by deposition of emissions from metallurgical pollutions sources, in case of Fe in combination of industrial and soil dust particles. Remaining elements are formed in a loose cluster. In this cluster the contents of V and Cr are more closely correlated (but less than contents of all elements included in the former cluster). Ni content correlates with the content variability of V and Cr, while Cu correlates the weakliest. The variability of Cu and Ni contents in the moss samples seem to be the most different, and it is caused probably by the operation of a few dominant (industrial) Cu and Ni sources.

Hungary

The cluster analyses of the HU analytical results showed (Figure 4 on the right) that two groups of elements could be recognized by the similarity of the element content variability. The contents of Fe and Cr were the most closely correlated while V and Ni contents were less correlated. These elements may belong to litophile elements taken up by moss mostly from soil particles. The variability of these elements is far from similar with the variability of Cd contents. Why the Cd content resembles the contents of litophile elements is not clear. Industrial sources of Cd may be situated in the areas with high soil dustiness. The said elements (Fe, Cr, V, Ni and Cd) form the first cluster. The remaining elements (Zn, Cu and Pb) create a loose cluster where Zn and Cu contents show the closest correlation. The contents of these elements may reflect distribution of industrial deposition loads. However, the variability of Pb content is different due to the effects of additional sources, such as combustion of coal and leaded petrol.

All V4 countries

Results of the cluster analysis for element variability of all moss samples (Figure 3) divided the elements contents by their variability into two clusters. The first cluster includes rather typical soil elements (Fe, Cr + Ni + V) and the second group rather chalcophile elements (Zn, Cd + Pb + Cd). The contents of elements from the former group may be controlled by the distribution of the deposition of soil particles while the content of elements from the latter group can be controlled by the distribution of the deposition loads of industrial sources of air pollution. Anyway, the diagram in the last figure is the result of heterogeneous contribution of element variability in moss of individual countries with the strongest effect of the CZ analytical results (n = 250).

Czech Republic								
	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
Cd	1.00	-	-	-	-	-	-	-
Cr	0.36**	1.00	-	-	-	-	-	-
Cu	0.42**	0.48**	1.00	-	-	-	-	-
Fe	0.53**	0.52**	0.45**	1.00	-	-	-	-
Ni	0.26**	0.76**	0.55**	0.47**	1.00	-	-	-
Pb	0.69**	0.28**	0.38**	0.42**	0.18**	1.00	-	-
V	0.25**	0.49**	0.56**	0.80**	0.52**	0.28**	1.00	-
Zn	0.62**	0.54**	0.58**	0.46**	0.54**	0.51**	0.36**	1.00

Slovak Republic								
	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
Cd	1.00	-	-	-	-	-	-	-
Cr	0.19	1.00	-	-	-	-	-	-
Cu	0.40**	0.21*	1.00	-	-	-	-	-
Fe	0.21*	0.74**	0.31**	1.00	-	-	-	-
Ni	0.26*	0.64**	0.25*	0.79**	1.00	-	-	-
Pb	0.50**	0.23*	0.63**	0.23*	0.20	1.00	-	-
V	0.26*	0.63**	0.27*	0.73**	0.75**	0.19	1.00	-
Zn	0.35**	0.13	0.61**	0.10	0.08	0.34**	0.10	1.00

Poland								
	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
Cd	1.00	-	-	-	-	-	-	-
Cr	0.40**	1.00	-	-	-	-	-	-
Cu	0.08	0.02	1.00	-	-	-	-	-
Fe	0.63**	0.52**	0.00	1.00	-	-	-	-
Ni	0.17	0.38**	0.18	0.28**	1.00	-	-	-
Pb	0.64**	0.47**	0.45**	0.67**	0.42**	1.00	-	-
V	0.24*	0.39**	0.10	0.44**	0.17	0.27**	1.00	-
Zn	0.82**	0.41**	0.07	0.61**	0.15	0.51**	0.23**	1.00

Hungary								
	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
Cd	1.00	-	-	-	-	-	-	-
Cr	0.40**	1.00	-	-	-	-	-	-
Cu	0.12	0.30*	1.00	-	-	-	-	-
Fe	0.50**	0.89**	0.34*	1.00	-	-	-	-
Ni	0.34*	0.56**	0.19	0.57*	1.00	-	-	-
Pb	0.20	0.14	-0.05	0.04	0.19	1.00	-	-
V	0.53**	0.60**	0.17	0.61**	0.81**	0.26	1.00	-
Zn	0.43**	0.51**	0.44**	0.51**	0.22	0.33*	0.31*	1.00

All V4 countries								
	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
Cd	1.00	-	-	-	-	-	-	-
Cr	0.18**	1.00	-	-	-	-	-	--
Cu	0.24**	0.15**	1.00	-	-	-	-	-
Fe	0.32**	0.75**	0.29**	1.00	-	-	-	-
Ni	0.21**	0.54**	0.26**	0.72**	1.00	-	-	-
Pb	0.49**	0.50**	0.39**	0.49**	0.33**	1.00	-	-
V	0.36**	0.53**	0.33**	0.65**	0.54**	0.48**	1.00	-
Zn	0.76**	0.17**	0.28**	0.24**	0.14**	0.39**	0.28**	1.00

Tab. 18. Correlation matrices for correlations of element contents in moss in individual countries and all V4 countries. Correlation coefficients, * means significant at the level $p = 0.05$ and ** at the level $p = 0.01$. Correlation coefficients $r \geq 0.75$ are marked in bold.

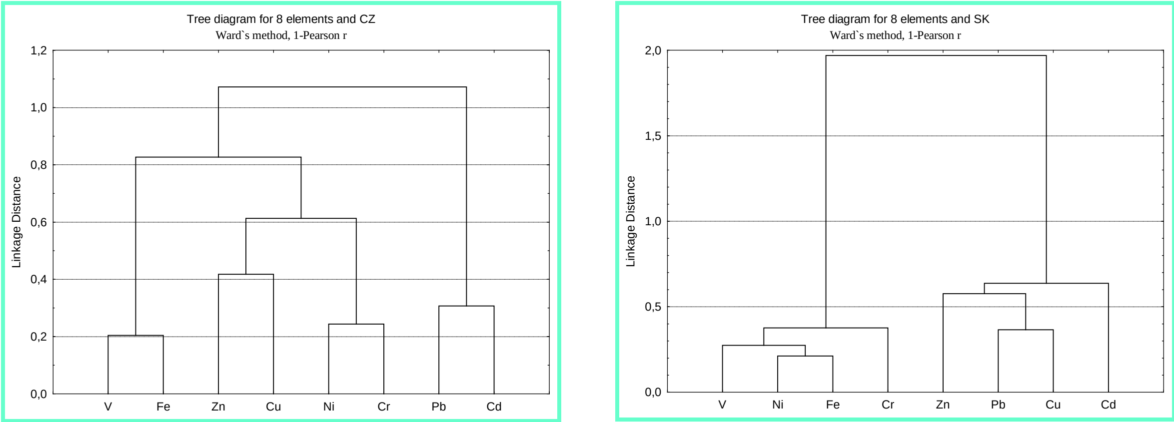

Figure 1. Results of the cluster analyses for contents of 8 elements in the moss samples (n = 250) from CZ (on the left) and in 86 moss samples from SK (on the right).

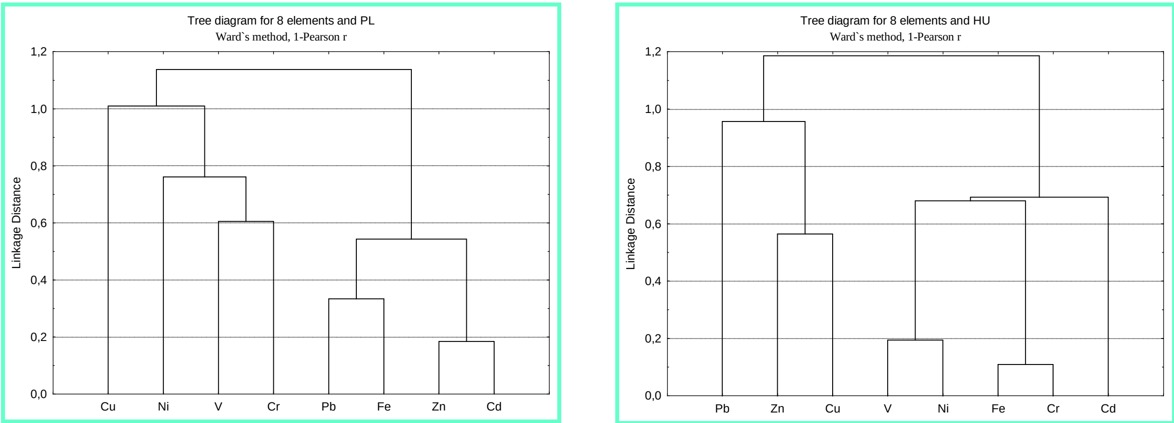

Figure 2. Results of the cluster analyses for contents of 8 elements in the moss samples (n = 116) from PL (on the left) and in 47 moss samples from HU (on the right).

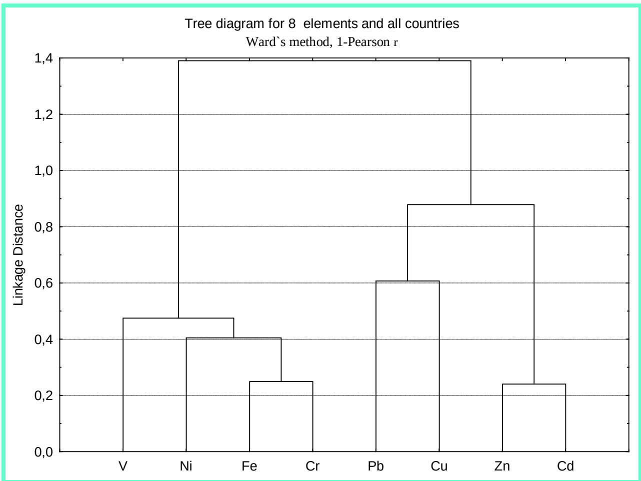

Figure 3. Result of the cluster analysis for contents of 8 elements in moss samples (n = 499) in V4.

4.5 Factors affecting the element content in moss

a) Altitude

Several factors such as geomorphology, local climate, land-use, etc. can influence atmospheric deposition loads of elements and their distribution in mosses. The most common and unambiguously defined variable in all V4 countries is the altitude of the sampling plots. That is why element composition of the moss samples was correlated with the altitude of the sampling plots.

Table 19 provides basic information of mean altitude of sampling plots in individual V4 countries and about the altitudinal variability.

