



JOINT INSTITUTE FOR NUCLEAR RESEARCH

# The 8<sup>th</sup> International Workshop on Biomonitoring of Atmospheric Pollution (BIOMAP 8)

Dubna, July 2 – 7, 2018

# **Programme & Abstracts**

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## PROGRAMME

## Monday 2<sup>nd</sup> July, 2018

**16:00 – 19:00** Registration (Hotel "Dubna")

## Tuesday 3<sup>d</sup> July, 2018

08:30	Late registration and putting up posters (International Conference Hall)			
09:30 - 11:00	Plenary session	Chair: Marina Frontasyeva		
09:30	Welcome address – JINR Director,	ome address – JINR Director, Academician Victor A. Matveev		
09:50	Welcome address – Bert Wolterbeet	k		
10:00	Sergey Gromov – Global air pollutie	on		
10:40 - 11:00	Conference photo			
11:00 - 11:30	Coffee/tea and poster view	ing		
11:30 - 12:50	Plenary session	Chair: Sergey Gromov		
11:30	Danas Ridikas et al. – Support of IA Past and present projects	s Ridikas et al. – Support of IAEA to studies related to atmospheric pollution: and present projects		
12:10	2	<i>na Frontasyeva et al.</i> – Twenty five years (1990 – 2015) of European moss ys: trends and remaining hotspots for heavy metals and nitrogen		
12:50 - 15:00	Lunch and poster viewing			
15:00 - 16:00	Session 1	Chair: Sergey Gromov		
15:00	<i>Ole William Purvis et al.</i> – Element in air pollution studies	signatures and lichens: a historical perspective		
15:20		<i>no Vieira et al.</i> – Lichens as biomonitors of long-range transported trace nents under different altitudes and different air mass influences		
15:40	<i>Eiliv Steinnes et al.</i> – Monitoring a Norway using terrestrial moss	<i>v Steinnes et al.</i> – Monitoring atmospheric deposition of organic pollutants in way using terrestrial moss		
16:00 - 16:30	Coffee/tea and poster view	ing		
16:30 - 17:50	Session 2	Chair: Richard Hoover		
16:30		element content of the lichen <i>Pseudevernia</i> ew. From the supranational state of art to a new assessment of regional benchmarks		
16:50	<i>Edyta Łokas et al.</i> – High airborne raregion	idioactivity in terrestrial environments of arctic		

- 17:10 Gergana Hristozova et al. - Atmospheric deposition studies in Bulgaria based on moss biomonitors, neutron activation analysis and inductively coupled plasma atomic emission spectroscopy
- 17:30 Omar Chaligava et al. - Distribution of major and trace element atmospheric deposition in Georgia (2014-2017 moss survey)
- 19:00 21:00Welcome party

#### Wednesday 4<sup>th</sup> July, 2018

#### **Plenary session:** 9:00 - 11:0009:00 Ilia Ilyin-Assessment of transboundary atmospheric pollution by heavy metals in the EMEP region using biomonitoring information and modelling results 09:40 Alexander Bolsunovsky et al. – Monitoring sources of radioactive contamination of the environment based on pine tree analysis 10:20 Boris Revich-Particulate matter, heat waves and wildfires as risk for health 11:00 - 11:30Coffee/tea and poster viewing

- 11:30 12:50Session 3 Chair: Ilia Ilyin
- 11:30 Bernd Markert et al. – Bioindication and biomonitoring (B & B) technologies with special consideration of lithium and its effects on human
- 11:50 Slavisa Popovic et al. - Development of ecosystem data base in Serbia
- 12:10 Murty P.V.S. Prabhakara et al. – Personal exposure monitoring of air pollution – priorities and challenges
- 12.30 Ilija Arsenic et al. - Kolmogorov complexity of heavy metals and radionuclide's spatial distribution
- 12:50 14.30Lunch and poster viewing
- 14:30 16:00Session 4

#### 14:30Yulia Aleksiayenak et al. - Biomonitoring study of trace elements atmospheric deposition in Belarus

- Sabina Dołęgowska- Uncertainty of selected steps of moss sample analyses for 14:50 trace elements
- 15:10 Pranvera Lazo et al. - Combination of naturally growing bryophyte moss biomonitoring, instrumental analyses, statistical analysis and GIS technique for evaluating trace elements atmospheric deposition – 2010, 2015 moss biomonitoring in Albania
- 15:30 *Claudia Stihi et al.* – Survey of heavy metal deposition in Romania; temporal trends and spatial distribution: 2010 and 2015

#### Chair: Danas Ridikas

Chair: Steinnes Eiliv

15:50 *Gevorg Tepanosyan et al.*– Atmospheric deposition of iodine and potential sources in Armenia

#### 16:10 – 16:30 Coffee/tea and poster viewing

#### 16:30 – 17:30 Session 5

#### Chair: Lazo Pranvera

- 16:30 *Zbigniew Ziembik et al.* Biomonitoring of heavy-metal contamination of forest areas in Southern and North-eastern Poland using moss
- 16:50 *Maria Zielińska et al.* The use of *Pleurozium schreberi* in biomonitoring of the forest areas of Southern and North-eastern Poland
- 17:10 *Dinesh K. Saxena* Mapping seasonal atmospheric metal precipitation of last 15 years from India using active moss approach

**19:00–20:30** Concert (The Boys' Choral School "Dubna")

## Thursday 5th July, 2018

Plenary session:		9:00 - 11:00	Chair: Bernd Markert	
09:00	Roeland Samson – Biomonitoring of particulate matter			
09:40	Richard Hoover et al Cosmic Dust in the Earth's Atmosphere			
10:20	Oldři	<i>ldřich Motyka</i> – Nanoparticle pollution and bryophytes – possibilities		
10:40		<i>ainer Schenk</i> – The dispersion model for air pollutants AUSTAL2000 understands eposition as loss and not storage		
11:00 – 11:30 Coffee/tea and poster viewing				
11:30 - 12:5	0	Session 6	Chair: Samson Roeland	
11:30		Ana Castanheiro – The PMF project; towards biomagnetic monitoring for source attribution of urban PM and associated early-health effects		
12:00		<i>Aničić Urošević et al.</i> – Moss bag biomonitoring of air pollution: urban vs. <i>Mira</i> agricultural scenario		
12:30		Valeria Spagnuolo et al. – A novel approach using moss bags to explore indoor vs outdoor elemental pollution sources		
13:00 - 15.00Lunch and poster viewing				
15:00 – 16:0	0	Session 7	Chair: Mira Aničić Urošević	
15:00	toxic	<i>Tijana Milićević et al.</i> – The grapevine leaves as bioindicators of air pollution by toxic elements and magnetic particles in experimental, commercial and organic vineyards		
15:20	Inga Zinicovscaia– Active moss biomonitoring of trace elements with Sphagnum girgensohnii in relation to atmospheric bulk deposition: Chisinau case study			

15:40 *Miodrag Krmar et al.* – Additional view in the moss technique by employing of some simple statistics

## 16:00 – 16:30 Coffee/tea, taking down posters

16:30 - 18:00	Session 8	Chair: Alexander Bolsunovsky
16:30	Alexandra Ioannidou et al. – Activity size distribution at different environments in Northern Italy	ution of radioactive <sup>7</sup> Be aerosols
	Silvana Munzi et al. $-\delta^{15}N$ in lichens reflects the source	e isotopic signature of ammonia
	<i>Önder Kılıç et al.</i> – Determination of <sup>210</sup> Po and <sup>210</sup> I in Thrace region of Turkey	Pb by moss monitoring technique
17:30 - 18:00	Closing procedure	

**19:00** Conference Dinner

## Friday 6<sup>th</sup> July, 2018

07:30 Excursion to Moscow by bus. Participants may either return to Dubna or stay in a hotel in Moscow or take a late flight on Friday.

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# **ORAL PRESENTATIONS**

#### BIOMONITORING STUDY OF TRACE ELEMENTS ATMOSPHERIC DEPOSITION IN BELARUS

Aleksiayenak Yu., A. Krakovska, M. Frontasyeva.

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The moss biomonitoring technique is widely used all over the Europe as a method to evaluate atmospheric deposition of metals more than 50 years (Frontasyeva, Steinnes, Harmens, 2016), but in Belarus it was applied for the first time at 2005. Every five years moss survey was conducted to see the difference between pollution levels in the country. During ten-year study samples of moss species of *Hylocomium splendens* and *Pleurozium schreberi* were collected over 280 sites all over country. Collection was carried out according to the sampling strategy adopted by the UNECE ICP Vegetation program on long-range atmospheric transport in Europe based on moss analysis (ICPVEGETATION, 2015). The moss samples were subject to instrumental neutron activation analysis (INAA) at the IBR-2 reactor of FLNP JINR in Dubna. A total of 32 elements were determined (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Hf, Ta, W, Th, U). Additionally, Cd, Cu and Pb were determined by atomic absorption spectrometry (AAS).

Comparison of the median values for various element from the three surveys in Belarus (in 2005/6, 2010/11 and 2015/16), showed that elements are mostly at the same levels. Although we noticed the increase of metal concentration at some sampling sites, the comparison of the results for Belarus with the analogous data for the other European countries showed relatively low contamination levels for the most of heavy and toxic elements. It could be explained by not so developed heavy industry as in nearby countries, and absence of extractive and processing industry. But still we reveal some polluted areas. In thus areas, the main pollution sources could be tractor plant in Minsk, engineering plant in Zhodino, farming, paintworks plants, iron and steel plant.

#### PERSONAL EXPOSURE MONITORING OF AIR POLLUTION – PRIORITIES AND CHALLENGES

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Undoubtedly, dedicated community of industrial hygiene (IH) / occupational health (OH) professionals are valuable contributors to society. The focus of best practice on industrial hygiene is to reduce risk, caring together, saving money and resources. Management of workplace risk factors such as indoor air quality (IAQ), biologic, chemical, ergonomic, and physical hazards is a challenging task for an industrial hygienist. A professional Industrial Hygienist must be able to anticipate, recognize and prevent potential job hazards, manage sampling plans and identify similar exposure groups (SEG) at workplace. Personal monitoring of exposure to workplace chemicals and ionizing radiation is a good tool in risk assessment of health. The result of personal exposure monitoring (airborne concentration of a given chemical in the breathing zone) is to be compared with occupational exposure limit (Reference 1).

Selection of the chemical substances and workers, assessment of personal exposure in SEG are challenging factors for an industrial hygienist. Number of samples, monitoring duration and frequency of reassessment are important in personal monitoring. Biological monitoring is another tool in personal monitoring, and is limited because of the small number of chemical substances whose biological exposure index (BEI) has been established.

Knowledge, skill and ability (KSA) is required for an industrial hygienist in reducing health risk at workplace to as low as reasonably practicable (ALARP). Ensure the application of appropriate professional judgement and ethical requirements in personal sampling techniques for health risk assessment. Without accurate exposure information, it is difficult to evaluate the health effects caused by air pollution in a specific environment (Reference 2).

#### References

1. Haruo Hashimoto, et al. Guidelines for personal exposure monitoring of chemicals: Part I. J Occup Health 2017; 59: 367-373.

2. Petro Terblanche. Personal monitoring of air pollution: How, what and why? The clean air journal 1991; 8(3): 3 - 5.

#### MOSS BAG BIOMONITORING OF AIR POLLUTION: URBAN VERSUS AGRICULTURAL SCENARIO

Aničić Urošević M.<sup>1</sup>, Milićević T.<sup>1</sup>, Vuković G.<sup>1</sup>, Relić D.<sup>2</sup>, Frontasyeva M.V.<sup>3</sup>, Popović A.<sup>2</sup>

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Urban and agricultural areas are highly anthropogenically devastated environments with diversely and densely distributed sources of pollution. These highly populated and cultivated areas represent in sum a big part of the Earth's surface and it is of crucial interest to monitor and control presumably high air pollution present there. Complex urban topography demands a high density of air quality monitoring stations while extensive agrochemical treatments in cultivated areas require often temporal measurements of pollution. The application of moss bags represents an easy-to-apply screening technique which has been used for biomonitoring of air pollutants. The technique has been mainly developed for application in areas where the naturally growing biomonitors are absent. It is successfully used for biomonitoring of potentially toxic elements including rare earth elements (PTEs) and persistent organic compounds, mostly polycyclic aromatic hydrocarbons (PAHs). In the last decade, we investigated crucial variables of the moss bag technique application (species-specific and the time- and site-dependent pollutant enrichment) through a series of studies performed in the urban area of Belgrade and agricultural areas in Serbia. Starting from 2017, we have been examined the moss bag technique for biomonitoring of PTEs at specifically polluted sites within the city such as crossroads<sup>1</sup>, street canyons, tunnel and garages<sup>2</sup>, and, finally, overall city area.<sup>3</sup> Thereafter, since 2015, we tested the technique application in commercial and organic vineyards.<sup>4</sup> The interchangeable use of two moss species, *Sphagnum girgensohnii* (a species of the most recommended biomonitoring genus) and Hypnum cupressiforme (commonly available) for biomonitoring of PTEs was discussed in the studies.<sup>3,4</sup> The results showed that the studied moss species could not be interchangeably used for airborne element assessment, except for Cr, Cu, and Sb.<sup>3,4</sup> In the urban area, 1-month bag exposure ensures accumulation of the elements and adequate replicability of the results even at air pollution background sites.<sup>5,6</sup> Otherwise, in the agricultural area, this period does not guarantee detectable element moss load if the bag exposure does not coincide with the agrochemical application time (which is variable in different vineyards). Hence, in a vineyard ambient, moss bags should be exposed during the whole vegetation period comprising unpredictable treatments of grapevine during the vegetation season. The moss bag technique enables uniformly biomonitoring of the air pollutants over all anthropogenically devastated areas since successfully overcomes the issue of lack naturally growing mosses.

<sup>&</sup>lt;sup>1</sup> Vuković G., Aničić Urošević M. et al., Sci. Tot. Environ. 542 (2016) 394–403.

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<sup>&</sup>lt;sup>3</sup> Vuković G., Aničić Urošević M. et al., Sci. Tot. Environ. 521–522 (2015) 200–210.

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<sup>&</sup>lt;sup>5</sup> Aničić M. et al., J. Haz. Matt. 171 (2009) 182–188.

<sup>&</sup>lt;sup>6</sup> Aničić Urošević M. et al., Urban For. Urban Gree. 25 (2017) 1–10.

#### KOLMOGOROV COMPLEXITY OF HEAVY METALS AND RADIONUCLIDE'S SPATIAL DISTRIBUTION

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With the development of mathematics as well as natural sciences and with the improvement of the human cognitive level, a new discipline dealing with complexity of different natural systems has been recognized. As a consequence, many complexity measures have been developed. One of the most promising is Kolmogorov complexity. These measures provided to scientific community a new insight into environmental processes. Spatial distribution of heavy metals and radionuclide's (HM&RN further) is forming by acting natural processes as well as human activities. Despite the fact that this distribution plays important role in environmental processes it has not been analyzed with deserving attention. The usual way to present the results obtained of some measurements having objective to describe environmental properties is to create a map of areal distributions of some characteristic quantity (or index). Attempts to introduce some quantitative (or numerical) measure which depict measured areal distribution (and obtained map) were not so frequent in scientific community. In this paper we made efforts to introduce some numerical parameters as new measure which can describe spatial distributions. This measure is based on application of Kolmogorov complexity.

#### MONITORING SOURCES OF RADIOACTIVE CONTAMINATION OF THE ENVIRONMENT BASED ON PINE TREE ANALYSIS

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Nuclear weapons tests, long-term operation of nuclear power plants, and accidents that have occurred at them have released considerable amounts of artificial radioactivity into the environment. It is well-known that Russia is one of the most forested countries in the world. Conifers make up the greater portion of the standing volume of forests in Russia, and they mostly grow in the Krasnoyarskii Krai (Siberia). Pine is among woody plants that show high sensitivity to radioactive contamination; it has been included in the list of Reference Animals and Plants by the International Commission on Radiological Protection.