Country	n	Mean	Min.	Max.	Median
CZ	250	479	160	930	460
SK	86	606	170	1285	580
PL	116	183	74	426	159
HU	47	152	66	334	128
V4	499	401	66	1285	370

Table 19. Basic statistics for the altitudinal data of the sampling plots in the individual countries of V4.

Correlations between contents of 8 toxic elements and altitudes of the moss sampling plots in individual V4 countries can be seen in Table 20. About one half or correlations were significant at level $p \leq 0.05$. Nevertheless, approximately only one third of correlations were significant at level $p < 0.01$. Such a correlations are marked (**). Obtained correlations are rather slight or moderately close. Only in one case the correlation coefficient exceeded the value 0.50 (coefficient of determination $R^2 = 0.25$, the altitude can explain maximally about 25 % of variability of the element content in the moss samples). Both the positive and negative correlations were obtained.

In CZ, all significant correlations were negative. With the increasing altitude of the moss sampling plots the content of Cr, Cu, Fe, Ni and V in moss significantly ($p < 0.01$) decreased. The altitude of sampling plots did not significantly affect the contents of remaining elements in the CZ moss samples. The similar relationships were found for the SK territory. With increasing the altitude of sampling plots the content of Cr, Fe, Ni and V significantly decreases ($0.01 < p \leq 0.05$). The altitude of sampling plots did not control the contents of Cd, Cu, Pb and Zn significantly.

Different relationships between elemental composition of mosses and the altitude of sampling plots were proved in PL and HU. Except for Cr and V contents of the remaining elements in moss significantly and positively correlated with the altitude. In contrast to the CZ and SK territories, contents of Cr, Fe, Ni, Pb and Zn, and more Cd in mosses increased with increasing the altitude of sampling plots. In HU, only Ni content in moss significantly ($0.01 < p \leq 0.05$) increased with the altitude. In evaluation of the whole Visegrad territory Cu and V content in moss significantly decrease with increasing or the altitude while for Cr was found the inverse relationship.

However, the variable altitude of sampling plots is covariable operating together with other dependent variables such as precipitation, forest cover, urbanisation, density of industrial sources of pollution, concentration of coarse particles in the atmosphere, etc., which can influence atmospheric deposition in opposite directions. To find the pure effect of the altitude (partial correlation), the effect of the covariables should be eliminated. However, there are not available values for the crucial covariables from individual countries. That is reason why we cannot explain the pure effect of the altitude exactly. For example, partial correlation revealed (Sucharová and Suchara 2004b) that in fact „pure“ effect of the altitude of sampling plots significantly and negatively affected also Cd, Pb and Zn contents in the CZ moss samples.

We could consider, for example, that with increasing altitude in SK and CZ content of coarse particles carrying heavy metals decreases, while in mainly lowlands of PL and HU protruding hills are better targets for atmospheric deposition. Anyway, for some details about effects of the altitude, precipitation and some other explanatory factors controlling the content of elements in the moss samples in CZ see literature (Sucharová and Suchara 2004b, 2004c).

Country	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
CZ	0.00	-0.23**	-0.19**	-0.33**	-0.21**	0.03	-0.25**	-0.06
SK	-0.02	-0.25*	-0.06	-0.24*	-0.27*	-0.20	-0.26*	0.04
PL	0.57**	0.37**	-0.12	0.47**	0.24**	0.49**	0.22	0.48**
HU	-0.03	0.17	-0.17	0.24	0.29*	0.10	0.03	-0.01
V4	-0.07	0.16**	-0.22**	-0.01	-0.10*	0.06	-0.18**	-0.04

Table 20. Correlation of content of chosen elements in moss with the altitude of sampling plots. Correlation coefficients, * significant at level $p < 0.05$, ** significant at level $p < 0.01$.

b) Factor analysis

The factor analysis (Principal Component Analysis, PCA) was applied for 8 elements (Cd, Cr, Cu, Fe, Ni, Pb, V, Zn) in the moss samples collected at all V4 countries. Maximally two factors (F1 and F2) controlling markedly the element contents in moss in these countries could be extracted (screening test). Results of the factor analyses of national and total moss data is available in the following Table 21:

CZ		SK		PL		HU		V4	
$F1_{CZ}$ (3.3%)	Cr, Ni, V	**$F1_{SK}$** (3.2%)	Cr, Fe, Ni, V	**$F1_{PL}$** (3.3%)	Cd, Fe, Zn	**$F1_{HU}$** (2.6%)	Ni, V	**$F1_{V4}$** (3.1%)	Cr, Fe, Ni, V
$F2_{CZ}$ (2.4%)	Cd, Pb	**$F2_{SK}$** (2.4%)	Cu, Pb, Zn	**$F2_{PL}$** (1.6%)	Cu	**$F2_{HU}$** (2.4%)	Cu, Fe	**$F2_{V4}$** (2.3%)	Cd, Zn

Table 21. Results of the PCA for 8 elements in individual countries of V4.

Czech and Slovak Republic

The PCA shows that the extracted factors can explain only about 2–3% of total variability of element content in the moss samples. Only contents of some elements in moss were substantially controlled by these two factors. The variability in contents of the remaining elements could not be explained substantially by operation of the F1 and F2. These factors F1 and F2 in individual countries need not be the same and they surely differ at least in some ways. Anyway, F1 seems to control variability in mainly litophile elements in moss: Cr, Ni, (Fe), V, while F2 controls rather chalcophile elements (Cd, Cu, Pb and Zn) in moss. We can consider that the F1 represents contamination of moss through deposition of eroded soil particles. The F2 may represent deposition of industrial dust and aerosol particles, mainly from metallurgical industry. Fe variability in moss can be controlled by deposition loads of both the soil and industrial particles.

Poland and Hungary

In PL, the F1 may be represented by the operation of F2 (metallurgy) in the remaining countries with an accompanying effect of F1 (soil dust). The $F2_{PL}$ may be the specific factor corresponding to a Cu metallurgy effect, which is specific for PL.

In HU, the Fe content variability in moss together with the Cu content are controlled by operation of the $F2_{HU}$. In the remaining countries the Fe content variability can be substantially explained by operation of the F1. It may be caused by different portion of Fe and other elements in deposited particles (soil and industrial dust). Nevertheless, the correlation analysis (Table 18) showed week correlation of Fe and Cu contents in moss in HU.

The PCA results show a little bit different situation in individual countries. Mainly contents of chalcophile elements were controlled by some factors operating in individual countries. Since some elements are presented both in the pollution of metallurgical industry and in soil covers it is difficult to distinguish the effects of these pollution sources. In order to distinguish portion of contamination of the moss samples through soil dust additional determination of other typical soil elements (e.g., Al, Si, Ti, U) would have been needed.

4.6 Comparison with other countries

Comparison of the average contents of the investigated elements in moss in individual countries of V4 (Table 9) indicates that the lowest accumulation of elements in moss was found at the CZ territory (Cd, Cu, Fe, Pb, V and Zn) and for Cr and Ni in PL. The highest average contents of most of the element in moss were determined in SK (Cr, Fe, Pb and V). In average contents of these elements were 4–5 times higher than in CZ and for Cr even 7 times higher than in PL. The mean content of Cd, Cu and Ni in moss in HU was highest of all V4 countries and reached twofold or triplicate contents than in CZ. The highest mean content of Zn was determined in PL and the mean was 1.6 times higher than the CZ mean. The reason of accumulation the elements in moss is atmospheric deposition of eroded soil and emitted industrial particles as mentioned in the previous chapter.

Table 22 provides information about content of elements in moss in chosen countries in Europe. The comparison of V4 data (Table 9) with the figures in Table 22 shows that there can be seen a decreasing gradient of the element content in moss from the southern Europe (Balkans) through Central Europe to Scandinavia. In the least affected parts of Europe (Arctic Europe) the typical element contents in moss were found 2–5 times lower than the mean element contents in moss from Germany, Austria and CZ, and 5–10 times lower than in SK, HU and Balkan countries. The main reason can be not only increasing amounts of industrial emissions emitted in Central Europe but also decreasing ratio of forest and increasing portion of arable or bare soil covers toward southern Europe.

In spite of an effort to harmonize (standardize) the moss monitoring campaigns in Europe, there operate some factors modifying analytical results under constant atmospheric deposition loads of elements. For example, acrocarpous moss species may uptake elements from soil covers and control partly element contents in plant bodies. Even recommend pleurocarpous mosses can uptake differently effectively atmospheric deposition. For example, moss *Hypnum cupressiforme* accumulates in CZ by 25–50% higher contents of elements than other pleurocarpous mosses occurring at the same plots. Usually, content of elements is increasing with the age of the moss plant segment. Analysis of younger parts of moss gives lower results than analyse of specimens containing old parts of moss plants. Finally, various analytical methods used can provide different results. Total analytical methods give higher results than subtotal methods used digestion of samples. The latter methods provide by 10–40% less contents of elements bound in primary silicates (e.g., Cr, Cu, Fe, Ni, V) and by 50–90% lower contents of hardly dissolved elements (e.g., Al, lanthanides, Sb, U, W, Zr). All these factors should be considered during comparison of results from individual countries.

Elem.	**Germany** *n = 1025–1028* (⊥⊥)		**Austria** *n = 221* (⊥⊥, *)		**Romania** ***n =214* (**⊥⊥), Cd, Pb 21(*)	
	Median	**Range**	**Median**	**Range**	**Median**	**Range**
Cd	0.21	0.07–1.53	0.18	0.08–1.27	0.46*	0.26–1.03*
Cr	0.91	0.41–4.57	0.73	0.25–3.69	8.46	0.50–51.9
Cu	7.14	2.92–25.9	6.13	3.40–-41.0	21.5	2.21–2420
Fe	343	111–2830	409	144–3590	2510	338–21300
Ni	1.13	0.39–5.07	1.26	0.35–7.95	3.35	0.26v31.9
Pb	4.62	1.61–29.4	5.76	1.98–22.6	14.3*	6.45–31.5*
V	1.06	0.15–16.3	1.27	0.38–10.2	7.99	1.93–31.9
Zn	41.0	15.8–23.4	31.5	11.8–11.4	79.5	20.1–2940
Elem.	**Finland** *n = 938* (⊥)		**Lithuania** *n = 138* (*)		**Norwav** *n = 462–464* (⊥⊥)	
	Median	**Range**	**Median**	**Range**	**Median**	**Range**
Cd	0.12	0.01–0.42	0.15	0.09–0.31	0.09	0.01–2.62
Cr	1.06	0.34–9.21	1.27	0.44–4.73	0.69	0.13–25.8
Cu	3.38	1.26–67.7	6.45	3.73–12.3	4.26	1.74–206
Fe	210	51–1950	623	291–2820	365	99–11200
Ni	1.38	0.46–68.8	1.36	0.75–7.08	1.11	0.06–302
Pb	2.96	0.65–10.0	8.25	3.75–22.6	2.70	0.50–27.7
V	1.24	0.17–7.54	3.44	1.88–54.5	1.36	0.28–22.6
Zn	27.6	11.5–88.0	34.5	18.0–87.0	29.4	9.71–661
*Analytical methods used: ⊥ = INAA, ⊥⊥ = ICP-MS/ES, * = AAS.*						

Table 22. Determined content of elements in moss ($\mu g.g^{-1}$) in chosen countries in 2000 (Buse et al. 2003).

4.7 Evaluation and utilization of results

Czech Republic

Distribution of element content in moss reflecting current atmospheric deposition loads of 8 toxic metals shows the following three main hot spots of increased element accumulation in moss: western Bohemia, northeastern Moravia and southern Moravia. The hot spot in western Bohemia is situated in brown coal basin where extracted coal is burnt in industrial furnaces (power plants, metallurgical and chemical plants). The area belongs to the former Black Triangle I area. In lower intensity the hot spot continues to the western part of central Bohemia (Kladno district), where metallurgical industry until the middle of the 1990s operated. Second hot spot in southeastern Moravia is situated in brown coal basin and still many metallurgical and engineering plants operate in this area (Czech part of the Black Triangle II area). The third important hot spot is located in southern Moravia. It is caused by deposition of soil particles of eroded soil covers on Carpathian flysch sediments. The area is relatively dry and percentage of arable or cultivated soil is more than 80 %. This hot spot may operate in adjacent area of southwestern Slovakia and northeastern Austria. This „dusty triangle“ is affected by geogenic and climatic factors. However, deforestation and ploughing the land is work of humans. Of a few more local hot spots the most important are the surroundings of Příbram (secondary lead smelter), cross border area near Frýdlant (operation of the Polish coal power plant near Bogatynia) and northeastern Bohemia between Pardubice and Česká Třebová (area of former operation of engineering and chemical industries). Position of the crucial hot spots of increasing accumulation of 8 heavy metals in mosses is depicted in Figure 4. In these areas monitoring of the health condition of residents and monitoring of the environmental contamination level is desired. The area of these hot spots is not large (Table 23). Figure 4 showes distribution of zones of average deposition loads of 8 elements bioindicated through the element contents in moss. The atmospheric deposition loads in individual deposition zones were classified by the multiple of reference element content in the cleanest part of Europe as follows: lowly loaded areas, medium loaded areas, highly loaded areas and very highly loaded areas (Sucharová and Suchara 2004b: 66). Table 23 provides percentage share of these zones of the CZ territory.

Element	**Reference Arctic Europe**	**Element content limits in moss defining atmospheric deposition loads in CZ**							
Loads	**“Unloaded”**	**Lowly loaded (level 1)**	**%**	**Medium loaded (level 2)**	**%**	**Highly loaded (level 3)**	**%**	**Very highly l. (level 4)**	**%**
Cd	< 0.07	< 0.3	76.3	0.3–0.6	19.9	0.6–0.8	1.7	> 0.8	2.1
Cr	< 0.60	< 1.5	34.5	1.5–4.0	62.1	4.0–6.0	3.1	> 6.0	0.3
Cu	< 4.0	< 6.0	40.4	6.0–9.0	56.1	9.0–12	3.5	> 12	0.0
Fe	< 250	< 500	68.2	500–1250	30.0	1,250–1,750	1.7	> 1,750	0.1
Ni	< 1.8	< 2.0	52.0	2.0–5.0	47.6	5.0–7.0	0.3	> 7.0	0.1
Pb	< 2.5	< 10	91.7	10–25	7.6	25–35	0.6	> 35	0.1
V	< 1.1	< 1.5	45.4	1.5–3.0	51.5	3.0–4.0	2.5	> 4.0	0.6
Zn	< 25	< 50	91.4	50–80	7.6	80–100	0.7	> 100	0.3

Table 23. Defining of zones of atmospheric deposition loads in CZ through element content in moss ($\mu g.g^{-1}$) and % share of CZ influenced by defined deposition loads of given elements.

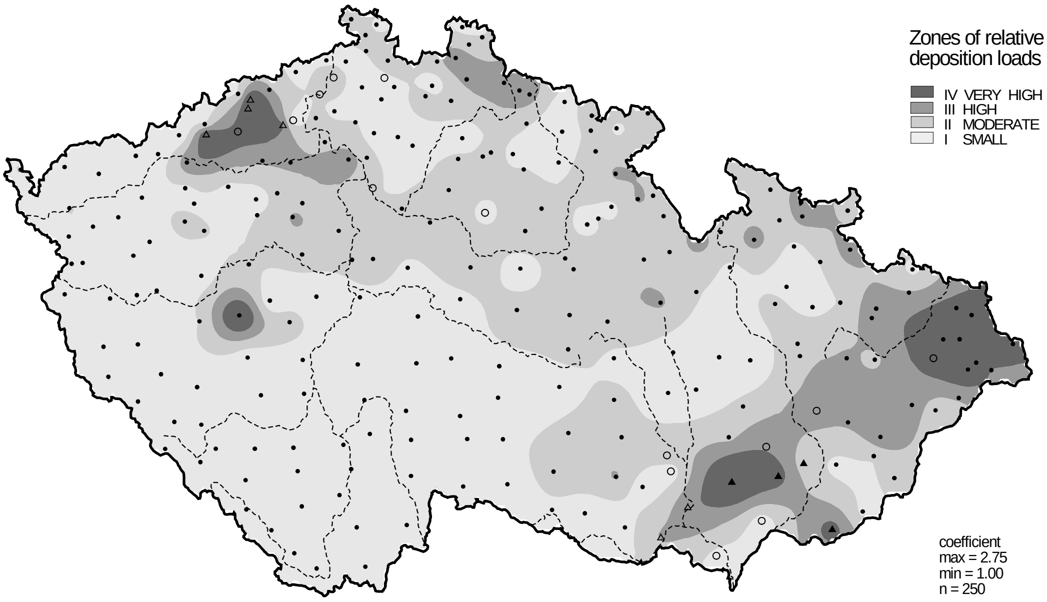

Figure 4. Distribution of deposition zones defined as mean load levels of 8 elements (Table 23) in the CZ territory in 2000. Zone I (mean level <1.35), zone II (1.35–1.69), zone III (1.70–2.05), zone IV(> 2.05). The zone IV mean deposition level >2.05 defines hot spots of increased deposition of 8 toxic metals.

Absolute atmospheric deposition loads of individual elements may be desiderating. In order to count atmospheric deposition levels *D* (µg.m^{-2}.year^{-1}) from the element content in moss *C* (ug.g^{-1}) either annual bulk deposition loads of elements trapped in collectors or efficiency of element uptake by moss *E* (% expressed in decimal terms) and annual production of the moss species *B* (g.m^{-2}.year^{-1}) must be known. Often the formula $D = C.B/E$ (Rühling 1994) is frequently used to assess the bulk deposition from the moss analyses. The uptake efficiency of some elements and moss *Pleurozium schreberi* in the conditions of central Europe are known and moss production in individual climatic regions can be easily determined. The mean production of *Pleurozium schreberi* in CZ was 130 g.m^{-2}.year^{-1} in 2000. The uptake efficiency of some elements by *Pleurozium schreberi* was measured in Scandinavia and in the Switzerland (e.g., Thöni et al. 1996). In order to assess the absolute deposition loads easily, for CZ general (average) coefficient $K_i = B/E_i$ can be introduced. Direct multiplication of the CZ moss element contents by this coefficient gives absolute deposition loads (annual bulk atmospheric deposition) $D_i = C_i.K_i$. The estimation of annual bulk atmospheric deposition of investigated 8 toxic elements is presented in Table 24.

Element	**Coefficient K_i**	**Bulk fall-out median**	**Bulk fall-out minimum**	**Bulk fall-out maximum**	**Element**	**Coefficient K_i**	**Bulk fall-ot median**	**Bulk fall-out minimum**	**Bulk fall-out maximum**
Cd	*181*	0.042	0.016	0.406	**Ni**	*283*	0.552	0.157	2.91
Cr	*217*	0.408	0.083	1.66	**Pb**	*130*	0.736	0.235	6.27
Cu	*283*	1.85	1.04	3.31	**V**	*221*	0.336	0.127	1.30
Fe	*217*	87	38	404	**Zn**	*153*	5.36	2.97	22.8

Table 24. Estimation of the bulk atmospheric deposition of chosen elements (mg.m^{-2}.year^{-1}) in CZ in 2000.

However, the comparison of atmospheric deposition loads determined through analyses of bulks trapped in collectors at measuring stations with the deposition loads estimated from the element content in moss in given area showed considerable differences for some elements or measuring stations (Sucharová and Suchara 2004b: 69–71). The moss production at the individual sampling plots can differ markedly from the assessment of the mean moss production introduced for the whole CZ territory. Determination of the production at all sampling plots is impracticable. More correct estimation of wet deposition of the elements through the moss analysis is being in progress in CZ.

Data of the former CZ moss surveys showed continual decreasing of element content in moss since 1991. A high decrease of element content in moss between 1991 and 1995 was recorded in Bohemia (western part of CZ) for Cd, Cr, Cu, Fe, Ni, Pb, V and Zn 16, 39, 24, 54, 50, 44, 65 and 23 %, respectively. The bio-indicated decrease in atmospheric deposition loads of all elements was significant (Sucharová and Suchara 1998: 109). This diminishing of atmospheric deposition levels was caused in CZ after political and economical changes in 1990 mainly by cancelling and selling of the most of state industrial plants and declaration of restructuring the industry in CZ. The decreasing accumulation of metals in moss went on between 1995 and 2000. In the moss samples repeatedly collected at the same 155 sampling plots mean the contents of Cd, Cu, Fe, Ni, Pb, V and Zn decreased by 26, 12, 0.7, 11, 55, 29 and 23 % in this period (Sucharová and Suchara 2004b: 74). Nevertheless, content of Cr increased by about 10 %. These changes in the elemental contents were significant at least at level of $p = 0.05$ except for Cr and Fe.

The distribution of the elements in moss in CZ indicates that the atmospheric deposition levels may be controlled through some environmental factors. Partial correlation between the altitude of sampling plots and element contents revealed that the "pure" effect altitude is significantly negative on the accumulation of Cd, Cr, Cu, Fe, Ni, Pb, V and Zn may be the result of decreasing density of industrial sources of pollution with the altitude in CZ.