In this study, samples from pine trees were investigated for artificial radionuclides; the samples were collected from pine (Pinus sylvestris) trees growing in the environs of the city of Krasnoyarsk (the administrative center of the Krasnoyarskii Krai) (Siberia, Russia) and at a distance of 80 km north-east of the city. Analyses were performed using a hyper-pure germanium detector. During 2011-14, both the global artificial radionuclide <sup>137</sup>Cs and the radionuclide <sup>134</sup>Cs were detected in pine samples. That suggested radioactive fallout from the Fukushima accident in Siberia. The pine needles contained the highest concentrations of the pine needles and branches but also in the new shoots in 2012, which suggested a transfer of Fukushima cesium isotopes from branches to shoots. In 2014, <sup>134</sup>Cs was only detected in the pine needle litter. Analysis of activity concentrations of cesium isotopes (<sup>137</sup>Cs and <sup>134</sup>Cs) and their ratio in pine samples from different regions may suggest different (aerosol or aquatic) pathways of radioactive contamination of forest ecosystems.

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#### BACKGROUND ELEMENT CONTENT OF THE LICHEN *PSEUDEVERNIA FURFURACEA*: A COMPREHENSIVE OVERVIEW. FROM THE SUPRANATIONAL STATE OF ART TO A NEW METHODOLOGICAL FRAMEWORK FOR THE ASSESSMENT OF REGIONAL BENCHMARKS

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In biomonitoring, the knowledge of Background Element Content (BEC) values is an essential pre-requisite for the correct assessment of pollution levels. Supranational BECs for the highly performing lichen biomonitor Pseudevernia furfuracea were estimated by a literature review integrated by an extensive field survey. Methodologically homogeneous element content datasets, reflecting different exposure conditions across 16 countries, were compiled and comparatively analysed. Element content in samples from remote areas was compared to that of potentially enriched samples, indicating that the former were unaffected by anthropogenic contributions, thus allowing to propose their metrics as a supranational benchmark. The literature survey revealed a huge methodological variability: in particular, the sample acid digestion was identified as one of the most neglected pieces of information. Indeed, such analytical step was never expressly considered in the built up of review-based lichen BEC values, introducing a bias due to the merging of data from highly heterogeneous sample digests. Therefore, limited to original data from Italy, we investigated the variability of 43 elements in remote mountain areas, after having digested samples with two acid mixtures, with and without HF (i.e. total vs. partial digestion), both associated to ICP-MS multi-element analysis. The digestion performance was evaluated by comparing analytical results of field samples with the accuracy obtained on the standard BCR 482 (P. furfuracea). Overall, the total digestion showed a better performance, especially for Al, As, Ba, Cd, Cu, Fe, Mn, Ni, Sn and Zn. Moreover, the sampling sites were characterized for anthropization, land use, climate and lithology at different scale resolution and the relationships between environmental descriptors and BECs based on partial sample digestion were tested by Principal Component Regression (PCR) modelling. Elemental composition resulted significantly dependent on land use, climate and lithology and regression models correctly reproduced the content of lithogenic elements at randomly selected sites. Finally, a methodological gap in biomonitoring procedures was filled by providing two sets of BEC values based on different sample digests for use as a reference in biomonitoring applications. Since BEC patterns were proved to be context-dependent, both sets referred to environmentally homogeneous macro-regions, thoroughly identified by a multivariate approach.

#### DISTRIBUTION OF MAJOR AND TRACE ELEMENT ATMOSPHERIC DEPOSITION IN GEORGIA (2014-2017 MOSS SURVEY)

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Moss biomonitoring, ENAA and AAS analysis were used to study major and trace element deposition in Georgia. Pleurozium schreberi, Hypnum cupressiforme, and Hylocomium splendens were chosen for the study due to their characteristic and occurrence. Overall, during 2014-2017 moss surveys, 122 moss samples distributed over the entire country were collected. Collection of samples was carried out in compliance with the Moss Manual of the UNECE ICP Vegetation [1]. For each sample concentrations of 39 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Sr, Zr, Mo, Pb, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Hf, Ta, W, Au, Th, and U) were determined by epithermal neutron activation analysis (ENAA) at the reactor IBR-2 of FLNP JINR. Concentrations of Cu, Cd and Pb were obtained by atomic absorption spectrometry. Different statistical analysis was applied for data interpretation. Factor analysis was used to find associations of chemical elements and to characterize the sources of element-pollutants. To visualize data GIS technologies were used. A comparison of determined values of elements with corresponding data from other Europe countries showed that the concentrations of heavy metals in mosses collected in Georgia are mostly higher. The obtained results evidence that there is a considerable problem in the Western Georgia, due to metal processing industry and mining enterprises allocated there.

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#### UNCERTAINTY OF SELECTED STEPS OF MOSS SAMPLE ANALYSES FOR TRACE ELEMENTS

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The first operations made on moss samples, just after sampling, such as preservation and physical treatment, lead to removal of particles deposited onto their tissues as well as to changes in the contents of major and trace elements. According to the international protocols each sample which cannot be cleaned just after sampling has to be dried and stored at a room temperature, or can be deep-frozen. Both these techniques are the most popular methods of preservation, however they may alter the membrane permeability and lead to removal or translocation of elements. To maintain the proper condition of the moss membrane permeability samples can be kept in the fridge but only if they are going to be cleaned within two weeks. In case of cleaning, the removal of elements is mainly related to washing, its duration, type of element and its position in a selected metal fraction (Aboal et al., 2008; Vázquez et al., 2015). To provide further insight into the impact of sample preservation and preparation, but also sampling, on the quality of measurement and the level of measurement uncertainty chemical analysis of Pleurozium schreberi (Brid.) Mitt moss samples for selected trace elements were done. After sampling, at the laboratory each primary sample (S1) was divided into three subsamples for preservation P1 (drying), P2 (frezzing) and P3 (acclimatization). After 7 days, samples were dried at 45°C in a forced air oven, and then divided into two sub-samples for preparation, P' (mechanical cleaning) and P" (rinsing). Subsequently, each sample was milled, sieved and digested in a close microwave system. The same procedure was undertaken for duplicate samples (S2).

After digestion, all samples were analyzed for Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn using the FAAS (for Fe, Mn, Zn) and GFAAS (for Cd, Co, Cu, Ni and Pb) techniques. According to the unbalanced methodology (Rostron, Ramsey, 2012), primary samples were analyzed twice, while duplicates only once. As standard reference materials, M2 and M3 were applied.

The following statistical methods: ANOVA, RANOVA, modified RANOVA and range statistics were harnessed to calculate uncertainty arising from sampling, sample preservation, preparation and analysis. The level of uncertainty varied from 0.3% for analysis to 20% for sampling and was dependent on: (i) type of element, (ii) its distribution in the environment, (iii) its intra- or extracellular distribution, and (iv) statistical method used for calculation.

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#### SPATIAL PATTERNS AND TEMPORAL TRENDS OF HEAVY METAL AND NITROGEN CONCENTRATIONS IN MOSSES (1990 – 2015)

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For more than 50 years, naturally growing mosses have been used as biomonitors of atmospheric deposition of heavy metals. The first European-wide moss survey was conducted in 1990/1 and has since then been repeated at five-yearly intervals. The most recent survey was conducted in 2015/16, with mosses collected from ca. 5,000 sites in 34 countries. In 2014, the coordination of the moss survey was handed over from the ICP Vegetation Programme Coordination Centre in the UK to the Moss Survey Coordination Centre at JINR in the Russian Federation. As a result, participation in 2015/16 has increased in countries in Eastern Europe, the Caucasus and Central Asia (EECCA region). Since 2005/6, some countries have also determined the nitrogen concentration in mosses, with 12 countries reporting nitrogen data in 2015/16. As in previous recent surveys, in 2015/16 the lowest concentrations of heavy metals in mosses were generally found in Northern and Western Europe, with some hotspots remaining near industrialised areas, and areas with current or historic mining activities. For the majority of metals, concentrations in mosses were highest in parts of Eastern and South-Eastern Europe. For some part this is due to current higher emissions of heavy metals from pollution sources, however, part of the higher deposition also seems to originate from a higher resuspension of historic heavy metal deposition via wind-blown dust as particularly the concentrations of metals such as aluminium, chromium and iron are high in those regions. Furthermore, many of the EECCA countries participating for the first time have preferentially sampled mosses in polluted regions. Nitrogen concentrations in mosses were generally highest in Central European countries.

Since 1990, the metal concentration in mosses has declined for all metals, however, the magnitude of decline varies per metal and was highest for lead (mainly due to the introduction of unleaded petrol) and lowest for copper. The rate of decline was generally highest in the 1990s but has levelled off since 2000 for most metals. Although some countries have reported a continued decline in concentrations in mosses for selected metals, this was not observed for all metals and some countries have even seen a slight rise of concentrations in mosses for some metals since 2010. Only a slight decline in the nitrogen concentration in mosses was observed between 2005 and 2015. Further details on spatial patterns of the 2015/16 moss survey and temporal trends since 1990 will be published in a report by the end of 2018.

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#### THE PMF PROJECT; TOWARDS BIOMAGNETIC MONITORING FOR SOURCE ATTRIBUTION OF URBAN PM AND ASSOCIATED EARLY-HEALTH EFFECTS

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Air pollution is now the world's largest single environmental health risk. Nevertheless, current air quality networks obtain poor spatial monitoring resolution due to high investment and maintenance costs. Especially in heterogeneous urban environments, spatial monitoring resolution is generally too limited. Biomagnetic monitoring has previously shown to be a promising monitoring approach to capture spatio-temporal variation of particulate air pollution (Hofman et al. 2017; Rai 2013; Matzka and Maher 1999; Hansard et al. 2011; Maher et al. 2008; Kardel et al. 2011); for both air quality monitoring and modelling applications, on both spatial (e.g. Hofman et al. 2013; Hofman and Samson 2014; Hansard et al. 2011) and temporal (e.g. Hofman et al. 2014; Mitchell et al. 2010; McIntosh et al. 2007) resolutions. Nevertheless, lacking information on source-dependent magnetisable composition and health-relevancy of atmospheric particles impedes the general application of biomagnetic monitoring in environmental air quality assessments. This ongoing study, therefore, aims at addressing this knowledge gap by evaluating atmospheric PM, originating from different sources (road and railway traffic, shipping, industry and background location) for its chemical composition, association with related pollutants (particle-bound metals, black carbon, ultrafine particles and PAHs), magnetic properties and early health response (pro-inflammatory potential) of human lung cells, combining a range of analytical techniques (a.o. SEM-EDX, ED-XRF, HR-ICP-MS, GCxGC-TOFMS and Coriolis). For each PM source environment, we combined sourcetargeted sampling with collection of atmospheric samples from conventional 24h pumped-air filters (Leckel SEQ47/50) and passively-deposited leaf biomonitoring. First results already identify source-specific metal and magnetic "fingerprints" from the loaded filter and leaf samples, with discriminating pro-inflammatory potential. This research hereby contributes to chemical source characterisation, its potential for source attribution in urban areas, and the health-relevancy of biomagnetic monitoring. While the magnetic mineralogy, grain size and concentration will reflect PM source-contributions, associations with heavy metals and/or elemental carbon might emphasize biomagnetic monitoring as a novel health-related PM proxy.

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#### COSMIC DUST IN THE EARTH'S ATMOSPHERE

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Cosmic dust exists throughout the Universe and is crucial to the recycling of chemical elements and organics - *from the early stages of the formation of stars and planets to the mass loss during the final stages of stellar evolution.* The *Hubble, Spitzer* and *Chandra Observatories* and telescopes provided data on Cosmic dust in diverse spectral regimes and astronomical locations: *Intergalactic Dust* (dust between galaxies/Okroy clouds); *Interstellar Dust* (diffuse interstellar medium; nebulae molecular clouds; circumstellar dust around young stars & Bok Globules); *Interplanetary Dust Particles* (IDP - comet dust tails/zodiacal dust; circumplanetary systems: *Mars* - dust tori of Phobos/Deimos; *Jupiter* - halo, outer diffuse & gossamer rings; *Saturn* - Rings & spokes; *Uranus* - narrow sheet, bands & gaps). While intergalactic and interstellar dust particles enter the Atmosphere; the dominant cosmic dust component entering Earth's atmosphere is from cometary ejecta, asteroidal collisions, micrometeorites and the disintegration of carbonaceous chondrites in Earth's upper atmosphere.

Discoveries about comets and carbonaceous meteorites have yielded important new insights into the origin of cosmic dust that enters Earth's atmosphere. The Vega and Giotto observations of comet Halley revealed that the Whipple cold "Dirty Snowball" model of cometary nuclei was incorrect and confirmed the Hoyle/Wickramasinghe prediction of hot, black cometary crusts [1]. The low albedo (~0.3) caused the jet-black Halley nucleus crust to become very hot (320 to 400 K) at 0.8 AU. Clearly, water-ices beneath this hot crust can melt to form near surface pools of liquid water that could support growth of chemolithotrophs and photosynthetic microalgae. Gas, water, ice, organics, mineral grains, ions and dust escaping slowly or explosively through weak regions or fractures in the crust could play a crucial role in the observed flaring, jets and the formation of the ion and dust tails of the comet. Therefore, the widely accepted hypothesis that liquid water (and life) could not exist in a comet is invalidated. This is consistent with the detection of indigenous microfossils in CI1 and CM2 carbonaceous meteorites and the recent studies indicating comets are likely parent bodies for these meteorites [2]. Asteroidal collisions were previously considered the primary source of cosmic dust, but recent IRAS observations suggest that asteroidal dust contributes <10% while the Jupiter Family of Comets produces up to 85% of the total mass influx (~100-300 tons/day) of cosmic dust into Earth's atmosphere [3] in agreement with the accumulation rates of cosmic-enriched elements (e.g., Ir, Pt, Os) in polar ice cores and deep-sea sediments. Cosmic dust particles and meteorites enter the atmosphere at high velocities and ablate forming nano-sized ironmagnesium silicate meteoric smoke particles (MSPs) in the upper mesosphere, which can remove sulfuric acid from the gas phase above 40 km [4]. Injected metals form layers of metal atoms and ions; nucleate noctilucent clouds, impact stratospheric clouds and Ozone layer, and fertilize oceanic plankton/diatoms with bio-available iron. We review Cosmic Dust in the Earth's Atmosphere and compare NASA/MSFC FESEM images & EDS data of element compositions of particulates from carbonaceous meteorites, Stardust cometary particulates and Apollo lunar dust samples with images and INAA analysis of element compositions of cosmic dust particles from moss [5].

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#### ATMOSPHERIC DEPOSITION STUDIES IN BULGARIA BASED ON MOSS BIOMONITORS, NEUTRON ACTIVATION ANALYSIS AND INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

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For the fifth time Bulgaria participates in the moss survey carried out in the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (the UNECE ICP Vegetation). In the summer of 2015, 115 moss samples (*Hypnum cupressiforme, Pleurozium schreberi* and *Pseudoscleropodium purum*) were collected in accordance with the sampling strategy. Concentrations of 37 elements in total were determined in moss biomonitoring species using instrumental epithermal neutron activation analysis (Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Eu, Fe, Hf, I, K, La, Lu, Mg, Mn, Na, Nd, Ni, Rb, Sb, Sc, Se, Sr, Ta, Tb, Th, Ti, Tm, U, V, W, Yb, Zn). Three additional environmentally important elements were analysed using inductively coupled plasma atomic emission spectroscopy (Cd, Cu, Pb). The determined concentrations were compared with data from a moss survey conducted in Bulgaria in 2005, as well as with data from other European countries participating in the ICP Vegetation programme in 2015. Multivariate statistical analysis (multiple factor analysis) was applied to characterize the sources of elements determined during the 2005 and 2015 moss surveys. Four groups of elements were differentiated. To illustrate the deposition patterns of element pollutants, GIS technology was used to produce distribution maps.

#### ASSESSMENT OF TRANSBOUNDARY ATMOSPHERIC POLLUTION BY HEAVY METALS IN THE EMEP REGION USING BIOMONITORING INFORMATION AND MODELLING RESULTS

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The main task of Meteorological Synthesizing Centre East of EMEP is to prove the EMEP countries with modelling information on atmospheric concentrations, deposition and transboundary transport of heavy metals (Pb,Cd, Hg). Concentrations and deposition fluxes of these metals are calculated over regular grid on annual basis. The modelling results are verified via comparison with available measurements collected from the EMEP monitoring network. Measurements of concentrations in mosses are characterized by high spatial density. Besides, these measurements are often carried out in regions where station-based monitoring data are not available. Therefore, the data on measured concentrations of HMs in mosses is important complementary information for analysis of pollution levels and their trends in the EMEP region. Concentrations in mosses and atmospheric deposition cannot be compared directly. Nevertheless, spatial distribution of modelled atmospheric deposition can be compared with spatial distribution of concentrations in mosses. Besides, long-term trends of these parameters can be compared.