The precipitation amounts correlated significantly and positively with the altitude. However, the contents of Cd, Cr, Cu, Fe, Ni, Pb, V and Zn in moss correlated significantly and positively with the biennial amounts of precipitations. The reason may be increased deposition speed of atmospheric deposition loads of elements during the rain episodes.

Surprisingly, no significant effect of geomorphology (protrusions, depressions, plains, orientation of slopes to the cardinal points) was determined on accumulation of the elements in moss in CZ. On the other hand, the land-use (percentage of forests, arable soil and build-up area) in a 5-km radius around the sampling plots controlled significantly the element contents in moss. The increasing forest cover significantly decreased content of litophile elements Cr, Fe and V. The increasing distance of the sampling plots from the forest boundary decreased content of these elements in moss (boundary effect, important filtering effect of larger forests). No significant effect of forest abundance in the landscape was found for Cd, Cu, Ni, Pb and Zn accumulation in moss. Forests protect probably local soil covers against wind erosion while the effect of forests to filter long-range transported fine industrial aerosols is much lower in CZ. The correlation of element content in moss with the percentage of the area of arable soil is in opposite to the correlations with the forest cover area. Increasing area of urbanised plots (including villages) in the surroundings of the sampling plots significantly increased accumulation of Cd, Cr, Cu, Fe, Pb and Zn in mosses due to locally increased combustion of fossil fuels, running of cars and operation of some industrial works. Increased accumulation of Ni and V near the settlements was not significant. Either no significant effect of bedrock types of the sampling plots on elemental composition of moss was determined. Six categories of rock types of similar chemical composition were introduced. Any element content in moss has not correlated significantly with these bedrocks types. Nevertheless, we believe that locally in southern Moravia and elsewhere the moss samples may be affected by the deposition of soil particles from soil covers of the local bedrock.

Efficiency factors show the difference in the proportionality of normalised element composition in moss against the normalised element composition of the surroundings matrices (humus, soil, bedrock). The element content in moss was compared with the Earth's continental crust. Aluminium was used as a normalizing element. The efficiency factors (EF) showed that the content of Cr, Fe, Ni, and V in moss corresponded with the content of these elements in the continental crust. However, EF for Cu, Pb and Zn were 50-85 and for Cd even 400 in *Pleurozium schreberi* in CZ indicating significant accumulation of these elements in moss due to anthropogenic activities. Anyway, in the hot spots the EF need not be the highest. Surprisingly, in the hot spots in southern Moravia and in the brown coal basin in western Bohemia the EF in moss was often low.

Additional details can be found in the CZ national moss survey 2000 (Sucharová and Suchara 2004b).

Slovak Republic

The map of the sampling sites is shown in the inserted map and in Figure 5. Concerning fixation of moss species (*Pleurozium. schereberi, Hylocomium. splendens* and *Dicranum* spp.) in forest ecosystem, it was possible only marginal pattern of other important pollution sources (Thermal power plant Zemianske Kostoľany and Vojany), because of the occurrence of the moss bio-indicators largely in coniferous forests the distribution of the sampling plots could not cover the whole SK territory, and hence effects of some pollution sources might be not indicated). The Danube and the East Slovak lowlands were almost uncovered by the sampling plots. The area affected by emissions from the oil plant Slovnaft was additionally included into the biomonitoring programme to find the effect of oil industry on the environment. In Figure 5 the SK sampling plots are arranged into groups I. - X. Specific effects of dominant industrial pollution sources characterize each group of the plots. Correct identification of the pollution sources affecting these plots is difficult due to an overlapping of their deposition fields and modification of the local atmospheric deposition by other anthropogenic activities (land-use, local municipal activities, etc.).

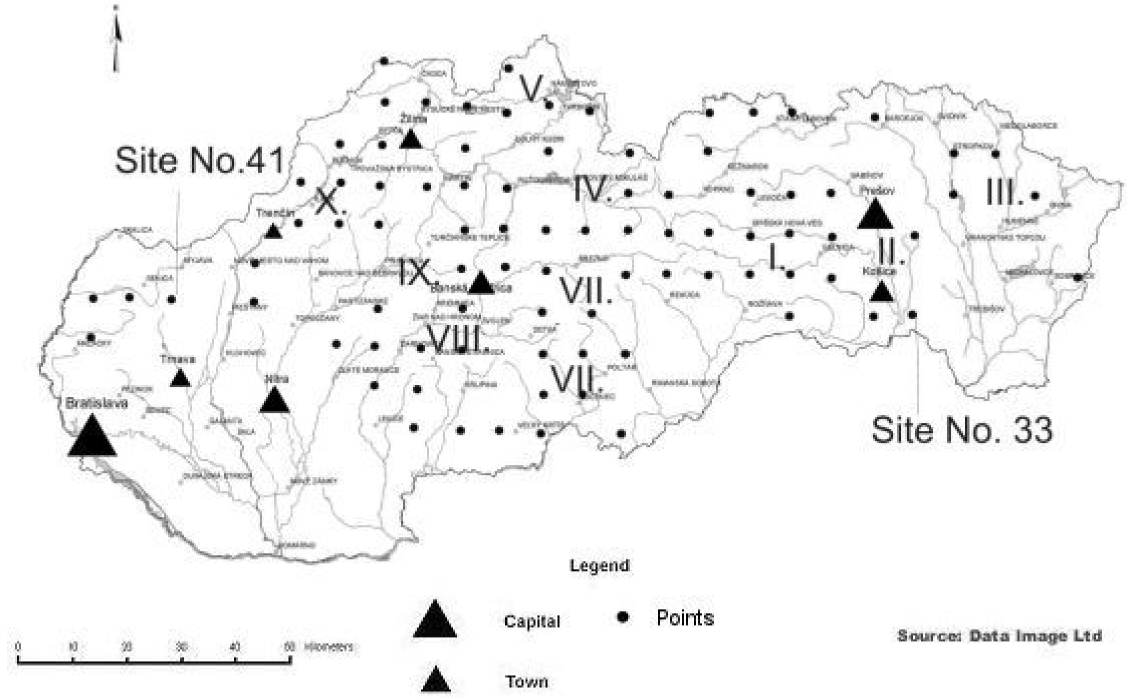

Figure 5. Distribution of the sampling plots and atmospheric deposition zones (cadastres) I-X in SK.

The total concentrations of 44 major and trace elements including the investigated 8 toxic metals were determined in 86 samples of mosses. For each element the mean, median, and range values were determined. These results are available in Table 9.

Comparison the element content in the SK moss samples with the element content in moss from a pristine area in Norway indicates considerably deposition loads of the most elements in SK. These bio-indicated atmospheric deposition loads (factors) in SK for 8 toxic elements are available in Table 25. These factors were evaluated through the coefficients of the relative deposition loads K_F. The value of the coefficient was counted as the ratio of the median value of element in the SK moss samples C_{iSl} and the median values of element contents in the Norwegian moss samples C_{iN} . The medians for the Norwegian moss samples were used from Steinnes et al. (2001)

$$K_{Fi} = \frac{C_{iSl}}{C_{iN}}$$

The median values of element contents for the SK moss samples in 2000 were for Cd, Cu and Pb lower approximately by 50 %, for Zn even by about 70 % in comparison with the respective medians in 1991 (Maňkovská, 1997; Maňkovská et al.2003). During the same period elements contents of Ni and V increased by about 50 %. Contents of Fe in moss did not show any significant change. The decrease in the concentrations of Cd, Cu and Pb are connected with a reduction of production of steel and non-ferrous metals in SK and with ceased distribution of leaded gasoline. The reason of the bio-indicated deposition loads of Ni and V is gradually growing of heavy oil combustion.

Relative atmospheric deposition factor K_{Fi}				
< 1	**1–2**	**2–5**	**5–10**	**> 10**
-	Ni, Zn	V, Cr, Fe, Cu,	Pb	Cd

Table 25. The ratio of medians for 8 element contents in the SK and Norwegian moss samples (K_{Fi}) in 2000.

Some bio-monitoring results related to the air pollution in SK are shortly discussed for chosen elements:

Cadmium

High Cd contents in moss were found almost on all SK territory, mainly around Košice (manufacture of basic metals and fabricated metal products), Štiavnické Mts., where is a long tradition of ore mining and in Orava region, which is affected by non-ferrous metal industry. Low levels values were found in the Low Tatra Mts.

Chromium

Relative enhanced concentrations of Cr were located also in the surroundings of the magnesite works (Lubeník – Jelšava). Elevated content of Cr was found near the Ferro-alloys works (Orava), works for metal chromium plating (Považská Bystrica), the town of Martin (manufacture of machinery) in the zone II (Snina – Stropkov -Strážske (manufacture of chemicals, chemical products, pulp and paper products), in surrounding town Svit and Ružomberok (zone IV) with chemical and pulp manufactures. Low levels values were found in the Low Tatra Mts. and the Krupinská vrchovina Mts.

Copper

About 75 % of Cu emissions come from metallurgy of nonferrous metals industry (Burda 1999), and ores reworking facilities surroundings of Krompachy, Gelnica, Slovinky (zone I) and Hnúšťa-Ľubeník-Miková (zone VII with magnesite ores and reworking facilities). High local value of Cu we found near town Martin (metal working factories).

Iron

High Fe contents in the moss were observed most frequently at the sites affected by the operation of Factor 1 (see later). In addition to area Snina-Stropkov, Košice and Martin as well as Dubnica (various metal-working industry) show elevated Fe level. Median value for Fe is considerably higher in SK than in neighbouring countries (Austria, Czech Republic and Poland).

Lead

Increased concentrations of Pb are related to soils of mineralised zones, areas where ore and smelters processing facilities (of base metals) were situated. Mainly the Volovské Mts were affected (deposition zone I) and the area near Banská Štiavnica (zone VIII), Kysuce and Lubeník-Jelšava-Poltár. Elevated Pb content was found in the area of the Pb-mine Lovinbaňa (zone VII).

Nickel

The median concentration of Ni in SK mosses (3.2 $mg.kg^{-1}$) is higher than in neighbouring countries (1.26 –2.06 $mg.kg^{-1}$). High correlation ($r = 0.8$) with Al, Sc, Ti, V, Fe and Co can be noted. Association of Ni with these elements indicates a dominant effect of the geochemistry on Ni accumulation in moss (Košická basin and around the old mining districts). Relatively high Ni contents in moss appeared at sites near Petrochema Dubová, towns Dubnica and Svit, Košice, Strážske (associated with the industry), around towns Lučenec-Poltár-Fiľakovo (engineering industry) and at sites in Northern Slovakia – transport from Poland. Crucial sources of Ni (> 60 %) in SK are burning of fossil fuels and automotive gases (Burda 1999).