Spatial Spearman correlation coefficients between modelled atmospheric deposition fluxes are more than 0.5 in few European countries. Similar comparison between concentrations in mosses and observed wet deposition fluxes measured at the EMEP network also revealed correlation varying from around 0.3 to 0.7 for lead and cadmium. Hence, concentrations in mosses depend not only on atmospheric deposition, but on other environmental factors which are needed to be considered.

Long-term trends of pollution levels for period 1990-2015 were reasonably well reproduced by the model. Magnitude of country-mean modelled deposition change for this period is comparable with the magnitude of change of concentrations in mosses (Fig. 1)

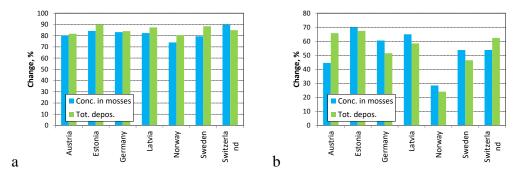


Fig. 1. Magnitude of change [ (1990-2015)/1990 x 100% ] of country-averaged concentrations in mosses and total deposition for the period 1990-2015.

#### ACTIVITY SIZE DISTRIBUTION OF RADIOACTIVE <sup>7</sup>BE AEROSOLS AT DIFFERENT ENVIRONMENTS IN NORTHERN ITALY

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In this work, the activity size distributions of the natural radionuclide tracer <sup>7</sup>Be are reported. They were obtained from measurements with two compatible 1ACFM 9 stage cascade impactor in outdoor air, under different meteorological conditions and at different environments in Northern, Italy covering all seasons of a year.

The activity size distributions of the natural radionuclide tracer <sup>7</sup>Be in different size fractions (<0.4  $\mu$ m, 0.4-0.7  $\mu$ m, 0.7-1.1  $\mu$ m, 1.1-2.1  $\mu$ m, 2.1-3.1  $\mu$ m, 3.1-4.2  $\mu$ m, 4.2-5.8  $\mu$ m, 5.8-9.0  $\mu$ m >9.0  $\mu$ m) were determined at different site places in Northern Italy during the four seasons of the year 2011. Four different locations were chosen, (a) a suburban - industrialised area (Segrate, Milan), (b) an urban area in downtown Milan (c) a rural-residential area (Ispra) and (d) a rural area at Monte Rosa mountain (1300 m asl). The first station at Segrate, Milan has been chosen as a reference station. Each sampling was conducted simultaneously at the reference station and at each one of the other stations.

At all stations the <sup>7</sup>Be activity concentrations present lower values during winter and higher values during summer, which is consistent with the general trend of <sup>7</sup>Be activity concentrations in Northern hemisphere throughout a year.

The greatest parts of <sup>7</sup>Be aerosol are associated with fine particulate. The <sup>7</sup>Be activity median aerodynamic diameter (AMAD) values ranged from 0.40 to 1.05  $\mu$ m.

The AMAD values were anticorrelated with <sup>7</sup>Be activities, while they are correlated with RH% in all stations, except the one in Ispra region near the lake Magoret,

Lower AMAD values are observed during summer and greater AMAD values during winter in all stations except the one near the lake. During all seasons of a year greater <sup>7</sup>Be AMAD values were observed in polluted environments. So, the <sup>7</sup>Be AMAD values could be used as an index of air pollutant conditions

#### DETERMINATION OF <sup>210</sup>PO AND <sup>210</sup>PB BY MOSS MONITORING TECHNIQUE IN THRACE REGION OF TURKEY

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Moss technique has been commonly used to monitor atmospheric dry/wet deposition of many groups of pollutants such as radionuclides, heavy metals and organic contaminants for 50 years. Moss is chosen for the determination of pollutants, since it has the important advantages which are wide surface area, nutrition by their surface directly from the atmosphere, without or thin cuticle layer and distributed in a wide geographical area.

In the natural radionuclides <sup>210</sup>Po and <sup>210</sup>Pb, which are decay products of the <sup>238</sup>U decay series, are major contributors to the internal radiation dose of human population. Although they are naturally present in the environments, the activity levels of <sup>210</sup>Po and <sup>210</sup>Pb increase by increasing human activities such as the burning of fossil fuels, using phosphate fertilizers in agriculture, and various industrial emissions.

In the present study, moss samples (Hypnum cupressiforme) were collected from the 44 sampling locations in Thrace region of Turkey. Activity concentrations of <sup>210</sup>Po and <sup>210</sup>Pb were measured using an alpha spectrometer (ORTEC).

This study presented the first data of <sup>210</sup>Po and <sup>210</sup>Pb activity concentrations in the Thrace region of Turkey. The activity concentrations of <sup>210</sup>Po from <sup>210</sup>Pb were at variable levels among the sampling locations. The higher activities of both radionuclides were found in northeast Thrace region in particular.

#### ADDITIONAL VIEW IN THE MOSS TECHNIQUE BY EMPLOYING OF SOME SIMPLE STATISTICS MIODRAG KRMAR, ILIJA ARSENIC, DRAGAN RADNOVIC.

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Terrestrial mosses are a very promising medium for investigation and monitoring of heavy metals (and airborne radionuclide) depositions due to their widespread occurrence and ease sampling procedure. A very dense network of sampling sites can be established to provide excellent spatial resolution on the maps of deposition which are usual way to present obtained results. The overall objective of the present study is to employ some simple statistical procedures to get additional analysis of the dataset of one standard moss survey. Several very specific patterns of scatter graphs were obtained in analysis of the correlation between concentrations of some heavy elements or radionuclides measured in mosses. Ratios of measured concentrations of some elements and their spatial distributions can offer additional interesting information. Distributions of obtained values of particular elements are usually lognormal and some analysis of these distributions was performed to get additional information concerning possible natural occurrence of some elements and anthropogenic impacts.

#### COMBINATION OF NATURALLY GROWING BRYOPHYTE MOSS BIOMONITORING, INSTRUMENTAL ANALYSES, STATISTICAL ANALYSIS AND GIS TECHNIQUE FOR EVALUATING TRACE ELEMENTS ATMOSPHERIC DEPOSITION – 2010, 2015 MOSS BIOMONITORING IN ALBANIA

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Moss biomonitoring in Albania (MBA) started on 2010 when a research group joined the ICP Vegetation Programme for evaluating trace elements atmospheric deposition. 44 elements were analyzed by INAA (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research. Dubna, Russia) and ICP-AES (Sts. Cyril and Methodius University, Skopje, Macedonia) techniques in 48 moss samples collected over the entire territory of Albania. 20 elements were analyzed by ICP-AES technique in 55 moss samples that cover the same territory on 2015 MBA. Hypnum cupressiforme (Hedw) moss that are present in all territory of Albania are selected as bioindicator of trace metal atmospheric deposition. High variations of trace metals were found for both MBAs indicating that the concentrations of elements are affected by different factors. Their spatial variability and distribution pattern may allow better understanding their natural and/or anthropogenic origin. This study induced that mineral particle dust from local emission sources is classified as the most important factor affecting the atmospheric deposition of elements accumulated in the current moss samples. The open slag dumps of mining operation in Albania is probably the main factor contributing to high contents of Cr, Ni, Fe, Ti and Al in the moss. It is confirmed by the presence of typical crustal elements in mosses that are mainly associated with local and long-term wind blowing mineral dust particles.

Enrichment factors (EF) of the elements were calculated to clarify whether the elements in the present moss samples were mostly originate from atmospheric deposition and/or local substrate soils. 2015 moss survey is compared with similar study of 2010. The results show an increase on Cr, Cu, As, Ni and Na, a decline on Ba, K and Mg, and the rest of elements remained mostly the same concentration level. Factor analysis (FA) is used to identify the most probable sources of the elements. Similar results were obtained from FA for 2015 and 2010 moss surveys. Five dominant factors are identified, i.e. natural contamination; dust emission from local mining operations; atmospheric transport of contaminants from local and long distance sources; contributions from air borne marine salts, and log-range transport of Hg.

Albania is exposed to high levels of heavy metal pollution particularly in western part that is exposed to high levels of heavy metal pollution linked with oil and gas industry and shipping traffic, and in the eastern part of exposed to high levels of metal pollution linked mostly with mineral operations, mineral dumps and mineral processing industry. It is highly recommended to continue the spatial distribution monitoring of trace elements in the future and the implementation of air pollution abatement policies for reducing heavy metal pollution.

## HIGH AIRBORNE RADIOACTIVITY IN TERRESTRIAL ENVIRONMENTS OF ARCTIC REGION

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Cryoconites are aggregates of mineral and organic substances on surfaces of glaciers, which are able to accumulate large amounts of airborne pollutants by binding them to extracellular polymeric substances secreted by microorganisms. The cryoconites are common in the ablation zones of glaciers, particularly those located at high latitudes and high altitudes. They accumulate dust eluted from the atmosphere by dry or/and wet precipitation. Because of their low albedo, cryoconites facilitate melting of ice leading to formation of holes on the glacier surface. The research carried out in five areas from the western and southeastern Spitsbergen coast. The cryoconites were collected. Measurements conducted in such a variety of localizations influenced by different environmental conditions provides an opportunity to study the impact of glaciological characteristics on contaminant accumulation in cryoconites. In this study contents of airborne radionuclides (<sup>137</sup>Cs, Pu isotopes, <sup>210</sup>Pb) in cryoconites were determined. The cryoconites collected from the two glaciers reveal the highest activity concentrations of the anthropogenic (<sup>137</sup>Cs, <sup>238,239,240</sup>Pu) and natural (<sup>210</sup>Pb) radionuclides. Activity concentrations of fallout radionuclides reaching 4500 Bq/kg, 14 Bq/kg, 179 Bq/kg for <sup>137</sup>Cs, <sup>238</sup>Pu and <sup>239+240</sup>Pu, respectively. Activity ratios of <sup>238</sup>Pu/<sup>239+240</sup>Pu, <sup>239+240</sup>Pu/<sup>137</sup>Cs are commonly used to identify and distinguish between global and regional sources of these radionuclides. The average activity ratios for <sup>238</sup>Pu/<sup>239+240</sup>Pu are 0.060 suggesting contributions from other than the global fallout sources of plutonium. Global fallout of radionuclides from the atmospheric nuclear weapons testing was characterized by the <sup>238</sup>Pu/<sup>239+240</sup>Pu activity ratios (for year 1973) of 0.025. The <sup>239+240</sup>Pu/<sup>137</sup>Cs activity ratios are 0.018 and are much lower than the decay-corrected value of ~0.06 expected for the year 2017, point to possible other sources of <sup>137</sup>Cs in these area. This study also reports evidence of <sup>240</sup>Pu/<sup>239</sup>Pu atomic ratios in the cryoconites. The average atomic ratio of  $^{240}$ Pu/ $^{239}$ Pu change within wide range between 0.117 and 0.229 with the mean value of 0.144. The results are higher and lower values of  $^{240}$ Pu/ $^{239}$ Pu atomic ratios than 0.180, indicating regional influences on Arctic fallout. Activity concentrations of airborne radionuclides in cryoconite samples from Spitsbergen were higher than in the soils from Spitsbergen. The main source of anthropogenic radionuclides in the Arctic is global fallout from atmospheric nuclear weapon tests and local fallout from tests conducted at Novaya Zemlya. <sup>210</sup>Pb in cryoconites is derived mainly from the atmospheric deposition and its activity concentrations reach high values up to 13000 Bg/kg. Occurences of seemingly cryoconite-derived material with high radionuclide contents in the glacier forefront indicate that the cryoconite granules can be retained on glacier surface and deposited at the terminus after ice melts out.

#### **BIOINDICATION AND BIOMONITORING (B & B) TECHNOLOGIES WITH SPECIAL CONSIDERATION OF LITHIUM AND ITS EFFECTS ON HUMAN**

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In recent years, a more intensive study of lithium has left a very significant insight into its effect on the human psyche. Since 1949 it has been successfully used in the treatment of manicdepressive (bipolar) disorders. A few years ago, it became apparent that higher concentrations of lithium in drinking water led to a reduction in the number of suicides. These results, first found in Japan, were soon confirmed in Austria and the USA.

Today, studies are already being conducted in which lithium deficiency is a possible and decisive factor in people's diseases such as dementia, Alzheimer's and others. But even in mentally influenced behavioural disorders, such as eating disorders due to personal dissatisfaction, lithium seems to play a physiological and biochemical function.

Lithium played no or only a subordinate role in bioindicative or biomonitoring investigations, for example to investigate atmospheric deposition with the help of mosses and lichens. This must change in the future, since lithium is relatively easily accessible analytically, for example via ICP/MS. However, particularly seasonal differences in lithium concentrations, such as those often found in ecto- and endrohydric mosses, must be taken into account.

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#### THE GRAPEVINE LEAVES AS BIOINDICATORS OF AIR POLLUTION BY TOXIC ELEMENTS AND MAGNETIC PARTICLES IN EXPERIMENTAL, COMMERCIAL AND ORGANIC VINEYARDS

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Biomonitoring of magnetic particles (PM) and potentially toxic elements (PTEs) using leaves could be suitable for the assessment of air pollution in an agricultural environment. The leaves of eight grapevine species (*Cabernet franc*, *Merlot*, *Prokupac*, *Cabernet sauvignon*, *Burgundy*, *Sauvignon blanc*, *Regent* and *Panonia*) were tested as biomonitors of PM and PTEs in three experiments performed in different vineyards (experimental, commercial and organic) in Serbia. Chemical and magnetic analyses were performed to determine PTE concentrations and magnetic particles (by saturation isothermal remanent magnetization, SIRM) in the leaf samples. *Experimental vineyard*. The study was conducted during 2013/2014. The associations between leaf species were identified. Applying ecological risk assessment formulas, the most polluted parcel in the vineyard was determined. In the case of all investigated species (*Cabernet franc*, *Merlot*, *Prokupac*, *Cabernet sauvignon* and *Burgundy*)<sup>7</sup>, there was found the influence of airborne Al, Cd, Cr, Cu, Fe, Ni and Zn (Ratio factor, RF>1) on the grapevine leaves from air pollution.

*Commercial vineyard.* During 2015, the experiment was conducted through the entire grapevine season. The influence of atmospheric deposition on the air-exposed leaves was observed  $(RF>1)^8$ . According to the correlations between biogeochemical index (BGI) and biological accumulation coefficient (BAC), bioaccumulation of B, Cd, Sb, Sr in the leaves was influenced by the atmospheric sources. The significant correlations between the element concentrations and SIRM values in leaves imply that the leaves (*Cabernet sauvignon* and *Sauvignon blanc*) indicate Co, Cr and Ni air pollution in the vineyard ambient. In addition, based on a comparison of the element concentrations in the grapevine leaves with those obtained by the moss bag biomonitoring in the same vineyard, significant correlations were observed between Co and Cr concentrations in the leaves and exposed mosses<sup>9,10</sup>.

*Organic* vineyard. The concentrations of PTEs in the organic grapevine leaves were lower than those measured in the studied experimental and commercial vineyards<sup>1,2,4</sup>. There was an indication that only airborne Al, Cr, Cu, Ni and Pb deposition have an influence on the outer parts of grapevine (leaf and grape skin) (RF>1).

Finally, all of the studies implied that the grapevine leaves could be a proxy for ambient air pollution by PM and PTEs in the vineyard ambient.

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### NANOPARTICLE POLLUTION AND BRYOPHYTES – POSSIBILITIES.

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Environmental concentrations of nanoparticles in the environment are continuously growing due to the increase in both the production of engineered nanomaterials and the nano-sized byproducts of other human activities. Monitoring of their presence in the atmosphere is, hence, important. Although bryophyte biomonitoring is widespread, not much attention has been paid to the possibilities of bryophyte application in the monitoring of nano-sized particulate pollution. Data on both the uptake mechanism and the distribution of the nanoparticles in the plant after the exposure are insufficient, nor have been the sample preparation and handling factors satisfyingly evaluated for their role in altering the nanoparticle accumulation patterns. Therefore, a series of studies was performed at the Nanotechnology centre (VSB-TU, Ostrava, Czechia): The differences in metal oxide nanoparticle accumulation following a simulated nano-pollution exposure of nano-ZnO and nano-TiO2 to samples of common biomonitoring bryophyte species Pleurozium schreberi and Hylocomium splendens were assessed. The impact of nanoparticle exposure on cell membranes integrity - by the assessment of potassium intra/extracellular ratio - and exposure-induced oxidative stress by L-ascorbic acid concentration determination in the tissue of the samples were also studied. Finally, factors of sample treatment affecting the distribution of the accumulated metals in the mosses – such as pre-exposure washing or oven-drying - were evaluated. Both the nanomaterials accumulated in the moss samples in similar, linear, rates while H. splendens was found to be mildly better accumulator. The nanoparticles were proved to not only adhere to the surface of the plants but to successfully penetrate the cells. Significant decrease of L-ascorbic acid concentration was observed following the exposure. The bryophytes assessed were found to be suitable possible biomonitors of nanoparticle air pollution as well as model organisms for the research of nanosized pollutant induced stress in plants.