Vanadium

The highest values in moss were observed in the vicinity of the industrial towns of Jelšava-Ľubeník-Rožňava. Higher V contents were observed in the surrounding of Martin (manufacture of machinery and equipment) and Lučenec-Poltár-Fiľakovo, Košice and Martin (engineering industry), Strážske and Svit with chemical and glass fibre industry (deposition zone IV). Probably the main source of V is a great incineration of wastes.

Zinc

The contamination by Zn is usually related to emissions of non-ferrous and ferrous metals industry (about 60 % of total Zn emissions in SK). Secondary main sources are combustion of coal and oil. Relative considerable input of Zn to moss is through atmospheric dust transport. High concentrations of Zn were observed in the vicinity of Martin, Piešťany, Košice, Banská Štiavnica, Podbrezová and area of Kysuce and Orava.

There were found 11 areas in SK where contentsof the 8 toxic elements in moss exceeded the median content twice at least. These areas and elements highly accumulated in moss are listed in Table 26. Marking of an element in bold indicates that this element reached absolutely maximal content in moss in this area. Localities Brezová pod Bradlom (site 41) and Slanec (site 33) are listed individually. The first locality is known by the geogenic anomaly in element contents (specific rock composition). The latter locality is heavily affected by extraction and grounding of rock.

Area	Location	Accumulated in moss	Area	Location	Accumulated in moss
I	Central Spiš region (Volovské Mts.), industrial activity metallurgy, nonferrous ores and processing factories	V, **Cr,** Ni, **Fe, Ni, Cu, Zn,** Cd, Pb	VIII	Kremnicko-Štiavnické Mts. (non-ferrous ores and smelters, old mining districts)	V, Ni,Cd,
II	Region Košice-Prešov (manufacture of basic metals and fabricated metal products)	Cr, **Zn,Cu,** Zn, **Cd, Pb**	IX	Horná Nitra and Martin (thermal power stations, manufacture of machinery and equipment).	V, Cr, **Ni,** Zn, **Cd, Pb**
III	Snina-Stropkov-Strážske (manufacture of basic metals and fabricated metal product, chemical products)	V, Cr, Ni, Cd	X	Kysuce and Považská valley (engineering and instrument industry, glass, tire and rubber industry (Small Black Triangle)	V, Cr, Ni, Cd
IV	Ružomberok-Svit (pulp, paper products, chemical and glass fibre industry).	V, Cr, Ni,		**Anomalous zones**	
V	Orava (ferro-alloys smelters, fabricated metal product)	Zn,	Site 41	Brezová pod Bradlom (geogenic anomalous zones)	**V**, Cr, Fe, **Ni**, Zn,
VI	Jelšava-Lučenec-Poltár (magnesite works, glass-ceramic production)	V, Cr,**Ni,** Pb	Site 33	Slanec (output and crumbled of stone)	V, Cr, Fe, Ni
VII	Detva-Brezno (manufacture of basic metals and fabricated metal products)	**Zn,** S			

Table 26. Areas in SK where element content in moss exceeded the related SK median twice at least.

The total pollution coefficient Z_i was calculated for all sampling sites to identify the most heavy metal polluted areas:

$$Z_i = \frac{1}{n}\sum_{k=1}^{n}\frac{C_{ik}}{C_{k\_bg}} = \frac{1}{n}\sum_{k=1}^{n} Cf_{ik}$$

Where Cf_{ik} is the content of k-pollutant in i-sampling site divided by baseline level C_{k_bg}. For value of background level we used the current median value in Norway, and n is the number of pollutants considered. The following pollutants were selected: As, Cd, Co, Cr, Ni, Cu, Fe, Hg, Pb, and Zn (n = 10). Distribution map of Slovakia shows that most high Z_c values are related to the above mentioned industrial areas in the metal industry in area Stropkov, Košice, Martin, Dubnica, where is 10–15 times high in comparison with Norway limit value and lowest (approximately twice) at eastern part of the High Tatra Mts.

The most heavy metal polluted areas

The total pollution coefficient (cumulative value) Z_i was calculated for all sampling sites to identify the heaviest metal polluted areas:

$$Z_i = \frac{1}{n}\sum_{k=1}^{n}\frac{C_{ik}}{C_{k\_bg}} = \frac{1}{n}\sum_{k=1}^{n} Cf_{ik}$$

Where Cf_{ik} is the content of k-pollutant in i-sampling site divided by baseline level C_{k_bg}. For value of background level we used the current median value in Norway (Steinnes et al. 2001) and n is the number of pollutants considered. The following pollutants were selected: As, Cd, Co, Cr, Ni, Cu, Fe, Hg, Pb, and Zn ($n = 10$).

Distribution map of SK shows that most high Z_c values are related to the above-mentioned industrial areas in the metal industry in area Stropkov, Košice, Martin, Dubnica, where it is 10–15 times higher in comparison with Norway limit value and lowest at eastern part of the High Tatra Mts. (Figure 6).

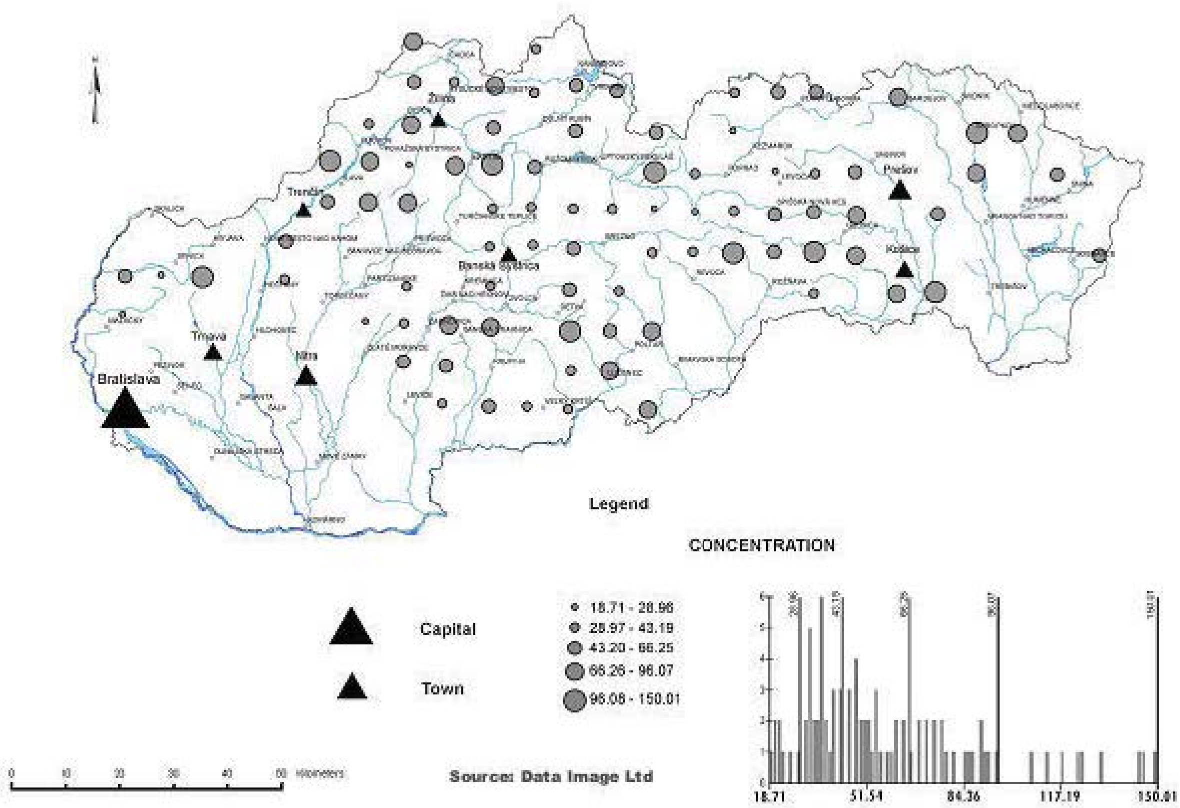

Fig. 6. The cumulative pollution value (Z_i) over the SK territory for elements As, Cd, Co, Cr, Ni, Cu, Fe, Hg, Pb and Zn. The pattern of the zones of relative general deposition loads in SK identified by mosses analyses.

Assessment of deposition rates

The mean absolute deposition rates of elements (mg m^{-2} yr^{-1}) for the individual zones of the contour maps have been assessed in accordance with the following formula (Rühling 1994a):

$$D = \frac{C.A}{E}$$

Where D is the atmospheric bulk deposition of given element (μg.m^{-2}.$year^{-1}$); C is the concentration of the element in a moss sample (μg g^{-1}), A is the biomass production of the moss at given locality (g.m^{-2}.$year^{-1}$); and E is the efficiency of element income by the moss (% in decimal expression). The available published coefficients for element uptake for the investigated elements in Norway and for *Pleurozium schreberi* (Berg and Steinnes, 1997) were used as presented in Table 27. The mean production of *Pleurozium schreberi* in conditions of CZ was found to be 129 $g_{\ d.w.}$.m^{-2}.$year^{-1}$ in 1995 (Sucharová and Suchara 1999). In accordance with the formula, the assessed annual average bulk atmospheric deposition values for the individual elements in the SR are presented as median, minimal and maximal values in Table 27.

Element	Uptake efficiency by moss	Bulk fall-out median	Bulk fall-out minimum	Bulk fall-out maximum	Element	Uptake efficiency by moss	Bulk fall-out median	Bulk fall-out minimum	Bulk fall-out maximum
Cd	*0.6*	0.1	0.02	0.3	**Ni**	*0.5*	0.9	0.18	3.3
Cr	*0.7*	0.25	0.2	7.9	**Pb**	*1.0*	3.6	1.2	14
Cu	*0.4*	2.5	1.3	12	**V**	*0.5*	1.2	0.45	7.8
Fe	*0.6*	335	0.9	2900	**Zn**	*0.65*	8	4	31

Table 27. Estimation of the bulk atmospheric deposition of chosen elements ($mg.m^{-2}.year^{-1}$) in SK in 2000.

Poland

The bio-indicated atmospheric deposition loads were determined in four areas representing the current atmospheric deposition cadastres in PL.

The highest atmospheric deposition loads of most investigated elements were bio-indicated in industrial areas in southern PL (Katowice). Increased deposition levels of some elements and very high Cu deposition levels were found in southwestern Silesia (between Wrocław and Góra). Eastern and western Silesia belonged to the so-called Black Triangle II and Black Triangle I areas. However, element contents in moss show gradual decrease. Central PL around the city of Warsaw is affected by low or moderate deposition loads of the investigated elements. In the eastern part of PL moss samples accumulated least amounts of all determined elements. The obtained results indicate a gradient of decreasing atmospheric deposition loads of elements in the direction south-north in PL. Accumulation of mainly metallurgical and chemical industries in southern PL are the reason of high or increased atmospheric deposition loads in Silesia. Mainly this area deserves regular monitoring of contamination of the environment and possibly health epidemiological study aimed to the effects of toxic metals. The element contents in moss in 2000 show decrease in element accumulation in moss in comparison with 1995 mainly in industrial southern part of PL.

In order to estimate the absolute deposition rates of elements in PL, the same coefficients for the uptake efficiency of *Pleurozium schreberi* and the mean production of this moss were used in the formula presented above in evaluation of the SK results. The obtained assessments of deposition rates of the investigated elements in PL are presented in Table 28.

Results of the correlation, cluster and factor analyses were discussed in the previous paragraphs.

Element	Uptake efficiency by moss	Bulk fall-out median	Bulk fall-out minimum	Bulk fall-out maximum	Element	Uptake efficiency by moss	Bulk fall-out median	Bulk fall-out minimum	Bulk fall-out maximum
Cd	*0.7*	0.066	0.040	1.32	**Ni**	*0.5*	0.405	0.187	0.746
Cr	*0.7*	0.164	0.062	1.94	**Pb**	*1.0*	1.28	0.508	8.46
Cu	*0.4*	2.59	1.46	12.8	**V**	*0.5*	1.50	0.392	2.14
Fe	*0.6*	92.2	46.4	912	**Zn**	*0.65*	8.28	5.64	117

Table 28. Estimation of the bulk atmospheric deposition of chosen elements ($mg.m^{-2}.year^{-1}$) in PL in 2000.

Hungary

The distribution of element content in moss reflecting the relative atmospheric deposition rates showed that northern half of HU suffers much more by increased deposition (Cd, Cu, Ni, Pb, Zn) than the southern part of the country. Northwestern HU is more affected by deposition of heavy metals than the eastern part. Reasons of the distribution of the hot spots are discussed in the comments to the maps. Determined element content in moss is similar as in SK. The absolute deposition rates of elements were estimated in the same way as presented above for the remaining countries. Nevertheless, the used bio-indicator *Hypnum cupressiforme* is known to accumulate elements much effectively than the other moss species. What is more, production of this moss species in dry climate of HU can be expected much lower than the production of other moss species in the remaining countries of V4. It means that the ratio B/E in the formula is in fact much lower than used. Hence the figures in the Table 29 should be treated as overvalued. On the other hand there were no available data about production of *Hypnum cupressiforme* and its uptake efficiencies for given elements in HU.

Marked decrease in element contents in moss was determined in the period 1995–2000. The main reason is restructuring of heavy industry, introduction of sophisticated technologies, decrease in industrial combustion of coal and cease of distribution of leaded petrol.

Element	Uptake efficiency by moss	Bulk fall-out median	Bulk fall-out minimum	Bulk fall-out maximum	Element	Uptake efficiency by moss	Bulk fall-out median	Bulk fall-out minimum	Bulk fall-out maximum
Cd	*0.7*	0.129	0.037	0.424	**Ni**	*0.5*	1.37	0.258	6.04
Cr	*0.7*	0.461	0.055	1.40	**Pb**	*1.0*	1.83	1.55	7.44
Cu	*0.4*	3.10	1.42	22.6	**V**	*0.5*	0.774	0.103	8.39
Fe	*0.6*	327	56.3	1510	**Zn**	*0.65*	9.55	4.86	30.2

Table 29 Estimation of the bulk atmospheric deposition of chosen elements ($mg.m^{-2}.year^{-1}$) in HU in 2000.

5 CONCLUSIONS

Content of 8 toxic elements in moss was determined for 499 sampling plots situated in the Visegrad space. The element contents in moss reflect the average relative atmospheric deposition loads of given elements at the sampling plots.

Evidently high relative deposition loads were bioindicated in the western and northeastern parts of CZ (former so-called Black Triangle I and Black Triangle II areas), in Silesia in southern Poland (former Black Triangle II area), in the western and eastern parts of Slovakia and in northern half of Hungary. In general, SK territory was bioindicated as the most affected by deposition loads of many elements of the all investigated V4 countries. In PL bioindicated deposition loads of these elements decreased in the direction from the south to the north, while in HU accumulation of these elements decreased rather from the north to the south and from the west to the east. Along SK/CZ borderline the bioindicated deposition levels dramatically decreased at CZ side of the boundary ridge of the White Carpathian Mts. and Javorníky Mts.

The comparison of the V4 moss data with similar surveys carried out in other countries showed that the average deposition loads of 8 toxic elements in the Visegrad space were about 3–5 times higher and in SK 5–7 times higher than in the cleanest parts of Europe, namely in northern Norway. On the other hand, the bioindicated deposition levels in V4 are comparable or for some elements even 2–3 times lower than in southern and southeastern Europe (the Balkans). In general, after political and economical changes in V4 in the 1990s, bioindicated deposition levels of the investigated elements have decreased substantially. At present, the main sources of the toxic metals have been still industrials furnaces combusting coal, municipal wastes and the operation of metallurgical, engineering and chemical industries. However, erosion and deposition of soil covers seem to contribute significantly to the increased atmospheric deposition rates of the litophile toxic metals (e.g., Cr, Fe, Ni, V) on the territories with low industrial activities but with extensive agriculture.

The altitude of sampling plots showed that it could influence significantly the element contents in moss. Usually in the countries with the territory at relatively high altitudes (SK and CZ), increasing altitude decreased element content of the investigated elements in moss. Decrease in the density of industrial pollution sources and concentration of coarse solid particles in the atmosphere related with the altitude may be the reason. Nevertheless, many other explanatory factors (covariables), which have not been yet investigated in our study, may correlate significantly with the altitude. In the countries with low average altitude (PL and HU) the accumulation of toxic elements in moss increased with the altitude, except for copper. Increased precipitation (wet deposition), wind erosion or other similar effects may be the reason.

The presented report provides the assessments of absolute annual mean deposition rates of 8 elements in V4. Bulks of the element deposition were not measured in collectors at the sampling plots hence the correctness of these assessments could not be checked. However, moss production and element uptake efficiencies generalised for the whole Visegrad territory being used in the calculation of the absolute element fallout caused errors in the deposition loads assessments. More reliable way of the calculation of the absolute deposition rates of the elements based on the moss analytical results should be carried out in V4 in future.

The bioindicated current atmospheric deposition loads do not seem to be dangerous for the health and fatal for the environment, except for areas with the main hot spots. In the hot spots with high contamination of the environment by toxic elements keeping of basic hygienic rules could be recommended. As many elements can effect in synergy, in the multi-element hot spots (e.g., former Black Triangle areas or in the most industrialized parts of SK), the health screening could be recommended.

The determination of element content in moss is cheap and effective tool of a large-scale biomonitoring the current atmospheric deposition loads in V4. Distribution of elemental content in moss is regularly evaluated in most of European countries. Harmonised activities of this biomonitoring enable the comparison of the atmospheric deposition loads among individual European countries and of time trend of the atmospheric deposition loads. The results of the biomonitoring campaigns may serve as a basis for strategic economic development, control of long-term sustainable land use, protection of the health of inhabitants and protection of the environment in the Visegrad space.

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Acknowledgements

The authors thank the International Visegrad Fund for supporting the project 11007-2006-IVF. Special thanks go to Mgr. J. Lieskovský and Mgr. P. Kenderessy for graphical processing of the analytical results and preparation maps for print. We would like to express our thanks to Dr. Z. Al-Attasová for revision and improving of English in the manuscript.

Executive summary

Since 1990 most of the European countries have been bio-indicated atmospheric deposition loads of toxic and risky elements using chemical analyses of moss samples. Moss experts from the Visegrad countries (Poland, the Slovak Republic, Hungary and the Czech Republic) accumulated and evaluated available results of the bio-indication campaigns carried in the Visegrad space with special reference to the moss survey 2000. The crucial air pollution sources and harmful effect of pollutants are generally stated. Important international conventions on air pollution control are mentioned. Especially the Convention on Long-range Transboundary Air Pollution (CLRTAP) and a system of International Cooperative Programmes (ICPs) for a monitoring the effects of air pollution are mentioned. Determination of levels of current atmospheric deposition carried our in the frame of the UNECE ICP-Vegetation programmes is described. Individual Visegrad countries, emission sources and checking of air quality at measuring stations and moss bio-indicators are introduced.

The activities of the bio-monitoring the atmospheric deposition loads and obtained results in 2000 are presented. Specimens of the moss bio-indicators were collected at 499 sampling plots in the Visegrad space (Czech Republic 250, Poland 116, Slovak Republic 86 and Hungary 47). Content of 53 elements was determined in the moss samples. Contents of 8 elements (Cd, Cr, Cu, Fe, Ni, Pb, V and Zn) were determined in all four V4 countries, contents of 21 elements were determined only in the Czech and Slovak Republic (Ag, Al, As, Ba, Ce, Co, Cs, Hg, In, La, Mn, Mo, N, Rb, S, Sb, Se, Sn, Sr, Th and U). Only in Slovak Republic and in Czech Republic were determined 17 (Au, Br, Ca, Cl, Hf, I, K, Mg, Na, Sc, Sm, Ta, Tb, Ti, W, Yb and Zr) and 7 elements (Be, Bi, Ga, Li, Pr, Tl and Y), respectively. Results concerning mainly the eight elements determined in all V4 countries are presented in the form of a printed publication. In parallel the presentation of all results was taken in the form of CD due to many colour maps included in the report.

The reports provide basic statistics of moss analytical data. Contents of investigated elements in moss correspond with relative atmospheric deposition loads of these elements. The investigated elements are characterized (chemical properties, occurrence in the environment, biological effects, sources of pollution and displays of toxicity or deficiency), districts of increased accumulation of these elements in individual countries is listed, causes of the appearing of these hot spots are explained (pollution sources) and remedy in the most affected areas are recommended. The colour maps depict position of sampling plots and distribution of the elements in moss in individual countries. The reports include results of correlation analysis, cluster analysis and factor analysis. Effect of altitude of the sampling plots on accumulation of the elements in moss was evaluated. In spite of bio-indicated decrease of atmospheric deposition loads in some areas of V4 increased deposition loads of toxic of risky elements have gone on (western, northeastern and southeastern parts of the Czech Republic, southern Poland, western and eastern parts of the Slovak Republic and northern part of Hungary. Estimation of absolute deposition loads of many elements ($mg.m^{-2}.year^{-1}$) is included. Besides effects of industrial emission sources (combustion of fossil fuels and municipal wastes, metallurgical and chemical industries) wind erosion of soil covers and increased deposition of soil and dust particles play important role in contamination of some areas in V4 by lithophile elements. Unfortunately, only contamination of the environment by few heavy metals is being investigated while health and environmental effects of remaining elements are rather ignored.