# δ<sup>15</sup>N IN LICHENS REFLECTS THE ISOTOPIC SIGNATURE OF AMMONIA SOURCE

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Although it is generally accepted that  $\delta 15N$  in lichen reflects predominating N isotope sources in the environment, confirmation of the direct correlation between lichen thalli and atmospheric  $\delta^{15}$ N is still missing, especially under field conditions with most confounding factors controlled. To fill this gap and investigate the response of lichens with different tolerance to atmospheric N deposition, thalli of the sensitive Evernia prunastri and the tolerant Xanthoria parietina were exposed for ten weeks to different forms and doses of N in a field manipulation experiment where confounding factors were minimized. During this period, several parameters, namely total N,  $\delta^{15}$ N and chlorophyll a fluorescence, were measured. Under the experimental conditions,  $\delta^{15}N$  in lichens quantitatively responded to the  $\delta^{15}N$  of released gaseous ammonia (NH<sub>3</sub>). Although a high correlation between the isotopic signatures in lichen tissue and supplied N was found both in tolerant and sensitive species, chlorophyll a fluorescence indicated that the sensitive species very soon lost its photosynthetic functionality with increasing N availability. The most damaging response to the different N chemical forms was observed with dry deposition of NH<sub>3</sub>, although wet deposition of ammonium ions had a significant observable physiological impact. Conversely, there was no significant effect of nitrate ions on chlorophyll a fluorescence, implying differential sensitivity to dry deposition versus wet deposition and to ammonium versus nitrate in wet deposition. Evernia prunastri was most sensitive to NH<sub>3</sub>, then NH<sub>4</sub><sup>+</sup>, with lowest sensitivity to NO<sub>3</sub><sup>-</sup>. Moreover, these results confirm that lichen  $\delta^{15}$ N can be used to indicate the  $\delta^{15}N$  of atmospheric ammonia, providing a suitable tool for the interpretation of the spatial distribution of NH<sub>3</sub> sources in relation to their  $\delta^{15}$ N signal.

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# DEVELOPMENT OF ECOSYSTEM DATA BASE IN SERBIA

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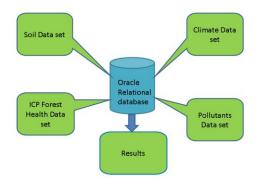
In SEPA we developed Oracle Relational database with 4 different data sets. The aim is Ecosystem data base creation. Main purpose is research of different environmental effects on vegetation.

Defoliation is one of the main forest health parameters monitored by the ICP Forests. The loss of assimilation organs during the summertime is an indicator of tree health condition, and the leaf loss percentage is evaluated on sample plots according to the methods and criteria for harmonized sampling, assessment and monitoring. All data were gathered annually at forested plots that were placed on a  $16 \times 16$  km grid, following harmonized methods for the period 2003-2014.

Wet, dry and total deposition and concentration of air pollutants was assessed using the standard methodology, specified by European Monitoring and Evaluation Program (EMEP). EMEP calculates National totals for Serbia for concentration and depositions of sulphur and nitrogen oxides and reduced nitrogen for the period 2004-2014.

We used climate data were collected by the Republic Hydro-meteorological Service of Serbia. Climatological standard normals are averages of climatological data computed for the following consecutive periods of 30 years. Usually it is used period from 1961 to 1990 as a standard normal, and calculated the normalized anomalies of temperature, precipitation and from the standard normals for each year and summer season from 2003 to 2014.

Soil data set includes soil map data from 1985, soil organic carbon content until 2010 and soil monitoring data until 2017.



For the start we analyzed sensitivity of dominant trees species in Serbian forest ecosystems to stress conditions caused by air pollution, acid deposition and unfavorable climate. The most sensitive species to increased level of air pollutants SO2 and HNO3 in 2003 and 2004, on the territory of Serbia are conifers Picea abies, Abies alba and Pinus sylvestris. Around cupper mining Bor (Eastern Serbia) total SOx has the greatest effect on Quercus frainetto and Quercus cerris defoliation and dead trees in 2014. The greatest defoliation of these species was observed in years with extended concentration of air pollutants and acid deposition.

## ELEMENT SIGNATURES AND LICHENS: A HISTORICAL PERSPECTIVE IN AIR POLLUTION STUDIES

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Since Oliver Gilbert's pioneering biomonitoring research carried out in and around Newcastle, UK, 40 years ago, studies highlight lichens as sensitive bioindicators of spatial and temporal patterns of element deposition. Biomonitoring at the local scale across point sources, including mining and smelting enterprises to the East of UK, provide natural laboratories to test biomonitoring methodologies. This has implications for policy and for assessing exposure to substances derived both locally, and from long distance aerosol transport, potentially harmful to human and environmental health. Examples include analysis of sulphur isotopes, investigating other biogeochemical signatures, including rare earth element patterns and rare element ratios in lichens and other materials as indicators of sources of geological materials.

## SUPPORT OF THE IAEA TO STUDIES RELATED TO ATMOSPHERIC POLLUTION: PAST AND PRESENT PROJECTS

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Through the Nuclear Science Programme the IAEA carries out activities to assist and advise its Member States (MSs) in assessing their needs for capacity building, research and development in the nuclear sciences and applications, as well as in supporting the MSs' activities for deriving benefits in specific fields of nuclear techniques and associated technologies.

During the last 20 years, the IAEA Physics Section has contributed to capacity building (knowledge and expertise) in the effective utilization of X-ray spectrometry and Ion Beam analysis techniques using a variety of accelerator based, laboratory and portable instrumentation. These techniques, often called nuclear and related analytical techniques (NATs), among other areas of applications, are also advantageous for the multi-elemental analysis of environmental samples used to assess the air quality, including airborne particulate matter collected on filters and species used for biomonitoring.

The IAEA has fostered the introduction of NAT in air quality studies. A summary of the past and present projects covering all geographical regions, supported and implemented by the IAEA is presented.

### THE DISPERSION MODEL FOR AIR POLLUTANTS AUSTAL2000 UNDERSTANDS DEPOSITION AS LOSS AND NOT STORAGE

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By the authors JANICKE(2000, 2002), Germany, for the calculation of the dispersion of air pollutants under the designation AUSTAL2000 a "model-based assessment system for the plant-related immission control" is developed. This propagation model is declared binding in the Federal Republic of Germany for application. All other model developers have to validate their algorithms on the provided reference solutions. However, SCHENK(2015, 2017), Germany, for example, demonstrates that these reference solutions are flawed. Principal and conservation laws are violated. The rigid rotation of a solid is confused with 3D wind fields. One speaks of the procedural basic operation homogenizing and means diffusion. After filling a control room with Luftbeimengungen one obtains a constant concentration distribution. One wants to make believe that then without energy input a redistribution takes place so that there is a barometric height distribution. For the calculation of the soil concentration results an indefinite expression, which is why one must calculate this deceptively. For two identical boundary value tasks different solutions are given. Air particles can not "see" and want to penetrate solid walls. One distinguishes "true" and "untrue" deposition rates. Finally, deposition is understood as loss, not storage, which is the subject of this work. Even GRAEDEL & CRUTZEN(1994), USA & Germany, believe that, for example, gas molecules can be lost through deposition. This view must also be corrected. In various publications and other statements of opinion of TRUKENMÜLLER(2015, 2016, 2017), Federal Environmental Agency Germany, the objections raised by SCHENK(2015, 2017), Germany, are denied and it is violently contradicted. One points to alleged misunderstandings and physical incomprehension. In this paper, the identified contradictions are analyzed in depth and the results of all studies are summarized. The authors of the AUSTAL refer to an allegedly universal agreement, which by VENKATRAM(1999), USA; should be justified. However, it turns out that it can not be read there with detrimental consequences for the modeling there. Moreover, the described relationship between deposition and sedimentation is flawed. The previously mentioned agreement, which is referred to below as the Janicke Convention, is intended to replace physically justified boundary conditions, but this contradicts the theory of ordinary differential equations. Chimerically, one tries to disguise the contradictions that have been recognized. Because other authors also use the erroneous results, e.g. in SIMPSON(2012), Norway imperatorily demands recognition of the Janicke Convention. It is also fabulated to have come up with a novel doctrine. It is shown by the author that all these claims are without object. It lacks the required knowledge in the field of momentum, heat and mass transfer. Only mathematics and mechanics as tools of incorruptible evidence are used for the assessment. The results are explained to the reader by means of formulas and graphics.\*

### Key words:

AUSTAL2000, dispersion calculations, particle model, sedimentation, deposition, air pollutants

### Summary

In Axenfeld et al. (1984) formulated a model for the calculation of dust spreading, which was later published by Janicke et al. (2002) was further developed into a "model-based pollution control system" called AUSTAL2000. In this context reference solutions are made available according to VDI (2000) and declared binding for other model developments within the Federal Republic of Germany. Schenk (2015-2) demonstrates that these reference solutions are flawed

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and not suitable for comparative calculations. The second law of thermodynamics and the law of mass conservation are violated. In Trukenmuller et 13alii. (2015) and Trukenmüller (2016) are contradicted. By means of an allegedly defined deposition rate and supposed convention according to Venkatram (1999) one wants to prove the opposite. However, it is true that no convention and definition of the deposition rate can be found there, and the derived connection between deposition and sedimentation is not correct. In addition, one imperatorically invokes other authors as well. Because in Simpson et 17alii. (2012) for the development of "The EMEP MSC-W chemical transport model - technical discription" also the erroneous connections according to Venkatram (1999) are used, obviously the own discussion with physical bases should be given up. For clarity, the term will be referred to as the Janicke convention. The present work is superficially concerned with these aberrations. It also shows that the authors of the AUSTAL in Janicke et al. (2002) deal only superficially with the convention they have introduced and others attributed to them. In fact, because of the boundary condition used in Venkatram (1999), they would only have a trivial solution with a vanishing concentration distribution. Even this fact is ignored in the already erroneous reference solutions. To demonstrate this, the author first derives the physically established deposition rate and explains its use in connection with the implementation of propagation calculations. The valid and faulty reference solutions are further analyzed and the background of the already described shortcomings revealed. The claimed violation of the Principles and Conservation Laws is due to the uncritical adoption of the results of Venkatram (1999) and the use of an alleged universal convention, which has only one aim, namely to disguise the inadequacy of its own considerations. Furthermore, in the present work, unlike Venkatram (1999), the physics-based relationship between sedimentation and deposition is given. The concept of GRAEDEL et al. (1994) according to which, for example, gas molecules could be lost by deposition is faulty. Finally, selected simulation results are compared with differently defined deposition rates. They exemplify all opposites. For the sake of clarity, all analytical correlations in formulas are described.\*

## A NOVEL APPROACH USING MOSS BAGS TO EXPLORE INDOOR VS OUTDOOR ELEMENTAL POLLUTION SOURCES

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Air quality is of primary importance for human health since a noticeable number of diseases, especially affecting respiratory and cardiovascular systems, are strongly correlated to air pollution. Although air biomonitoring is mostly focused on the assessment of outdoor pollution, such an approach shows a limited effectiveness, since people spend most of their time indoors. Therefore, the evaluation of human health risk should include the personal exposure to indoor pollution. In view of this perspective, this study investigated by the moss-bag approach the pattern of air dispersed elements in 12 coupled indoor/outdoor exposure sites, all located in urban and extra-urban residential areas. The aims were: i) to test moss-bag sensitivity in discriminating indoor vs. outdoor trace element composition in coupled exposure sites; ii) to compare the indoor and outdoor element patterns; iii) to relate the differences to environmental characteristics. Fifteen elements out of 53 considered (As, B, Ca, Co, Cr, Cu, Mn, Mo, Ni, Sb, Se, Sn, Sr, V, Zn) were enriched in moss exposed outdoor, whereas only 7 of them (As, B, Cr, Mo, Ni, Se, V) were also enriched in indoor moss samples. The cluster analysis of the sites based on all element contents, clearly separated samples in two groups corresponding to mosses exposed indoor and outdoor, with the latter generally exceeding the first.

In outdoor environment a higher number of element was enriched in mosses exposed in urban sites (12-25) than in extra-urban sites (9-15); by contrast, no clear pattern was observed for indoor moss samples, suggesting that several specific factors (e.g., heating and cooking systems, building material, furniture, time and ventilation system,...) could contribute to the element fingerprint of indoor environments. Based on the site specific Indoor/Outdoor ratio, As, B, Mo and Se were mostly enriched in outdoor sites, whereas Ni, Cr and V were mostly enriched in indoor samples, supporting the presence of indoor emitting sources for these elements. These results show the high sensitivity of mosses transplanted in bags in discriminating outdoor and indoor levels of air dispersed elements, indicating the validity of this approach to provide crucial information for a more wide-ranging assessment of health risk exposure.

## MONITORING ATMOSPHERIC DEPOSITION OF ORGANIC POLLUTANTS IN NORWAY USING TERRESTRIAL MOSS

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Following initial studies on air concentrations of persistent organic pollutants (POPs) at a limited number of sites, some groups of compounds were incorporated in the national deposition program for air pollutants based on sampling and analysis of moss samples. In this presentation selected data from the 2010 and 2015 moss surveys are discussed, based on samples from 20 sites distributed over the country. Groups of compounds studied include polynuclear aromatic hydrocarbons (PAH), polychlorinated diphenyls (PCB), polybrominated diphenyl ethers (PBDE), chlorinated paraffines, and selected pesticides. 3-litre samples of Hylocomium splendens are collected with clean hands at 20 selected sampling sites all over the country and transported to the laboratory in portable coolers with ice packs. Portions of moss are then extracted with selected organic solvents prior to analysis by GC-MS techniques. Combustion products such as PAH are generally higher in the south of the country, and at least in part associated with long-range atmospheric transport of pollution aerosols from other countries of Europe. Chlorinated compounds such as PCB are fractionated during the atmospheric transport as evident by relative enrichment of lower-mass members with northern latitude. A corresponding fractionation is observed among members of the PAH group. Most compounds included in both surveys showed a decline from 2010 to 2015. The fractionation patterns observed in the moss surveys confirm geographical trends previously observed in air sampling of POPs at a smaller number of sites in Norway.

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## SURVEY OF HEAVY METAL DEPOSITION IN ROMANIA; TEMPORAL TRENDS AND SPATIAL DISTRIBUTION: 2010 AND 2015

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Data on concentration of heavy metals (Al, V, Cr, Fe, Ni, Cu, Zn, As, Cd, Sb and Pb) in moss collected on the territory of Romania in 2010 and 2015 were used to estimate the contribution of local pollution sources to the total metal air pollution level and to define tendencies in the changes of atmospheric deposition of heavy metals in moss.

Concerning the air pollution with heavy metals, the moss data sets, acquired using the standardized methodology established in the framework of the European Moss Survey coordinated by the UNECE ICP Vegetation, have revealed that there is still a problem in the northern and north-western parts of Romania.

A strong decrease in median concentration in mosses between the two Romanian moss survey was recorded for Cd (-78%), Cu (-68%) and Pb (-86%). For Al, Cu, Fe, Ni, Sb, V and Zn a small concentration decrease was found (-5% to -14%). For As, a considerable increase of concentration was found (+37%).

In comparison to median heavy metal concentrations in the other (Eastern) European countries, the heavy metal concentrations in mosses collected from Romania were comparable or relatively higher.