These reports provide first thorough evaluation of the bio-indication of atmospheric deposition loads in the Visegrad space. The publication of this data was from one half funded by the Visegrad International Fund (Project 11007-2006-IVF).

Streszczenie

Od roku 1990 większość krajów europejskich prowadzi pomiary atmosferycznej depozycji pierwiastków stosując mchy jako wskaźniki biologiczne. Biomonitoring przy użyciu mchów jest również prowadzony w krajach Grupy Wyszehradzkiej (V4) (Polska, Słowacja, Węgry i Republika Czeska). Niniejsze opracowanie zawiera wyniki badań bioindykacyjnych przeprowadzanych w krajach V4 ze szczególnym uwzględnieniem pomiarów z roku 2000.

W raporcie omówiono podstawowe źródła zanieczyszczeń powietrza i ich szkodliwy wpływ na środowisko. Wyniki odniesiono do postanowień ważnych międzynarodowych konwencji dotyczących kontroli zanieczyszczeń powietrza. Szczególny nacisk położono na postanowienia Konwencji w sprawie transgranicznego zanieczyszczania powietrza na dalekie odległości (CLRTAP) w nawiązaniu do systemu Międzynarodowego Programu Współpracy (ICPs) do monitorowania wpływu zanieczyszczeń powietrza. Opisano aktualny poziom atmosferycznej depozycji zanieczyszczeń wykonywanej w ramach programu UNECE ICP-Vegetation. Opracowanie zawiera także krótką charakterystykę poszczególnych krajów Grupy Wyszehradzkiej, opis źródeł emisji i systemów kontroli jakości powietrza na stacjach pomiarowych oraz informacje o mchach-wskaźnikach.

Raport opiera się głównie na wynikach monitoringu biologicznego rejestrującego atmosferyczną depozycję zanieczyszczeń przeprowadzonego w roku 2000. Mchy stosowane jako biowskaźniki zebrano w 499 stanowiskach rozmieszczonych na obszarze 4 krajów tworzących Grupę Wyszehradzką (w tym w Republice Czeskiej liczba stanowisk wynosiła 250, w Polsce 116, na Słowacji 86 i na Węgrzech 47). W próbach mchów oznaczono stężenia 53 pierwiastków. Stężenia 8 pierwiastków (Cd, Cr, Cu, Fe, Ni, Pb, V i Zn) zostały określone w próbach pochodzących ze wszystkich 4 krajów Grupy Wyszehradzkiej, zawartość 21 pierwiastków określono tylko w próbach z Czech i Słowacji (Ag, Al, As, Ba, Ce, Co, Cs, Hg, In, La, Mn, Mo, N, Rb, S, Sb, Se, Sn, Sr, Th i U). Kolejne 17 pierwiastków (Au, Br, Ca, Cl, Hf, I, K, Mg, Na, Sc, Sm, Ta, Tb, Ti, W, Yb and Zr) analizowano tylko w próbach z Czech, a 7 pierwiastków (Be, Bi, Ga, Li, Pr, Tl and Y) tylko w próbach zebranych na Słowacji. Wyniki zawierające dane wysokości stężeń ośmiu pierwiastków wspólnych dla wszystkich krajów V4 zostały opublikowane w formie raportu drukowanego, natomiast opracowanie zawierające kolorowe mapy rozkładu stężeń pozostałych pierwiastków upowszechniono tylko w formie elektronicznej (CD).

Opracowanie zawiera podstawowe analizy statystyczne przeprowadzone dla wyników analiz chemicznych mchów. Stężenia analizowanych pierwiastków w mchach odpowiadają ich względnej depozycji atmosferycznej. Scharakteryzowano analizowane pierwiastki (chemiczne właściwości, występowanie w środowisku, wpływ na organizmy, źródła zanieczyszczeń, efekt ich toksyczności lub niedoboru), wyszczególniono obszary o podwyższonej akumulacji poszczególnych pierwiastków dla wszystkich krajów V4, wyjaśniono przyczyny występowania skażonych terenów (źródła zanieczyszczeń) oraz zalecono podjęcie środków naprawczych dla najbardziej obciążonych rejonów.

Kolorowe mapy pokazują położenie stanowisk zbioru prób mchów i rozkład wysokości stężeń pierwiastków w poszczególnych krajach. Raport zawiera wyniki analizy korelacji, analizy klasterowej i czynnikowej. Oszacowano wpływ wyniesienia (wysokości n.p.m.) stanowisk zbioru prób na akumulację pierwiastków w mchach. Pomimo obniżającej się od początku lat 90. atmosferycznego opadu zanieczyszczeń nadal w kilku regionach na obszarze krajów V4 stwierdzono ich wysokie poziomy (zachodnia, północno-wschodnia i południowo-wschodnia część Republiki Czeskiej, południowa część Polski, zachodnia i wschodnia część Słowacji oraz północna część Węgier). Do opracowania włączono także oszacowanie całkowitej depozycji szeregu pierwiastków ($mg.m^{-2}.rok^{-1}$). Stwierdzono, że obok wpływu emisji zanieczyszczeń ze źródeł przemysłowych (spalanie paliw kopalnych i komunalnych śmieci, emisji z przemysłu metalurgicznego i chemicznego) erozja wietrzna gleb, powodująca wzrost opadu cząstek gleby, odgrywa ważną rolę w zanieczyszczeniu pierwiastkami litofilnymi niektórych obszarów wchodzących w skład grupy V4. Niestety, w badaniach uwaga zwykle zwracana jest na zanieczyszczenie środowiska przez kilka metali ciężkich, natomiast wpływ na zdrowie i środowisko pozostałych pierwiastków jest raczej pomijany.

Opracowanie niniejsze stanowi pierwszą całościową ocenę atmosferycznej depozycji zanieczyszczeń przy użyciu metod bioindykacyjnych w obszarze krajów tworzących Grupę Wyszehradzką. Publikacja ta była w połowie finansowana przez Międzynarodowy Fundusz Wyszehradzki (Projekt 11007-2006-IVF).

Souhrn

Od roku 1990 většina evropských zemí bioindikuje úrovně atmosférických spadů prvků pomocí chemických rozborů vzorků mechu. Odborníci na biomonitoring využívající mech z jednotlivých visegrádských zemí (V4: Polsko, Maďarsko, Česká republika a Slovenská republika) shromáždili a vyhodnotili dostupné výsledky těchto biomonitorovacích aktivit probíhajících na území visegrádského prostoru se speciálním ohledem na výsledky biomonitoringu z roku 2000.

Obecně se uvádějí rozhodující zdroje znečišťování ovzduší a škodlivé účinky látek znečišťujících ovzduší. Jsou zmíněny důležité mezinárodní úmluvy o kontrole znečišťování ovzduší. Zvláštní pozornost byla věnována Úmluvě o snižování znečištění ovzduší přecházejícím hranice států (CLRTAP) a soustavě společných mezinárodních projektů (ICP) na kontrolu dodržování úmluvy a sledování dopadů znečištění ovzduší. Je popsáno určování úrovní aktuálních atmosférických spadů prvků probíhající v rámci programu OSN/EHK ICP-Vegetace. Tato zpráva stručně představuje jednotlivé visegrádské země, jejich důležité emisní zdroje a systémy pro kontrolu kvality ovzduší na měřících stanicích a pomocí analýz mechu.

Uvádějí se činnosti biomonitorování atmosférických depozičních zátěží pomocí analýz mechu a dosažené výsledky v roce 2000. Vzorky mechu byly odebrány na území visegrádského prostoru na 499 odběrových plochách (Česká republika 250, Polsko 116, Slovensko 86 a Maďarsko 47). Ve vzorcích mechu byl stanoven obsah 53 prvků. Obsahy 8 prvků (Cd, Cr, Cu, Fe, Ni, Pb, V a Zn) byly stanoveny ve vzorcích ze všech zemí V4, obsahy 21 prvků byly zjišťovány jen v České a zároveň ve Slovenské republice (Ag, Al, As, Ba, Ce, Co, Cs, Hg, In, La, Mn, Mo, N, Rb, S, Sb, Se, Sn, Sr, Th a U). Pouze ve Slovenské republice byly v mechu zjištěny obsahy 17 prvků (Au, Br, Ca, Cl, Hf, I, K, Mg, Na, Sc, Sm, Ta, Tb, Ti, W, Yb, Zr) a v České republice obsahy 7 prvků (Be, Bi, Ga, Li, Pr, Tl a Y).

Výsledky týkající se především obsahu 8 prvků v mechu ve všech zemích V4 jsou prezentovány formou tištěné zprávy (část I). Distribuce všech 53 prvků v mechu (část II) jsou publikovány formou souběžně vydávaného CD vzhledem k velkému počtu prezentovaných barevných map a omezeným prostředkům na jejich vytištění.

Zprávy podávají základní statistiku výsledků chemických analýz mechu. Obsahy sledovaných prvků v mechu odpovídají relativní atmosférické depoziční zátěži místa růstu mechu. Pro určované prvky se uvádí základní charakteristiky (chemické vlastnosti, výskyt v životním prostředí, biologické účinky, zdroje jejich emisí a projevy toxicity nebo nedostatku), uvádějí se seznamy území v jednotlivých zemích V4 se zvýšenou akumulací jednotlivých prvků v mechu, předpokládané vysvětlení vzniku těchto ohnisek znečištění (identifikace zdrojů znečištění) a případná doporučení nápravných opatření v nejvíce zatížených regionech. Barevné mapy zobrazují umístění odběrových míst vzorků mechu a rozložení obsahu jednotlivých prvků v mechu na území visegrádského prostoru. Zprávy prezentují výsledky korelační analýzy, shlukové analýza a analýzy hlavních komponent. Byl hodnocen také vliv nadmořské výšky odběrových ploch vzorků na míru hromadění prvků v mechu. Navzdory dlouhodobě bioindikovanému poklesu depozičních zátěží zemí V4, na některých místech visegrádského prostoru přetrvávají zvýšené spady některých toxických a nebezpečných prvků (západní, severovýchodní a jihovýchodní část ČR, jižní Polsko, východní a západní část SR, a severní polovina Maďarska). Uvádějí se odhady absolutních depozičních spadů mnoha prvků ($mg.m^{-2}.rok^{-1}$). Vedle dopadů průmyslových emisních zdrojů (spalování fosilních paliv a komunálních odpadů a metalurgického a chemického průmyslu) hrají důležitou roli v kontaminaci životního prostředí zemí V4 depozice litofilních prvků ze spadů erodovaných půdních a prachových částic. Běžně se sleduje kontaminace životního prostředí pouze několika těžkými kovy a zdravotní a environmentální vlivy zbylých prvků se ignorují.