# ATMOSPHERIC DEPOSITION OF IODINE AND POTENTIAL SOURCES IN ARMENIA

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Iodine concentrations in 76 moss samples collected during the 2015/2016 moss survey in the Republic of Armenia (Fig. 1) were assessed to reveal spatial patterns and potential sources of origin. Iodine content ranges from 0.5 to 9.4 with a mean of 3.6 mg/kg, coefficient of variation is 58.5%. The Shapiro-Wilk test showed that iodine is abnormally distributed, and a boxplot revealed an outlier spatially located in the slope of Geghama Mountains near the shore of Lake Sevan. The spatial distribution of iodine values showed that 25% of the samples had values greater than 5 mg/kg. These samples are located mostly in the mountain regions of Armenia: in the Geghama Mountains and the Syunik highland. This may be explained by the fact that the

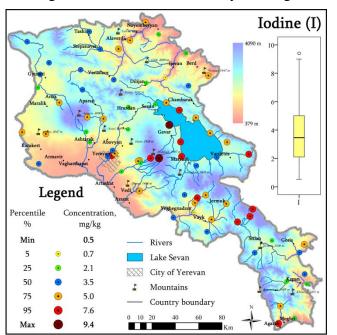


Fig. 1. Iodine contents spatial distribution in Armenia

northern regions of Armenia are partly influenced by the Black Sea, and the northeastern and south-eastern regions by the Caspian Sea. Besides it is known that the highest levels of precipitation are observed territories in these suggesting that atmospheric deposition can be a potential source of iodine. The correlation analysis of I with the sampling point altitudes showed significant Spearman correlation coefficient (0.368, p<0.01). According to a previous study [1] Iodine contents in the 0-25 cm of brown soils of Armenia are within the range 1.6-3.4 mg/kg whereas in chernozems the corresponding range is 2.2-7.5 mg/kg. Moreover, positive correlation between soil iodine concentration and altitude was also observed. This is verified by the results of the present study.

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### LICHENS AS BIOMONITORS OF LONG-RANGE TRANSPORTED TRACE ELEMENTS UNDER DIFFERENT ALTITUDES AND DIFFERENT AIR MASS INFLUENCES

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A set of transplanted lichen Parmotrema bangii were exposed for 5, 7 and 12 months to assess the deposition of trace elements and their possible origins in Pico mountain. The elemental concentrations of 38 elements were determined in 28 locations over the mountain surface between sea level (50 m - baseline of marine layer) up to the summit (2,250 m - low free troposphere). The EC ratio showed that the concentrations of almost all the elements increased with respect to the control, at all mountain surfaces, especially during winter, with winds causing soil re-suspension and consequent accumulation. Local soil was also analyzed to calculate EF to further assess atmospheric pollution. Samples showed high soil enrichment with exception of Ba, Br, Ce, Cl, I, Hg, Sb, Th and Zn, for which high values were found mainly in the western surface, corresponding to the prevailing air masses origins from North America. Moreover, PCA results showed that major sources of atmospheric elements are soil with anthropogenic contamination, Sahara particles from dust events, re-suspension of local soil, marine elements. Transplanted lichens showed a distinct accumulation of atmospheric elements under the two different layers in accordance with aerosols studies previously completed, suggesting the usability of transplanted lichen as biomonitors of long-range transported elements at high altitudes (LFT).

# THE USE OF *PLEUROZIUM SCHREBERI* IN BIOMONITORING OF THE FOREST AREAS OF SOUTHERN AND NORTH-EASTERN POLAND

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Forest ecosystem is highly degraded by human activity, but it is perfectly able to clean and regenerate by itself. Therefore, plants growing in forests are an excellent material for understanding the mechanisms of translocation.

The aim of the study was to assess the contamination and the seasonal changes in accumulation of selected heavy metals (Ni, Zn, Cd and Pb) in *Pleurozium schreberi* moss growing in the forest of southern and north-eastern Poland. The research was focused on the assessment of sources (primary and secondary) of contaminants accumulated in plants and the assessment of the impact of ecosystems` contamination and seasonal changes on the concentrations of heavy metals in the studied samples.

The three-year biomonitoring study indicated that among the studied areas the greatest accumulation of heavy metals in the studied species of moss was present in the Beskidy Mountains. The samples in which the lowest concentrations of heavy metals were determined were collected in the north-eastern areas of Poland. Also, seasonal changes in metal concentrations were observed, but they differ in particular years, which may be the result of differences in meteorological conditions during the research. The PCA method did not show the relationship between the studied heavy metals, but proved good lead accumulation properties of the *Pleurozium schreberi* moss.

The study was performed within the framework of the project: *Ecosystem stress from the combined effects of winter climate change and air pollution - how do the impacts differ between biomes?* (WICLAP) Polish Norwegian Research Programme (NCRD) POL-NOR/ 198571/83/2013.

# BIOMONITORING OF HEAVY-METAL CONTAMINATION OF FOREST AREAS IN SOUTHERN AND NORTH-EASTERN POLAND USING MOSS

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In the years 2014–2016 biomonitoring studies were conducted in the forest areas of south and north-eastern Poland: the Karkonosze Mountains, the Beskidy Mountains, the Borecka Forest, the Knyszyńska Forest and the Białowieska Forest. In this study epigeic moss *Pleurozium schreberi* was used. Samples were collected in spring, summer and autumn.

In the samples, Mn, Ni, Cu, Zn, Cd, Hg and Pb concentrations were determined. Based on the obtained results, the studied areas were ranked by extent of heavy-metal deposition: Beskidy > Karkonosze Mountains > forests of north-eastern Poland.

In data analysis a mixed effect model was used. In the model changes in a metal concentration were related to year, season and forest location. Significance of the parameter in the model was verified.

Influence of parameter on metal's concentration depend on the element type. This effect indicates different sources of metals. There was observed, i.a., an increase in Cd concentration at the beginning of the growing season, which may be related to low emissions during the heating season. Analysis of the surface distribution of deposition of metals in the studied areas showed a significant contribution of nearby territorial emissions and unidentified local emission sources. The contribution of distant emission to Zn, Hg and Pb deposition levels in the Karkonosze and Beskidy region was also indicated.

Using methods of Compositional Data Analysis common relationships between metals' concentrations were studied. Some patterns in data were observed.

### ACTIVE MOSS BIOMONITORING OF TRACE ELEMENTS WITH SPHAGNUM GIRGENSOHNII IN RELATION TO ATMOSPHERIC BULK DEPOSITION: CHISINAU CASE STUDY

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For the first time active moss biomonitoring was used to assess trace element deposition in the capital of the Republic of Moldova, Chisinau. Moss *Sphagnum girgensohnii* samples were exposed in bags at three sites of Chisinau from October, 2016 to March, 2017. The content of 30 elements: Na, Mg, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Br, Rb, Mo, Sr, Sb, Ba, La, Ce, Hf, Th, Cu, Cd, Pb, and U in the exposed and unexposed mosses was determined by neutron activation analysis and atomic absorption spectrometry. According to the relative accumulation factor, the most abundant elements in the samples were V, Cr, Fe, Ba, La, As, Sb, U, and Pb. Such elements as Cl, K, and Rb were depleted from the moss tissue during the time of exposure. Principal component analysis was used to identify and characterize different pollution sources. The obtained results indicate that the use of *S. girgensohnii* moss bags is a simple and inexpensive technique to monitor major and trace element content in the air of urban area.

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# POSTERS

# MAGNETIC FINGERPRINT OF PARTICLE AND PARTICLE-BOUND AIR POLLUTION ON DECIDUOUS TREE LEAVES IN URBAN AREA

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Magnetic biomonitoring using tree leaves has been proven as proxy for airborne particle matter (PM) pollution and may acts as an ecosustainable tool for environmental protection management. As a complex mixture, PM carries multiple chemical species, such as trace elements, which contributes to the toxicity of PM. The leaf entrapment of PM is species-specific and it is of importance to select tree species which reliably reflects PM pollution. In this study, four tree species common in urban areas of Europe and wider (Aesculus hippocastanum, Acer platanoides, Betula pendula and Tilia cordata) were investigated to select the appropriate biomonitor that enables the most consistent 'signal' to a particle and particle-bound toxic elements. The tree leaves were sampled in the central urban and suburban parks in Belgrade (Serbia) in May and September from 2011 until 2014. Magnetic PM fraction in the leaf samples was quantified by Saturated Isothermal Remanent Magnetization (SIRM) while the concentrations of Al, Cr, Cu, Fe, Ni, Pb and Zn were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Magnetic and elemental measurements were considered in a relation to the regulatory PM10 data performed by local authorities. The median leaf SIRM values of T. cordata, A. hippocastanum and A. platanoides (174, 140, and 123 ×10<sup>-</sup>  $^{5}\times$ A m<sup>2</sup> kg<sup>-1</sup>, respectively) implied the considerable capacity of these species for capturing magnetic particles contrary to *B. pendula* ( $68 \times 10^{-5} \times A \text{ m}^2 \text{ kg}^{-1}$ ). However, *B. pendula* leaves showed the significant correlation of the SIRM and PM10 values (r=0.75), the SIRM and element concentrations, and spatio-temporal differences in the SIRM/element content between the studied parks/years. These results recommend B. pendula as a valuable biomonitor of PM and its associated elements. Nevertheless, both the results (high SIRM values, the significant correlation between SIRM and PM10 - r=0.71) and literature findings (abundance, adaptability, PM removal efficiency), favour A. platanoides over B. pendula in magnetic biomonitoring of particles.<sup>11</sup> These results can be an important achievement concerning the recognition and control of air quality as well as environmental protection in urban areas.

<sup>&</sup>lt;sup>11</sup> Aničić Urošević M., Vuković G., Stević N., Deljanin I., Nikolić M., Tomašević M., Samson R., 2018. Tree leaf magnetic biomonitoring of particle(-bound) air pollution: An ecosustainable tool for environmental protection management. Ecological Indicators, *submitted for publication*.

# EFFECT OF TEMPERATURE AND HUMIDITY ON THE PERFORMANCE OF CHARCOAL CANISTER PASSIVE <sup>222</sup>RN DETECTORS

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The dependence of radon adsorption on the temperature up to 35  $^{\circ}$ C was studied for 4" open face (OF) charcoal canister at different values of relative humidity using a radon calibration chamber which was previously constructed. This carried out using variable and controlled radon concentration, humidity, and temperature. Sets of calibration factor (CF) and adjusting factor (AF) curves were established at different temperatures (T= 20, 25, 30, and 35  $^{\circ}$ C) at different humidity (RH=20, 50, and 80%). These curves are used to extend the use of open-faced charcoal canisters for higher temperature and humidity applications. The optimum exposure time to achieve the best detection accuracy was estimated between 2 and 4 days depending on relative humidity. The open-faced canisters have higher efficiency of radon absorption at low temperature.

**Keywords:** Radon; Charcoal canisters; Calibration factor; Humidity, Temperature dependence.

# NATURAL AND ARTIFICIAL RADIONUCLIDES IN MOSS SAMPLES FROM THE REGION OF NORTHERN GREECE

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Terrestrial mosses obtain most of their nutrients directly from precipitation and dry deposition. They can be used as biological indicators of airborne radionuclide depositions.

Ninety-five (95) samples of *Hypnum Cupressiforme* Hedw. were collected in Northern Greece in a short time interval during the end of summer 2016, covering a regular grid of 30 km x 30 km. Samples were collected from different altitudes, from 30 m to 1450 m above the mean sea level. After sampling and preparation of samples, mosses were measured using gamma spectrometry. They were measured in a low-background HPGe detector with relative efficiency 32%.

The activity concentrations of different radionuclides were determined. <sup>7</sup>Be ranged from 69 to 1280 Bq kg<sup>-1</sup>, and the concentrations of <sup>137</sup>Cs ranged from 0 to 425 Bq kg<sup>-1</sup>. The concentrations of <sup>210</sup>Pb were between 147 and 1920 Bq kg<sup>-1</sup> and for <sup>40</sup>K were between 120 and 750 Bq kg<sup>-1</sup>. Differences have been observed in the activity concentrations between mosses collected from different surface types such as ground surface, rocks, branches and near roots. Mapping of <sup>7</sup>Be and <sup>210</sup>Pb activity in mosses provide information about aerosols deposition and help tracking their pathway. Finally, no correlation between the concentrations of <sup>7</sup>Be and <sup>210</sup>Pb has been found.

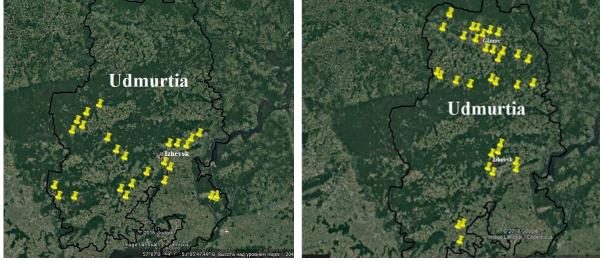
# MOSS MONITORING OF TRACE ELEMENTS IN THE REPUBLIC OF UDMURTIA, RUSSIA

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Results on atmospheric deposition of trace elements in the moss survey in 2016-2017 in the Republic of Udmurtia, Russia, are reported. Udmurtia is an industrial region allocated in the east of the East-European Plain, where it goes to the Western Urals. An important role in its economy belongs to enterprises of the military-industrial complex, machine tools and automotive, building materials and mining. Samples of moss were collected over the territory Republic in accordance with the guidelines of the Moss Manual 2015/2016 of the UNECE ICP Vegetation. Coordinates of the sampling sites were very close to those used in the first moss survey in Udmurtia carried out in 2005-2006 (Pankratova et al., 2007, 2008). Conducted research to Supplement and expand the information charges of the samples of moss that were conducted in 2005 and 2016 (Pankratova et al., 2007, Bukharin, etc., 2017). A total of 39 elements were determined by neutron-activation analysis and atomic absorption spectrometry (Pb, Cd, and Cu). Multivariate statistics (factor analysis) and geochemical mapping were applied for data interpretation.



Moss monitoring network in Udmurtia, Wester Urals, in 2016

Moss monitoring network in Udmurtia, Wester Urals, in 2017

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# LONG TERM TREND EVALUATION OF MERCURY CONCENTRATIONS IN AIR AND PRECIPITATION AT THE BACKGROUND AREA OF CENTRAL EUROPEAN PART OF RUSSIA

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Mercury is one of the priority pollutants been selected for monitoring in environmental media by international organizations and research programs. The lifetime of mercury in its elemental form is estimated to be from days to months which is longer than for many other pollutants. Being emitted into the atmosphere mercury could be transported for long distance and are detected far from sources, including remote areas and background territories such as biosphere reserves. The program of integrated background monitoring network (IBMoN) in the Russia incudes the measurements of Hg in atmosphere and other environmental media. However, there is only one IBMoN station, in Prioksko-Terrasny biosphere reserve, provided long term data on concentrations of mercury both in air and precipitation for the period since 1980s. The sampling area is located in remote area of Central European Russia to the south from Moscow at the boundary of forest zone. The samples are collected in glass tube absorber by low-volume force pumping of air through the silver amalgam sorbent. In laboratory a mercury concentration is determined by means of atomic absorption spectrometry. In this research on trend estimation we paid more attention to the period since 1990s by using two approaches. The first way is the application of well-known linear trend analysis with the Mann-Kendall test and Sens slope approach to the averages. It was realized into MAKESENS package within Excel software. The results were prepared for both whole time series and their sub-periods of different tendencies. The second approach is the approximation of trend by bi-exponential curve with filtering periodic (seasonal) fluctuations. The monthly average values were tested and evaluated with the use of ad hoc MSC-East data tool (special FORTRAN program prepared by Modeling Center of EMEP, Moscow). Presented results of estimation are ambiguous for interpretation and demonstrate various tendencies for different time periods.

Key words: Background monitoring, atmospheric mercury, air pollution, precipitation, trend analysis

# LEAF-DEPOSITED SEMI-VOLATILE ORGANIC COMPOUNDS (SVOCS): AN EXPLORATORY MONITORING STUDY USING GCXGC-TOFMS ON LEAF WASHING SOLUTIONS

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Airborne particulate matter (PM) includes semi-volatile organic compounds (SVOCs), which can be deposited on vegetation matrices such as plant leaves. In this study, leaf washing solutions from ivy leaves exposed during one-month period at different land use classes were explored via comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-TOFMS), after an online sample preparation with solid-phase extraction. The composition of leaf-deposited SVOCs was compared against routinely monitored air pollutants concentrations (PM10, PM2.5, O3, NO2, SO2) which were measured at co-located air quality monitoring stations.

A total of 911 different organic compounds were identified for all study sites. While no significant land use effects were observed, increasing exposure time resulted in a higher number and diversity of SVOCs, suggesting cumulative time-integration to be more relevant than variations between study sites. After one day, leaf-deposited SVOCs were mainly due to alcohols, N-containing compounds, carboxylic acids, esters and lactones, while ketones, diketones and hydrocarbons compounds gained relevance after one week, and phenol compounds after one month of exposure. As leaf-deposited SVOCs became overall more oxidized over time, SVOCs transformation at the leaf surface is suggested to be an important phenomenon. Confirmed the applicability of GCxGC-TOFMS to analyze SVOCs from leaf washing solutions, further research should include validation of the methodology and comparison with atmospheric organic pollutants.

# NUCLEAR AND RELATED TECHNIQUES USED FOR POLLUTION INVESTIGATIONS IN ENVIRONMENT AND HEALTH RISK ASSESSMENT

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The paper is reviewing several applications of multi-elemental nuclear and related techniques for the determination of elemental composition of selected environmental and pollution biomonitor samples: soils, cultivated plants, mushrooms, mosses, tree leaves.

The employed techniques were: instrumental neutron activation analysis (INAA), inductivelycoupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), energy dispersive X-ray fluorescence (ED-XRF), and ion beam techniques particle-induced X-ray emission (PIXE) and particle-induced gamma-ray emission (PIGE), The environmental and biomonitor samples were investigated using validated techniques at partner institutions Dunarea de Jos University of Galati (UDJG), Valahia University of Targoviste (UVT), Institute of Multidisciplinary Research for Science and Technology, and Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), Romania, and Frank Laboratory of Neutron Physics (FLNP) of Joint Institute of Nuclear Research (JINR) at Dubna, Russian Federation.

A discussion is made regarding their suitability to be used in environmental studies, for the investigation of contamination with metals, inorganic toxicants occurence in environmental factors, as well as for pollution studies using biomonitors. The advantages are highlighted for each technique concerning the sensitivity, selectivity, level of matrix effects, cost of analysis, etc.

Based on the obtained results, coefficients of transfer of metals from environment to plant tissues have been assessed and a calculation of health risk for population by consuming food items from industrial areas has been done.

# FIRST MOSS SURVEY IN TAJIKISTAN

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Within the framework of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops, the distribution of heavy metals and radionuclides in mosses in Tajikistan were investigated. The concentrations of heavy metals and radionuclides are determined by the neutron-activation analysis method. Many small industries located in Tajikistan are important sources of heavy metals emissions. Especially, aluminum, cement and antimony factories, as well as heat-electric central operating in coal combustion, are the main sources (especially for Al, Hg and Pb). Currently, due to improper disposal of industrial waste and the filtration process, the spread of heavy metals has become one of the main factors of atmospheric pollution. Most of these enterprises are very close to the settlements and adversely affects the state of the inhabitants of a given region [1].

The Republic of Tajikistan for the first time took part in the European moss survey in 2015/2016. In May 2015, were collected 25 moss samples at 23 sampling sites distributed over the territory of Tajikistan. The most dominant and widespread moss species in Tajikistan are Pleurozium schreberi and Hylocomium splendens. The study was conducted to assess air quality in the territory of Tajikistan, to generate information necessary for better identification of pollution sources, and to create a database for future surveys.

Fluctuations in the level of pollution of the air basin occur to a large extent under the influence of atmospheric conditions that determine the transport and scattering of impurities. To assess this phenomenon, a characteristic called the potential for atmospheric pollution is used and determines the ability of the atmosphere to scatter or accumulate pollutants in a given area. In mountainous areas of Central Tajikistan, the wind regime depends, first of all, on orographic features, which in turn stimulate the potential for air pollution. In large cities, there is a significant amount of exhaust emissions from cars, which increase the flow of heavy metals into the atmosphere. Therefore, it is necessary to know the current state of the air environment, its potential capabilities and ways to overcome or reduce side effects.

A total of 45 elements (Na, Mg, Al, Cl, K, Sc, Ca, Ti, Cr, V, Mn, Ni, Fe, Co, Zn, Pb, Cu, Se, As, Br, Sr, Rb, Zr, Mo, Cd, Sb, I, Ba, Cs, La, Ce, Nd, Eu, Gd, Sm, Tb, Yb, Tm, Hf, Ta, W, Au, Hg, Th and U) were determined using the instrumental epithermal analysis of neutron activation and atomic absorption spectrometry [2]. The results for some selected elements are shown in Figure 2a and 2b. The diagram in Figure 2a shows a high content of Al and Fe almost in all sampling points. If one of the main reasons are factories for the production of aluminum and cement (affecting the areas of Khanako, Luchob and Kharangoni Bolo), then another reason can be called the often occurring in the warm season the dust-storm from Afghanistan. Light fractions of dust storms can reach up to the South and Central part of Tajikistan.

From the data obtained, it can be concluded that main anthropogenic sources of heavy metals are heat-electric center, transport and small industrial activities. Three different indicators, the C<sub>F</sub> pollution factor, the I<sub>geo</sub> geocoding index and the pollution load index used to quantify the degree of pollution indicate moderate or severe industrial pollution located around the main industrial centers - the municipalities of Ziddi, Sioma, the Gorge of the river Adzhuk 1 and 2, Iskandarkul, Artuch, Kharangoni Bolo.

The methodology of moss biomonitoring proved to be an effective method for studying the atmospheric deposition of heavy metals, as well as other trace elements and identification of pollution sources [3]. The study showed that a relatively inexpensive method of moss can be

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used to determine regional differences and temporal changes in the deposition of several elements. This allows documenting the effectiveness of emission reduction measures. ilogy of moss biomonitoring proved to be an effective method for studying the atmospheric deposition of heavy metals, as well as other trace elements and identification of pollution sources. The study showed that a relatively inexpensive method of moss can be used to determine regional differences and temporal changes in the deposition of several elements. This allows documenting the effectiveness of emission reduction measures.

With a view to a detailed study of the state of the atmosphere proceeding from the small number of investigated territories, it can be concluded about the need to increase the sampling area and further work on the entire territory of the Republic of Tajikistan It is important to continue the moss survey in all of the territories of Tajikistan

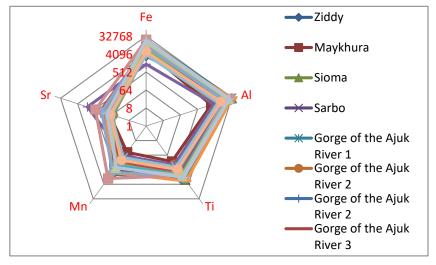


Figure 2 a. Concentration charts (mg / kg) of more common main environmental pollutants in Tajikistan

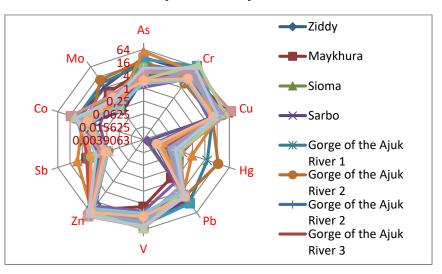


Figure 2 b. Concentration charts (mg / kg) of more common main environmental pollutants in Tajikistan

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# TERRESTRIAL ISOPODS AS POTENTIAL BIOINDICATORS OF ANTHROPOGENIC POLLUTION OF SOIL – COMPARISON OF TWO METHODS OF ANALYSES

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Terrestrial isopods (woodlice and pill bugs) have been proved to be reliable as indicators of pollution of environment. They are widespread throughout Europe, relatively large, conspicuous and they have short life-cycle. Mainly, they can cumulate heavy metals into their bodies. This research is focused on heavy and toxic metals which are noxious for the environment. The purpose of this project is to find out heavy metals in soils using terrestrial isopods as potential bioindicators of anthropogenic pollution in Czech Republic. Multi-elemental instrumental epithermal neutron activation analysis at the reactor IBR-2 in FLNP, JINR is used for assessment of heavy metal contamination which belongs among environmental problems in Czech Republic. Concentrations of heavy and trace elements are determined in terrestrial isopods and soils collected in Moravian-Silesian region in Czech Republic. High concentrations of calcium and zinc was find out in isopods. Over limited values of zinc, cobalt and copper was observed in the most of soil samples. It can be due to the excessive load from industrial production. This overview of elemental composition is useful for public safety in Czech Republic and for protection of soils.

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# TEMPORAL TRENDS OF HEAVY METALLS CONTAMINATION OF TULA REGION AIR (MOSS MONITORING)

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Using the method of passive moss biomonitoring of air pollution, the major industrial region of Central Russia - Tula region - was studied. The sampling of mosses in the territory of the region was carried out in 2015-2016 with a network of 17x17 km<sup>2</sup>. A total of 47 elements in 116 moss samples from the Tula region were determined by instrumental epithermal neutron activation analysis at FLNP JINR. A high content of a number of elements of anthropogenic origin V (mean deposition value 7.7 mg/kg), Fe (2527 mg/kg), Zn (54 mg/kg), As (0.77 mg/kg), Sm (0.44 mg/kg), Tb (0.07 mg/kg), Hf (0.84 mg/kg), W (0.2 mg/kg), Th (0.86 mg/kg), and U (0.21 mg/kg) compared to other regions of Russia was revealed. Compared with data of passive moss biomonitoring for the EU, the air of Tula region contains 1.5-7 times more of V, Cr, Fe, Zn, As, and Cd. Temporal trends for Tula region for 10-15 years (Ermakova et all, 2004) shows increase of atmospheric pollution by such elements as Fe (12%), Ba (17%), Cr (23%), Co (28 %), As (13 %), Cd (32 %), Sr (18 %), Sm (15 %), Tb (12 %), Yb (45 %), Ta, (8 %) W (7 %), Th (15 %). The concentrations of such elements as Cl, Mn, V in atmospheric deposition decrease by 23 %. High content of As was found in the Kireyevsky and Uzlovsky districts of the region; Cd in Tula city (region center) (probably due to the influence of the vehicle emissions); Cr in the mosses of the Efremovskiy area, Fe in Tula and the Kireevskiy area, Ni in the Chernskiy and Efremovskiy areas, V in the Leninskiy area. The maximum content of Zn was observed inTula, the Kireevsky district and southern districts of the region. Mn deposition was revealed in the east of the region. Such a redistribution of toxic elements from the main sources of pollution with air masses can be associated with wind transfer in the southern direction, depending on the mobility of the elements. Contamination factor (CF) is more than 5 compared to the region background for such elements as As, Cr, Fe, Ni, V, Mn, Ce, Sm, W, U, Ba, Tb, Th, Sc, Ti, La, Zr, Hf, Ta, and Tm. Geo-accumulation index for heavy metals and metalloids is 1.34-2.87 and it is maximal for such elements as Cr, Fe, V, Ce, W, Th, Sc, La, Ce, Hf, and Tm (more than 2.11). Results of the factor analysis revealed four groups of factors: Factor 1 is associated with soils, industrial pollution of soil and weathering processes; Factor 2 (V, Fe, Zn, Se, Mo) can be attributed to the industrial pollution; Factor 3 is associated with physiological activity of mosses (vegetation factor) ; Factor 4 is associated with the extraction and processing of ores. The reason for high level of anthropogenic air pollution in Tula region is the activity of enterprises of metallurgical, defense, engineering and chemical industries.

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# HEAVY METALS CONCENTRATIONS IN MOSS SAMPLES IN GREECE

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Mosses can be used as biomonitors of atmospheric deposition of heavy metals. They are geographically widespread species and they can provide a better understanding of spatial and temporal variations in atmospheric metal deposition. Mosses receive most of their nutrients directly from wet and dry deposition. The lack of a rooting system means that uptake from the substrate is normally not significant. These properties make mosses an ideal way of monitoring and evaluating the concentrations of heavy metals deposited from the air to terrestrial systems in a quite economic way.

Ninety five (95) samples of *Hypnum cupressiforme* Hedw. were collected in Northern Greece in a short time interval during the end of summer 2016, covering a regular grid of 30 km x 30 km. The sampling sites were located from  $39.97^{\circ}$  to  $41.65^{\circ}$  North and from  $20.97^{\circ}$  to  $26.26^{\circ}$  East. All the samples were collected according to the instructions of the Protocol of the European Survey ICP Vegetation and were analyzed to the content of heavy metals using INAA.

The concentrations of 33 elements were determined. High concentrations of Al and V are noticed in areas where metal industries, coal fired power plants and lignite mining exist. Areas with manufacturing, electricity and heat production activities, show an additional increase in concentrations of As, Cr and Ni elements. Therefore, a high sampling density was achieved, providing information for the elemental deposition from the atmosphere to terrestrial systems over the region of Northern Greece.

# HEAVY METALS AND <sup>210</sup>PB IN AIR FILTERS FROM FINLAND FOR YEARS 2005-2010

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In the present work weekly filters collected in Helsinki, Finland during 2000 – 2005 underwent energy dispersive X-ray Fluorescense (ED-XRF) analysis for the determination of their content in Pb, Br, Zn, Cu, Ni, Fe, Mn, Cr, V, Ti, Ca, K, Cl, S, Si, Al, and Na. More specifically, one weekly filter per month and per year was analyzed.

The analysis indicated that there is a decline trend with the time for Fe and a slight decrease for Ti, Si. The observed concentrations of Pb remain relative stable throughout the time period 2000-2005.

High average concentration of Pb 500 ngr m<sup>-3</sup> was typical of the air in central Helsinki throughout the '60s, but after '70s was decreased to around 150 ngr m<sup>-3</sup>. The observed average concentration of lead in the present study equal with 17.7 ngr m<sup>-3</sup>, reveals a decrease of its concentration of the order of one magnitude since '70s.

Other observed mean concentrations in ng m<sup>-3</sup>: Cu: 34.5, Zn: 44.9, Br:15.8, are also lower almost half of those observed during '70s (Cu: 70, Zn: 172, Br:49 ng m<sup>-3</sup>).

The high correlation coefficient observed between the Cu-Zn (R=0.89) is an index of traffic source. The relative high correlation coefficient between the Ni-V observed values (R=0.66) is an index of heavy oil source. Finally the relative high correlation coefficient between the three elements (Fe-Si-Ti) is a clear index of soil source.

Airborne <sup>210</sup>Pb is a decay product of <sup>222</sup>Rn emanating from the soil. Due to its long half-life (22.3 years) <sup>210</sup>Pb accumulates relatively into the atmosphere. Thus it can be used as an atmospheric tracer for long-range transported air masses. Anthropogenic lead emissions has low content of <sup>210</sup>Pb, so the anthropogenic lead emissions tend to decrease the specific activity of <sup>210</sup>Pb in the atmosphere. The <sup>210</sup>Pb specific activity is the ratio of the <sup>210</sup>Pb activity concentration to the total concentration of stable lead. The observed values of this ratio vary between 3.5-58 kBq g<sup>-1</sup>. Previous reported values in Southern Finland ranged between 0.67-39 kBq g<sup>-1</sup> and between 3.9-91 kBq g<sup>-1</sup> in Northern Finland with minimum values during the cold winter, due to the increased lead emissions from energy production.

# STUDY OF AIR DEPOSITION OF TRACE ELEMENTS USING VASCULAR PLANTS AS BIOINDICATORS

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Heavy metal (HM) environmental pollution is a global problem that may pose serious problems for human health and ecosystem. During the last decades the awareness about the effects of HM atmospheric pollution has attracted several researches due to the toxicity effects of heavy metals, such as carcinogenicity, mutagenicity and endocrine disruption character. The cities of Tirana (capital city) and Durres (costal city) are being moderately polluted due to the high vehicular emissions, and the use of adulterated fuel in vehicles. We have tried to investigate and evaluate the pollution level on the basis of the HM concentrations in the vascular plants and data statistical treatment. Most heavy metals are fixed at the surface of leaves of vascular plants and as the plant grows, the particles of deposited dust (including heavy metals) appear an integral accumulation and the concentration level of HM in plant is usually higher than the dedectable limit of analytical method (flame or furnace AAS) by promissing good quality of the results.

Leaves of Ligustrum lucidum, Fam: Oleaceae were collected according to a network of 62 stations (20 stations in Tirana and 42 stations in Durres) distributed uniformly along the main streets of the cities during the last week of March 2013. Heavy metals such as Cu, Zn, Mn, Fe, Ca, Mg, Na, K, Pb, Cd and Hg were analyzed in composite leave samples collected in different trees of the same species at the same road. Sample digestion was realized by wet digestion technique in half-pressure Teflon tubes HNO3 (9:1). Chemical analysis were performed using FAAS technique (Cu, Zn, Mn, Fe, Ca and Mg), ETAAS technique (Pb and Cd), CV-AAS technique (Hg) and with AES technique (Na and K).