Předkládané zprávy poskytují pro V4 poprvé souhrnně zpracované a vyhodnocené výsledky bioindikací úrovní atmosférického spadu prvků. Publikování těchto dat bylo z poloviny finančně podpořeno Mezinárodním visegrádským fondem (Projekt 11007-2006-IVF).

Összefoglaló

A legtöbb európai állam 1990 óta a bioindikációs technika alkalmazásával vizsgálja a légkörből kiülepedő veszélyes és toxikus nehézfémek mennyiségét a bioindikátor mohák kémiai analízisével. A Visegrádi Országok összegyűjtötték a hozzáférhető kiértékelt eredményeket a Visegrádi térségben folytatott bioindikációs tanulmányokból, különös figyelemmel a 2000. év moha-vizsgálataira. Meghatározták a fő szennyező-kibocsájtókat és káros hatásait a szennyezőanyagoknak. Fontos nemzetközi egyezmények tesznek említést a légszennyezés nyomon követéséről, ilyen a különösen nagy távolságra jutó országhatárokon átterjedő légszennyezettségről szóló egyezmény (CLRTAP) és a Nemzetközi Együttműködési Programok (ICPs). Az aktuális légköri kiülepedés meghatározása az UNECE ICP vegetációs programja alatt valósult meg. Bemutatásra kerülnek a Visegrádi Országok moha-bioindikátor és levegő minőségmérő állomásai, valamint a kibocsátó források is.

Bemutatásra kerül a 2000. év minden elérhető eredménye a légköri biomonitoring felmérésekből. A Visegrádi térségből összesen 499 mintavételi helyen lett gyűjtve bioindikátor anyag (Cseh Köztársaság: 250; Lengyelország: 116; Szlovák Köztársaság: 86; Magyarország: 46). Összesen 53 elem meghatározására került sor a moha mintákból. Az 52 elemből 8 elem (Cd, Cr, Cu, Fe, Ni, Pb, V és Zn) vizsgálata történt meg mind a négy országban, a többi elem vizsgálata (Ag, Al, As, Ba, Ce, Co, Cs, Hg, In, La, Mn, Mo, N, Rb, S, Sb, Se, Sn, Sr, Th, U, Au, Br, Ca, Cl, Hf, I, K, Mg, Na, Sc, Sm, Ta, Tb, Ti, W, Yb, Zr, Be, Bi, Ga, Li, Pr, Tl, Y) a Cseh- és a Szlovák Köztársaságban került vizsgálatra. A nyomtatott kiadvány eredményei jobbára a nyolc elem meghatározására vonatkoznak mind a négy Visegrádi Országból. Emellett a CD kiadványban minden eredmény bemutatásra kerül, számos színes térkép illusztrációjával.

A beszámoló tartalmazza az eredmények főbb statisztikai adatait. A vizsgált elemek mohákban található mennyisége arányos ezen elemek légköri kiülepedésének mértékével. A vizsgált elemeket jellemezzük (kémiai tulajdonságuk, előfordulásuk a természetben, élő szervezetre gyakorolt hatásaik, lehetséges szennyezőforrásaik, valamint mérgezési vagy hiánytünetek), felsoroljuk az egyes országok növekvő szennyezést mutató területeit a szennyezőforrások feltüntetésével. Színes térképek ábrázolják a mintavételi pontok helyzetét és az elemek eloszlását az egyes országokon belül. A beszámoló továbbá tartalmazza a korreláció-analízis, csoportanalízis és faktoranalízis eredményeit. Elemeztük a mintavételi pontok tengerszint feletti magasságának hatását az elemek felhalmozódására. Annak ellenére, hogy a légköri ülepedés csökkent, a Visegrádi Országokban számos területen belül növekedett a veszélyes elemek terhelésének mértéke (Csehország nyugati, észak-keleti és dél-keleti része, Dél-Lengyelország, a Szlovák Köztársaság nyugati és keleti része, valamint Észak-Magyarország). Becslést adunk a teljes kiülepedés mértékére számos elem esetében (mg.m^{-2}.év^{-1}) is. A szennyezőanyag-kibocsájtó források hatásai mellett (fosszilis tüzelőanyagok elégetése, kohászat, fémfeldolgozó és vegyipari üzemek), a szél okozta talajerózió, a növekvő mennyiségű kiülepedő talaj- és por részecskék fontos szerepet játszanak a Visegrádi Országok néhány területén belül a mohák és zuzmók elem-felhalmozásában. Sajnos csupán néhány nehézfém környezetre gyakorolt hatásának vizsgálata történt meg, míg a többi elem egészségre és környezetre gyakorolt hatását nem került sor.

Ez a jelentés az első átfogó értékelése a légköri nehézfémszennyezés bio-indikációjának a Visegrádi Országokon belül. Ezen adatok publikálásában nélkülözhetetlen segítséget nyújtott a Visegrádi Nemzetközi Alap (VIF) (11007-2006-IVF).

Súhrn

Od roku 1990 väčšina európskych krajín bioindikuje úroveň atmosférických spadov prvkov pomocou chemických rozborov vzoriek machu. Odborníci na biomonitoring, ktorí využívajú mach z jednotlivých visegrádských krajín (V4: Poľsko, Maďarsko, Česká republika a Slovenská republika) zhromaždili a vyhodnotili dostupné výsledky týchto biomonitorovacích aktivít prebiehajúcich na území visegrádského priestoru so špeciálnym zreteľom na výsledky biomonitoringu z roku 2000.

Obecne sa uvádzajú rozhodujúce zdroje znečistenia ovzdušia a škodlivé účinky látok znečisťujúcich ovzdušie. V texte sú spomenuté dôležité medzinárodné dohovory o kontrole znečisťovania ovzdušia. Osobitá pozornosť bola venovaná Dohovoru o znižovaní znečistenia ovzdušia, ktoré prechádza cez hranice štátov (CLRTAP) a sústave spoločných medzinárodných projektov (ICP) na kontrolu dodržovania dohovoru a sledovaniu dopadov znečistenia ovzdušia. Je uvedené určovanie úrovní aktuálnych atmosférických spadov prvkov prebiehajúce v rámci programu OSN/EHK ICP -Vegetácia. Táto správa stručne predstavuje jednotlivé visegrádske krajiny, ich dôležité emisné zdroje a systémy pre kontrolu kvality ovzdušia na meracích staniciach a pomocou analýz machu.

Uvádzajú sa činnosti biomonitorovania atmosférických depozičných záťaží pomocou analýz machu a dosiahnuté výsledky v roku 2000. Odber vzoriek machu bol vykonaný na území visegrádského priestoru na 499 odberových plochách (Česká republika 250, Poľsko 116, Slovensko 86 a Maďarsko 47). Vo vzorkách machu bol stanovený obsah 53 prvkov. Koncentrácie 8 prvkov (Cd, Cr, Cu, Fe, Ni, Pb, V a Zn) boli stanovené vo vzorkách zo všetkých krajín V4, koncentrácie 21 prvkov boli zisťované len v Českej a zároveň v Slovenskej republike (Ag, Al, As, Ba, Ce, Co, Cs, Hg, In, La, Mn, Mo, N, Rb, S, Sb, Se, Sn, Sr, Th a U). Iba v Slovenskej republike boli v machu zistené koncentrácie 17 prvkov (Au, Br, Ca, Cl, Hf, I, K, Mg, Na, Sc, Sm, Ta, Tb, Ti, W, Yb, Zr) a v Českej republike koncentrácie 7 prvkov (Be, Bi, Ga, Li, Pr, Tl a Y).

Výsledky týkajúce sa predovšetkým obsahu 8 prvkov v machu vo všetkých krajinách V4 sú prezentované formou tlačenej správy (časť I). Distribúcia všetkých 53 prvkov v machu (časť II) je publikovaná formou súbežne vydávaného CD vzhľadom k veľkému počtu prezentovaných farebných máp a obmedzeným prostriedkom na ich tlač.

Správy podávajú základnú štatistiku výsledkov chemických analýz machu. Obsahy sledovaných prvkov v machu odpovedajú relatívnej atmosférickej depozičnej záťaži miesta rastu mechu. Pre určované prvky sa uvádzajú základní charakteristiky (chemické vlastnosti, výskyt v životnom prostredí, biologické účinky, zdroje ich emisií a prejavy toxicity alebo nedostatku), uvádzajú sa zoznamy území v jednotlivých krajinách V4 so zvýšenou akumuláciou jednotlivých prvkov v machu, predpokladané vysvetlenie vzniku týchto ohnísk znečistenia (identifikácia zdrojov znečistenia) a prípadné doporučenie nápravných opatrení v najviac zaťažených regiónoch. Farebné mapy zobrazujú umiestnenie odberových miest vzoriek machu a rozloženie obsahu jednotlivých prvkov v machu na území visegrádskeho priestoru. Správy prezentujú výsledky korelačnej analýzy, zhlukovej analýzy a analýzy hlavných komponent. Ďalej bol hodnotený tiež vplyv nadmorskej výšky odberových plôch vzoriek na mieru hromadenia prvkov v machu. Napriek dlhodobe bioindikovanému poklesu depozičných záťaží krajín V4, na niektorých miestach visegrádskeho priestoru pretrvávajú zvýšené spady niektorých toxických a nebezpečných prvkov (západná, severovýchodná a juhovýchodná časť ČR, južné Poľsko, východná a západná časť SR, a severná polovica Maďarska). Uvádzajú sa odhady absolútnych depozičných spadov veľa prvkov ($mg.m^{-2}.rok^{-1}$). Popri dopadoch priemyselných emisných zdrojov (spaľovania fosilných palív a komunálnych odpadov a metalurgického a chemického priemyslu) hrajú dôležitú úlohu v kontaminácii životného prostredia krajín V4 depozície litofilných prvkov zo spadov erodovaných pôdnych a prachových častíc. Bežne je sledovaná kontaminácia životného prostredia iba niekoľkými ťažkými kovmi a zdravotné a environmentálne vplyvy ostatných prvkov sa ignorujú.

Predkladané správy poskytujú pre V4 prvý krát súhrnne spracované a vyhodnotené výsledky bioindikácií úrovní atmosférického spadu prvkov. Publikovanie týchto dát bolo z polovice finančne podporené Medzinárodným visegrádským fondom (Projekt 11007-2006-IVF).