The data matrix of analytical parameters was statistically treated with Descriptive Statistics and multivariate analysis by using MINITAB 17 software package. The distribution trend of trace elements in the vascular plants of Tirana and Durres urban areas followed different distribution orders. such as Hg<Pb<Cu<Zn<Fe<Mn<Na<Mg<Ca<K for Tirana, and Hg<Pb<Cu<Zn<Mn<Fe<Mg<Ca<Na<K for Durres. Significant differences were found between Na level in Tirana and Durres, by indicating high impact of marine environment. Elements such as K, Na, Ca and Mg mainly originate from natural sources. Their concentration levels were higher in Durres compared to Tirana, by confirming the effect of marine environment. A smaller median value of Cu, Pb, Zn, Hg, Mn and Fe in Durres city explains a greater influence of anthropogenic factors in Tirana city compared to the marine sea salts influence in the city of Durres.

Aiming to check the association of the parameters under investigation Cluster Analysis (CA) was conducted. Based on the CA, the sampling stations were classified into 3 main clusters. Cluster 1 were composed with the main streets of Tirana, Cluster 2 were composed with the main streets of Durres, and Cluster 3 were composed with the most pulluted streets of Tirana, by indicating different origin of the pollution in the studied areas.

Key words: Vascular plant, heavy metals, SAA, pollution, Cluster analysis, urban area, Albania

# AN INVESTIGATION ON CONCENTRATION LEVELS OF POLLUTANTS IN MOSSES AT BACKGROUND TERRITORIES OF CENTRAL AND NORTHERN EUROPEAN RUSSIA

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The research screening analysis was performed for data on pollutant concentrations received during regular moss monitoring survey in 2016 by Russian ICP-Vegetation team. The region of this study was correspondent mainly the territory covered by atmospheric measurements of different background monitoring networks (IBMoN and EMEP), however, the most of sampling points are placed at the areas of central and northern Russia.

During the screening of data we had divided sampling points into ranges of three groups based on the values of heavy metal concentrations. Spatial distribution of ranged data demonstrates a clear growing of concentrations from north to south. Also one undistributed point (exception) was found with extremely high concentrations of pollutants - Voronezh Biosphere reserve.

To estimate the roles of natural and anthropogenic sources in the formation of the sample composition, the enrichment factors (EF) were calculated for element in mosses relatively to the average abundance of chemical elements in the earth's crust.

For the seven elements EFs show the lithogenic character of pollution; ones of two elements indicate mixed sources - lithogenic and anthropogenic. Based on the results of calculations an assumption could be made on anthropogenic nature of remaining elements determined in mosses.

We present also the preliminary results of comparison between atmospheric deposition of some metals and their concentrations in mosses for the most areas of survey territory of this study.

# DEFENSE MECHANISM OF ORGANISMS IN THE ENVIRONMENT OF NOBLE METALS IONS

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The environment is exposed to metals and metallic particles continually. This exposure is proved to be both at algal and cyanobacterial levels but also at plant level (1). Over the last few years, our research team has been intensively engaged in metal nanoparticle biosynthesis and, on the basis of natural defensive cellular mechanisms, we observed the ability of various biomasses to form nanoparticles (NPs) upon contact with metal cations. For biosynthesis of Ag and Au, various organisms were used such as silica algae Diadesmis gallica and Mallomonas kalinae, cyanobacterium Anabaena mendotae and moss Pleurozium schreberi. Despite the differences among the organisms, we have found one common feature – bioaccumulation of metallic ions and the simultaneous reduction and stabilization into the form of metallic NPs.

Organisms are rich in organic compounds such as proteins, polysaccharides and other metabolites. All these compounds contain functional hydroxyl, carbonyl or carboxyl groups playing an important role during redox reactions with metallic ions.  $Ag^+$  and  $Au^{+3}$  ions are reduced to zero-valent forms ( $Ag^0$ ,  $Au^0$ ); these forms can act as growth nuclei for subsequent nanometric structures. Their sizes are strongly dependent on the content of the functional groups and the local environment (additive salts, residual elements and so on).

The mesoporous biosilica with unique 3D hierarchy is an attractive material in terms of interfacial phenomena. Diadesmis gallica biosilica surface acts as a bio-template for AgCl (3-51 nm) and Au nanoparticle (9-27 nm) biosynthesis. On the other hand, Au NPs synthesized using Mallomonas kalinae offered more uniform size distribution with mean size about 10 nm. These materials can be used both as solution and in powder form. We noticed similar mechanism of Ag and Au NPs synthesis (10 and 23 nm) using Anabaena mendotae and NPs were attached intra- and extracellularly. Finally, moss acted as strong bioaccumulator and Au accumulation was both visually and analytically proved. Moreover, the use of terrestrial mosses as biomonitors in multi-element studies of metal deposition is a well-established technique (2). The synthesized NPs are interesting material for the catalytic decomposition of organic pollutants such as organic dyes, nitro-aromatic and pharmaceutical compounds; Ag NPs are known for their antibacterial properties against human pathogens. These bio-based materials, however, has to be produced with respect to the natural habitat and their remedial environmentally friendly degradation has to be considered.

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# LITHOPHYLIC ELEMENTS ATMOSPHERIC DEPOSITION STUDY IN KALININGRAD REGION (USING MOSS-BIOMONITORING TECHNIQUE)

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The biomonitoring technique was applied to pollution studies in Kaliningrad region. Samples of the terrestrial moss Pleurozium schreberi and Hilocomium splendens have been collected on regular network of 10x10 km.

The elements were determined by epithermal neutron activation analysis (ENAA) at the IBR-2 pulsed fast reactor FLNP JINR Dubna, Russia. Samples for ENAA, about 0.3 g, were pelletized and heat sealed in polyethylene foil for analysis based on short-lived radionuclides, as for elements with long-lived radionuclides the samples were packed in aluminum cups. The samples were irradiated for 3 min for short-lived radionuclides and to determine elements associated with long-lived radionuclides the samples were irradiated for 100 h. After irradiation, gamma-ray spectra were measured by high-purity Ge detector.

Statistical processing of data included the calculation of these descriptive statistics: mean content, standard deviation, minimum and maximum content, median, variance, and coefficient of variation. The Pearson and Kolmogorov criterions were applied to test the hypothesis of normal distribution of the elements in the sample. For normal distribution, the Pearson correlation coefficients were used to characterize the ratio of two chemical elements. Different pollution sources were identified and characterized with the help of multivariate statistics (factor analysis). Principal component analysis was used.

For spatial distribution mapping the IDW (inverse distance weighting) method within QGIS 2.18 (Interpolation module) software package was applied. Given a small number of points, no RMSPE (root-mean-square "prediction" error) was done. The number of columns and rows was 500 x 500; the distance coefficient was 1. Opting for spatial distribution mapping instead of mere point mapping is justified by the key factors responsible for heavy metal distribution in Kaliningrad region. For the region of strong cyclonic activity, with a high frequency of westerly air-mass trajectories, atmospheric transport is of great importance. In winter, the western and south-western directions of atmospheric transport prevail, while the summer mainly enjoys the north-western and southern wind currents. Western and southern cyclones causing rainy weather contribute to the deposition of pollutants into the region's territory. Airborne transport with deposition plays a dominant role, which led us to prefer visualizing the surface distribution in lichens using a continuous (interpolated) spatial distribution rather than individual data points. The interpolation method of mapping provides a good visualization for relative metal accumulation, but not of actual absolute metal deposition on ecosystems.

# BIOINDICATION OF POLYCYCLIC AROMATIC HYDROCARBONS PAH IN KALININGRAD REGION. THE FIRST STEP

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Moss samples were collected in the Kaliningrad region to study atmospheric deposition of PAHs for the first time, in 2017 year.

Only pleurocarpous mosses were sampled in pine forests: Hylocomium splendens (Hedw.) Schimp and Pleurozium schreberi (Brid.) Mitt. There were only four plots with suitable conditions Each sampling point was situated at least 3 m away from the nearest projected tree canopy, at sites representative of non-urban areas, at least 300 m from main roads (highways), villages and industries and at least 100 m away from smaller roads and houses. There were composite sample from each sampling point, consisting of ten subsamples, collected within an area of about 50 x 50 m. The total amount was 3 liters. Samples were collected in glass jars and covered with metal caps. Samples were kept cool and in the dark at all times.

Content of 16 Polycyclic aromatic hydrocarbon (PAH) atmospheric deposition was evaluated in the mosses y samples by high-performance liquid chromatography. Sum of PAH varied from 80 to 120 ng/g DW. The main contribution is made by PAHs: fluoranthene, pyrene and phenanthrene, their content was more than 10 ng/g DW.

There is the feature of PAH distribution – plots with maximal content of PAH are situated in the East part of the region.

# ELEMENTAL CONTENT ASSESSMENT IN ATMOSPHERIC DEPOSITION BY MOSS MONITORING TECHNIQUE AND NEUTRON ACTIVATION ANALYSIS IN THE SOUTH PART OF SILESIAN COAL BASIN

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The Czech Republic had extremely high emissions and atmospheric deposition of pollutants in the second half of the 1980s. After political changes in 1989/1990, there was a restructuring of industry and introduction of new more environmentally friendly technologies. The main hot spots of air pollution are situated in coal basins in the northwest and northeast part of the country. The research is focused on Moravian-Silesian Region in the NE, which is highly affected by extraction and processing of black coal and metallurgical industry operation, numerous domestic and nearby polish sources.

For improvement of monitoring system in industry region regular network of sampling points was created by geographic information system. Bioindicator using for monitoring were moss. In years 2015/2016, 85 moss-sampling points were used. Samples were analyzed by neutron activation analysis in Frank Laboratory of Neutron Physics in Department of Neutron Activation Analysis and Applied Research. As results, 46 elements were determined.

Factor analysis was used for grouping elements. Cattell's scree test shown ideal scenario for three and less ideal but acceptable for four factors. In case of three factors, six elements constitute factor 2 (Zn, As, Br, Sb, I, Ba). The most significant samples that are consider in factor 2 are situated around mining cities with plenty of power plants. Factor 3 is composed by four elements (Ca, Se, Mo, Cd). Research works on assumption that Ca, Se and Mo are from vegetation origin. Distribution of significant samples in factor 3 contribute to previously supposition. All these samples are situated in unpolluted localities even in nature reserve.

In case of results for four factors, is group of elements contain in factor 2 in previous case, extended by Sb and Mn for same localities. Factor 3 contain elements Ca, Cr, Fe, Rb, Sr and Mo. Most significant sampling point is near ironworks however others in mountains. Last group of elements is consisting of Se, Cd, W. All significant localities are in middle cities with light industry.

# GREEN TECHNOLOGY OF SYNTHESIS OF LANTHANIDE OXIDES NANOCRYSTALLITES AND THEIR TOXICITY TESTING

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Lanthanide oxides have gained a lot of attention due to their diverse use for applications and between of the significant rare earth oxides belongs Gd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, and Er<sub>2</sub>O<sub>3</sub>. Gd<sub>2</sub>O<sub>3</sub> is characterized by good crystallographic stability, high mechanical strength, excellent thermal conductivity, and a wide band gap and are used as new contrast agents during magnetic resonance [1]. Further, thermally stable Sm<sub>2</sub>O<sub>3</sub> is characterized by high refractive index and wide band gap and are used in solar cells, semiconductors, infrared absorbing glass, catalysts, and sensors [2]. Finally, antiferromagnetic Er2O3 is characterized by good mechanical properties, high electrical resistance, and excellent chemical stability and are used in effective photoelectrochemical materials or gas sensors [3].

For these reasons is important to select a suitable method, precursors and reaction conditions, because all these attributes affect properties of the prepared nanomaterials. One of the ecofriendly, simple, and inexpensive method for preparation of lanthanide oxides nanocrystallites is glycine-nitrate processed. Our group has recently published an article [4] describing a method of the preparation of three dilanthanide trioxides (Gd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, and Er<sub>2</sub>O<sub>3</sub>) in a shape of nanocrystallites via thermal decomposition of a transient complex formed in situ from suitable lanthanide nitrates. Ultra-fine powder of the samples was obtained via this method. The resulting nanocrystallites were characterized using X-ray powder diffraction analysis, which showed the nanocrystallites having the crystallite size equal to 10 (Gd<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>) and 11 nm (Sm<sub>2</sub>O<sub>3</sub>). Morphology of the samples was examined by scanning and transmission electron microscopy. Electron diffractions observed in transmission electron microscopy corresponds to the results obtained from X-ray diffraction analysis. Moreover, acute aquatic toxicity tests of prepared nanocrystallites were driven revealing the moderate toxicities against Desmodesmus subspicatus peaking with EC50 0.47 g·dm<sup>-3</sup> (Er<sub>2</sub>O<sub>3</sub>).

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# CONCENTRATION OF HEAVY METALS IN DOMINANT MOSS SPECIES OF NORTHERN TAIGA AS AN INDICATOR OF AERIAL TECHNOGENIC LOAD

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The method of indication of aerial technogenic pollution by heavy metals using different types of mosses, widely distributed in European countries since the beginning of 1970-ies. Studies carried out in Sweden [1], Norway [2, 3], Finland [4] and Poland [5] have shown that two dominant mosses, *Hylocomium splendens* and *Pleurozium schreberi*, can replace each other and adequately reflect the level of environmental pollution with heavy metals.

The aim of this work is a comparative assessment of the concentration of heavy metals (Ni, Cu) in two dominant species of the moss cover of the North taiga ecosystems – *Pleurozium schreberi* and *Hylocomium splendens* – in the period of high (1991) and low (2011) intensity of aerotechnogenic load.

Sample living parts of mosses *Pleurozium schreberi* and *Hylocomium splendens* were collected in 1991 and 2011, at 17 stations located on the territory of the Lapland biosphere reserve at different distances from the Copper-Nickel combine (Kola Peninsula, Russia). In these samples, the content of Ni and Cu was measured by atomic absorption spectrometry.

The studies have shown that the content of Ni and Cu in the living parts of the studied moss species (Pleurozium schreberi, Hylocomium splendens) adequately reflects the intensity of air pollution of the Lapland biosphere reserve by atmospheric emissions of heavy metals by Copper-Nickel combine. Therefore, both moss species can equally be used to monitor aerial technogenic pollution of environment with heavy metals. The absence of a direct correlation of the concentration of heavy metals in the studied moss species with the distance to the combine and the ambiguous picture of the changes in the content of Ni and Cu in mosses for two periods of observation confirm the influence of other factors (wind rose, orography of the area) on the processes of incoming of heavy metals from the polluted air into the mosses and their accumulation in plant tissues. In this regard, when laying the network of monitoring sites, it is necessary to take into account not only the direct distance to the source of aerotechnogenic pollution, but necessarily the rose of winds prevailing in this territory, and the orography of the terrain. The disproportion and non-synchronicity of the decrease in the content of heavy metals by the studied species of mosses in response to a sharp reduction in the volume of atmospheric emissions by the Copper-Nickel combine are due to numerous reasons, not all of which are known to date and require further research.

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### AIR POLLUTION STUDY IN BAKU WITH MOSS BAGS USING NAA and AAS ANALYTICAL TECHNIQUES

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Ambient air pollution is mainly caused by emissions from motor vehicles, the energy and industrial sectors. The main source of pollution in urban areas is undoubtedly motor transport. It should be noted that during recent years, fuel consumption by motor transport has increased, and consequently, emissions of harmful substances into air have also increased. The present research was conducted to assess the air pollution in Baku – the capital of Azerbaijan. Baku characterizes with intensely transportations, construction of buildings, and oil and gas industries that associate to it human health hazard and the natural releasing from active mud volcanoes.

Moss bags technique (*Sphagnum girgensohnii*) as an active biomonitor was implemented to (in bags) characterize the different sources of air pollution in Baku. Moss bags were exposed at twenty-one urban sites for 3 and 6 months starting from December 2016, respectively. The concentration of elements was determined by means of two complementary analytical techniques were used: neutron activation analysis (NAA) and atomic absorption spectrometry (AAS).

A total of 38 elements were determined namely; Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Ni, Cu, Co, Fe, Zn, As, Se, Br, Sr, Cd, Rb, Mo, Sb, I, Ba, Cs, La, Ce, Sm, Tb, Hf, Ta, W, Au, Pb, Th and U. Out of 38 elements 3 elements were determined by using AAS namely; Cd, Cu, and Pb. Descriptive statistics, and principal component analysis were calculated. Spatial and temporal distribution of selected elements were constructed by using ArcGIS. Multivariate Statistical Analysis (Factor Analysis) allowed characterization of potential pollution sources. Factor 1 represents light (Mg, Al, Sc, Ti,) and heavy (Cr, Fe, Co, Sr, Ba, Cs, La, Sm, Tb, Hf, W, Th, U) crust components. It also contains crude oil metals (V and Ni) which can be associated with the close-lying oil wells and long-range transport of petroleum oil pollutants from the oil rigs allocated in the Caspian Sea. Oil industry has a similar geographical distribution as the dominant source of terrestrial dust in the area. Factor 2 is a vegetation factor (K, Ca, and Rb) associated with the green areas of Baku city. Factor 3 is characterized by seasalt (NaCl), and other marine element, Br, whereas I, another marine element, is splitted into all four factors (0.44; 0.51; 0.35; and 0.15). Factor 4 most probably, reflects nonferrous metal ores mining (Zn (0.70), Se (0.77), and Au (0.76)).

### TRACE ELEMENT ATMOSPHERIC DEPOSITION STUDY IN AZERBAIJAN BASED ON MOSS ANALYSIS

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Azerbaijan is the largest agro-industrial country of the Caucasus with an extensively developed industry and a large agricultural sector with a dynamically developing economy, providing significant human impact on the environment. The national policy of Azerbaijan for protection of the environment is compliance with requirements of the International Conventions ratified by the Republic of Azerbaijan. Implementation (transfer of the European technology) of the moss-biomonitoring technique by scientists from JINR, Dubna, Russia, in Azerbaijan began in cooperation with the Azerbaijani specialists in the spring of 2015. The first systematic study was undertaken in the summer of 2015 of atmospheric deposition of man-made heavy metal pollutants in the area of mining and processing plant in Dashkesan and Kedabek mining district, where mining of non-ferrous metals has an ancient history. At the same time samples were collected in the Gey-Gel State Reserve in the Lesser Caucasus. The 85 moss samples (predominantly Pleurosium schreberi) collected in both environmentally contrast area were studied by neutron activation analysis at the reactor IBR-2 of FLNP JINR. A total of 44 elemental concentrations were determined (Na, Mg, Al, Si, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Tm, Yb, Hf, Ta, W, Au, Th, U). Pb, Cu, and Cd will be later determined by atomic absorption spectrometry. Multivariate statistical analysis of the analytical results obtained will make it possible to identify the main sources of pollution and to assess the role of long-range transport of pollutants. Given the importance and actuality of this work, it is planned to study atmospheric deposition of heavy metals and radionuclides by means of moss biomonitoring in most of Azerbaijan (about 60% of the territory where proper moss species grow). New data on Azerbaijan will make a great contribution to the scientific understanding of the current environmental condition of the country and serving as an enrichment of the scientific methodology of biomonitoring using mosses in a subtropical zone (out of 11 possible climate types in the area, 9 occur within the relatively small territory of Azerbaijan). Due to these studies Azerbaijan intends to become a participant of the UN Program on air pollution in Europe in the framework of the Convention on Long-Range Transboundary Air Pollution (CLRTAP).

### THE STUDY OF THE MICROELEMENTS IN MOSSES FROM THE MOUNTAIN CRIMEA

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The mountain part of the Crimea peninsula is a unique ecological forest region with subtropical and moderate climate which situated in the center of the Black sea region. The main natural sources of studied microelements are the occasional industries on the western, northern and eastern borders of the forest areas. The studied zone includes territories of Crimean mountain forest reserve, Yalta's mountain forest reserve and several small reserves and other protected areas.

The 26 sampling sites were chosen according to monitoring manual of International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops. Besides that the samples were collected along transects (cross-sections) through the Crimean mountains. The concentrations of 40 elements was determined in mosses from mountain part of the Crimea peninsula in 2015. *Pleurozium shreberi, Hylocomium splendens* and common local species as *Homalothecium philippeanum* Kindb., *Rhytidiadelphus triquetrum* were used for complex analysis. The neutron activation analysis was used as analytical technique for determination of concentrations of microelements.

Such elements as Mg, K, Ca, Zn, Se, Br, Sr, Sb and I had an relative equal distribution among all sites ( $C_{max}/C_{min} < 5$ ) with the local accumulation at the several station. Mo, Sn, Sm and Au had an outliers due to particles of anthropogenic origin and specific rock materials.

Mg, Ca, Ni, Se and I accumulated to the higher values than in mosses from Bulgaria and Macedonia. It's could be explained by specific contribution of aerosols of marine origin (Se and I), carse (cavern) rocks (Ca, Mg) and shales (Ni). The last ones were accumulated due to anthropogenic impact in processes of producing of concrete and rock mining at the several places. The such halogens as Br and I reached the maximal concentrations in the coastal areas (on the south of the region) and in the places with the highest altitude due to wind actions.

In general the presence of anthropogenic traces was found in small excesses of concentrations such elements as Mg, Ca and Ni. Other microelements as Mo, Sn, Sm and Au could indicate the rock mining and processing industries in the studied zone.

## ATMOSPHERIC DEPOSITION OF HEAVY METALS IN KAZAKHSTAN

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The moss biomonitoring technique was applied to assess the atmospheric deposition of heavy metals in the South-Eastern, North-Eastern, Northern and Central parts of Kazakhstan. The fifty-eight moss samples were collected in summer and autumn of 2014 and 2015 growth period, thirty-five moss samples were collected in summer 2016 growth period. A total of 46 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Zr, Nb, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Hf, Ta, W, Au, Th, U) were determined by epithermal neutron activation analysis. Multivariate statistical analysis of the results obtained was used to assess the pollution sources in the study area of the Almaty, Pavlodar, Ust'-Kamenogorsk, Shymkent, Semey and Akmola region. In Akmola region, near the lake Borovoe, a climate-koumiss-healing resort called "Pearl of Kazakhstan" and "Kazakhstan Switzerland" is situated. It is considered one of the most beautiful and pristine places in the country. These preliminary results of our study in different areas of Kazakhstan, in spite of a small number of investigated territories, look very promising for assessing air pollution in Kazakhstan and serve the ground for extending sampling areas in the moss survey in 2020.

### DETERMINATION OF BE-7, PO-210 AND PB-210 RADIONUCLIDE ACTIVITIES IN ISTANBUL AIR PARTICULATE MATTER

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The activity concentrations of Be-7, Po-210 and Pb-210 were determined first time in the İstanbul surface air particulate matter (PM2.5 and PM10). The samples were provided by Istanbul Metropolitan Municipality Air Quality Laboratory. Briefly surface air particles were collected on quartz and/or EPM filters by using a gravimetric sampler (Sequential Sampler SEQ 47/50; capacity 55.2 m<sup>3</sup> d<sup>-1</sup>) throughout the four seasons (2017-2018). Two samplers were employed in Anatolia and European side of Istanbul (Kadıköy and Aksaray, respectively). Be-7 activities in particulate matter were measured by using a gamma spectrometer equipped with high purity germanium detector (CANBERRA). For measurement of <sup>210</sup>Po, filters were dissolved in concentrated acid mixture in a microwave digestion system, and then known activity of <sup>209</sup>Po was added to the solution as a standard tracer. After digestion, <sup>210</sup>Po was spontaneously deposited on rotating silver disc. Activity concentrations of <sup>210</sup>Po in the filters were replated and measured in order to calculate <sup>210</sup>Pb activity from in-grown <sup>210</sup>Po.

The average activity concentration of Be-7 was found to be  $5.17 \pm 2.35$  mBq m<sup>-3</sup>. This value is comparable to other studies held in similar latitudes. Po-210 and Pb-210 activities in particulate matters found to be higher compared to similar studies carried out in urban areas and big cities. Combustion of fossil fuels such as gas, oil, coal and biomass was supposed to be the main reason of enhanced Po-210 and Pb-210 deposited on Istanbul air fine particles.

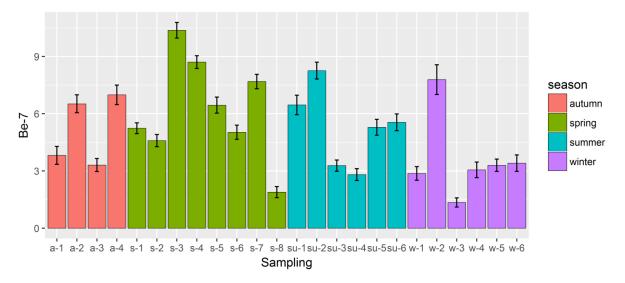


Table 1. Temporal change of Be-7 activity (mBq m<sup>-3</sup>) in PM10 at Anatolia side of İstanbul

### TREND ESTIMATION FOR ICP IM DATA SERIES OF CONIFEROUS STANDS PARAMETERS

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The problem of air pollution and its effects on the natural environment or particular ecosystems is one of the greatest global challenges faced by mankind. The earlier studies [1] proved that Pinus sylvestris L. and Picea abies L. are good indicators of background environment state. It was shown that particularly for northern and central parts of European Russia there is significant correlation between wet deposition and tree stands conditions.

Our research was performed in areas of Russian ICP IM sites RU04, RU16, RU13, located at Russian national reserves (RU04– Oka-Terrace Biosphere Reserve, RU13– Central-Forest Biosphere Reserve, RU16– White Sea Biological Station). The main objectives were to evaluate defoliation and discoloration of Pinus sylvestris L. and Picea abies L. stands. The main goal of presented study was to recognize whether some tendencies could be determined in measured parameters or not. The MAKESENS tool with realized Mann-Kendell test and Sensslope application for trend estimation was used for time series analysis.

There are no co-directional trends for those parameters found for whole data sets. Two trends of high significance were identified only (one increasing and one decreasing) allowing to suppose that air quality at RU04 is getting better while in contrary, state of environment at RU13 is getting worse. For both cases Pinus's stands seem to be more sensitive to air quality conditions, and it corresponds to earlier studies for the same territories.

The short data series and rare (or absence of) measurements during 1990s for other parameters did not possibly allow to disclose any significant trends.

### Summary

The study is devoted to the trend analysis of air pollution bioindicators condition. Data serise were obtained by the standart method of "Forest damage" subprogram of International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM). Multidirectional significient trends were detected.

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### CHARACTERIZATION OF THE AUTOMOTIVE BRAKE WEAR DEBRIS AND ITS EFFECTS ON BIOSYSTEMS

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Braking processes have been extensively studied and discussed in the relation to the creation of the brake wear. Wear debris represents a major source of non-exhaust emission from road traffic and its production increases with the number of cars worldwide. However, the contribution to the environmental pollution is still not clear and there is not a unified procedure for the evaluation of the potential risk of the brake wear to the environment and human health.

Brake pad materials are complex composites formed of 10 up to 30 different constituents typically bound by polymer matrix (modification of phenolic resin). Braking process leads to the release of wear particles to the environment. Part of the released particles preserves the original chemical composition and morphology, part differs considerably because high temperature and pressure during the braking process cause changes both in composition and morphology.

The aim of this study was to perform characterization and evaluation of the potential toxicity of airborne fraction of wear brake debris generated during standard dynamometer test. Elemental and phase composition were determined by scanning electron microscopy, and X-ray powder diffraction. Carbon in graphitic and amorphous form, copper and iron in form of oxides were identified as major components. Characteristic number particle size distribution shows the interval range of 0.7 to 2.3  $\mu$ m. Effect of brake wear debris to biosystems was evaluated by its potential to induce oxidative stress via lipid peroxidation and protein carbonylation in the non-cellular system. Airborne wear showed ability to induce oxidative stress. Acute aquatic toxicity of the tested material to the freshwater green algae Raphidocelis subcapitata and the inhibition of root elongation of Sinapis alba was determined. Airborne brake wear particles caused growth inhibition in both proved tests. All these results indicate that the release of wear particles from brake systems is a risk to the environment.

### ACTIVE MOSS BIOMONITORING USING THE MOSS BAG TECHNIQUE IN THE PARK OF MOSCOW

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Quality control of atmospheric air is a priority topic for monitoring the environment [1]. There is a great need for rapid and cost-effective control of atmospheric pollution. The protected and park zones play a recreational role, therefore the assessment of air quality in this area is especially important. For the first time active biomonitoring (moss bags technique) was applied in Moscow, at the state museum-reserve Tsaritsyno. As a bioindicator the moss *Sphagnum girgensohnii* was chosen. This species was collected in a pristine wetland area Domkino Bay, near Dubna, Russia. *S. girgensohnii* was bagged and exhibited at 3 locations of Tsaritsyno from June to September of 2017. The goal of this pilot study was to assess air pollution with trace elements from potential pollution sources in Moscow. A total of 34 chemical elements: Na, Mg, Al, Cl, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Zn, Se, As, Br, Rb, Mo, Sr, Sb, I, Ba , Cs, La, Sm, Tb, Ce, Hf, Ta, W, Au, Th, and U were determined in the exposed samples by neutron activation analysis at the reactor IBR-2 of FLNP, JINR, and three environmentally meaningful elements: Pb, Cu, and Cd were determined by atomic absorption spectrometry in the same laboratory. The obtained results were compared with the analogous ones for Belgrade, Serbia, carried out with the same moss and exposure time [2].

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### HANDLING MISSING VALUES IN BIOMONITORING SURVEYS

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In the field of biomonitoring, dealing with compositional data, such as chemical composition of biomonitor, are common. This type of data contains a difficult mathematical problem of constrained sample space (the simplex). To resolve this problem, the log-ratio transformations have been developed in the last two decades to project the data into a real space, thus, allowing the application of standard multivariate techniques for compositional data analysis. However, zero and missing values commonly occur in compositional data, which are troublesome for logratio transformation as well as for the consequent multivariate analysis itself. Many researchers have suggested nonparametric replacement methods of zero and missing values.

This study demonstrates the importance of dealing with missing values showing two types of zeros in dataset from biomonitoring: i) values below the detection limit and ii) measurement error. Incomplete dataset containing both types of zeros from three biomonitoring surveys was assessed. The zeros were imputed using specialized algorithms and multivariate analyses (Principal component analysis and Hierarchical clustering on Principal components) were performed on the original dataset and on the dataset with imputed values which were, then, compared. Analyses of the dataset with imputed data proved to be much more revealing concerning the intended purpose of the survey.

### COMPARISON OF ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS IN ARMENIA AND GEORGIA USING THE MOSS BIOMONITORING TECHNIQUE

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The results of a trace element atmospheric deposition study in Armenia and Georgia in the frame of the UNECE ICP Vegetation moss survey 2015/2016 are compared and discussed. Two complementary analytical techniques: neutron activation analysis and atomic absorption spectrometry allowed determination of Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Pb, Cd, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Hf, Ta, W, Au, Th, and U in the moss samples. To characterize potential pollution sources and deposition patterns of pollutant elements, multivariate statistical analysis and geospatial mapping were performed. According to the Shapiro-Wilk test, V, Zn, As, Se, Br, Pb, and Cd in Armenia and As, Pb, Sb, and Au in Georgia showed abnormal distribution. The rest of the elements were normally or log-normally distributed. Independent T-test and Mann-Whitney U test indicated that Rb, I, Cs, and Pb in moss samples of Armenia and Georgia from similar sources. Closer scrutiny of the spatial distribution of these elements showed that high concentrations of Rb, I, and Cs were arbitrarily distributed throughout the whole studied territory, whereas high concentrations of Pb occurred in densely populated areas. Cluster analysis showed that in both cases Rb and Cs appeared in the same group of cluster with the other geogenic elements. In case of Pb and I, though both appeared together, the elements included in this group were different in the two countries. In Armenia Cd, As, Sb, Cu, Zn and Se were in the same group as Pb and I, whereas in the case of Georgia the two elements occurred in the same group as Se, Br, and Au. This implies that the sources of Pb and I may be different in the two countries. Local Moran's I index was used to reveal spatial clusters (hot spots) in Pb and I distributions. Such clusters were observed in Georgia, in the west near the Black Sea and in the east in direction of the Caspian Sea, indicating that iodine contents are mainly associated with marine precipitation. In the case of Pb a hotspot was identified in the territory of Armenia near the city of Yerevan. This fact confirmed that significant contribution of Pb is mainly from the local anthropogenic sources.

# Plan of Dubna

