





## 29th Task Force Meeting

29<sup>th</sup> February – 4<sup>th</sup> March 2016 Dubna, Russian Federation



# **Programme & Abstracts**



#### **Organizers:**

#### ICP Vegetation Programme Coordination Centre Centre for Ecology & Hydrology Bangor, UK

Harry Harmens Gina Mills

#### **Local organizers:**

Marina Frontasyeva
Inga Zinicovscaia
Otilia Culicov
Tatyana Donskova
Konstantin Vergel
Alexandra Kravtsova
Pavel Nekhoroshkov
Nikita Yushin

#### **PROGRAMME**

#### Monday 29<sup>th</sup> February, 2016

JINR will provide transport per bus between Sheremetievo or Domodedovo international airports and the hotel (travel time: ca. 2 and 4 hrs respectively). The departure time of the bus will depend on flight arrival times.

**16:00 onwards** Registration

**20:00** Welcome reception in the restaurant of hotel Dubna.

#### Tuesday 1<sup>st</sup> March, 2016

Plenary and moss survey sessions will be in the room in the main hall of ICH (International Conference Hall)

Ozone sessions will be in the Blue room on the ground floor of ICH

#### 08:30 Late registration and putting up posters

<b>Session 1:</b>	9:15 – 10:50	Plenary session	Chair: Marina Frontasyeva		
09:15	Welcome address – JINR Director. Academician Victor A. Matveev.				
09:30		<i>enski</i> – Update from Pollution Convention.	the Secretariat of the Long-range		
09:45	<i>Harry Harmens et al.</i> – Overview of the achievements of the ICP Vegetation in 2015 and future workplan (2016-2018).				
10:10	Walter Seidling - ICP Forests - platform for monitoring and research.				
10:30	•	C	atmospheric heavy metal pollution in lata and modelling results.		

#### 10:50 – 11:50 Coffee/tea and poster viewing (with authors at poster)

Session 2:	11:50 – 13:00 Harmens	Plenary session	Chair:	Harry
11:50	Marina Frontasye preliminary results.	va et al. – Information on t	he moss survey in 202	15: some
12:10		Preparations for ozone critica om the epidemiology worksho	1 '	mn 2016,
12:25	<i>Ignacio González I</i> biodiversity.	Fernández – Establishing critic	cal levels for effects of	ozone on
13:40	U	<ul> <li>Applicability of artificial hemical elements in various en</li> </ul>		predicting

#### 13:00 – 14.00 Lunch

Session 3:	14:00 – 15:30 (Two parallel sessions: Ozone and Moss survey)			
Session 3a:	Ozone effects on crops  Chair: Gina Mills			
14:00	Introduction to ozone sessions (Gina Mills) and introductions by participants.			
14:20	Kent Burkey et al. – Updates on studies on ozone-temperature interactions in the field.			
14:40	Vicky Bermejo et al. $-$ O <sub>3</sub> -sensitivity of the Mediterranean Spanish bread wheat: from the old cultivars to the current market-dominant. Preliminary results.			
15:00	<i>Ignacio González Fernández</i> – Ozone effects on the marketable biomass of leafy crops under Mediterranean conditions.			
15:20	General discussion.			
Session 3b:	Moss survey in the EECCA region Chair: Eiliv Steinnes			
14:00	Aleksander Alekseev – Spatial analysis of the area damaged by heavy metals released from smelter industrial plants: case study for Kola Peninsula, Murmansk region, Russia.			
14:20	Inga Zinicovscaia et al. – Multi-element atmospheric deposition study in the Republic of Moldova.			
14:40	Yulia Koroleva et al. – Trace elements accumulation by mosses, lichens and mushrooms in South-Eastern Baltic.			
15:00	Pavel Nekhoroshkov et al. – Atmospheric deposition of major and trace elements in the mountain Crimea studied by the moss biomonitoring technique.			
15:20	General discussion.			
15:30 – 16.00 Coffee/tea and poster viewing				
Session 4:	on 4: 16:00 – 17:30 (Two parallel sessions: Ozone and Moss survey)			
Session 4a:	Ozone: Global outreach activities - (1) Effects on food security Chair: Vicky Bermejo			
16:00	Gina Mills et al. – Modelling the global impacts of ozone on wheat.			
16:20	Discussing, including:			
	<ul> <li>Report from HTAP (Gina); What do we know? What do we need to know? Future ICP Vegetation activities.</li> </ul>			
Session 4b:	Moss survey: improvements and making more use of the data Chair: Aleksander Alekseev			
16:00	<i>Lotti Thöni</i> – Reduction of the number of sampling sites in Switzerland for the survey 2015.			

- 16:20 Emeline Lequy et al. Assessment of the uncertainty associated with heavy metal concentrations in mosses measured in France (1996 to 2011).
- 16:40 *Mitja Skudnik et al.* Spatial interpolation of N concentrations and  $\delta^{15}$ N values in mosses collected within or outside the area of the canopy drip line.
- 17:00 General discussion:
  - Improving moss monitoring manual (see Spanish paper);
  - Publications German colleagues and MossMet data;
  - How can we make more use of ICP Vegetation moss data.

#### Wednesday 2<sup>nd</sup> March, 2016

Session 5: 09:00 – 10:30 (Two parallel sessions: Ozone and Moss survey)

#### Session 5a: Ozone: concentrations and effects Chair: Klaudia Borowiak

- 09:00 *Pierre Sicard et al.* An epidemiological assessment of stomatal ozone flux-based critical levels for visible ozone injury in Southern European forests.
- 09:20 Evgenios Agathokleous et al. Growth, physiology and productivity of willow (Salix sachalinensis L.), an energy crop, exposed to ethylene di-urea under O<sub>3</sub>-enriched free air.
- 10:00 Samia Madkour Different bean (*Phaseolus vulgaris* L.) genotypes exhibit different modes of tolerance against ozone injury.
- 10:20 Discussion

#### Session 5b: Mosses as biomonitors of radionuclides Chair: Trajce Stafilov

- 09:00 *Eiliv Steinnes et al.* Use of mosses for monitoring atmospheric deposition of radionuclides possibilities and limitations.
- 09:20 *Miodrag Krmar et al.* Spatial distribution of some radionuclides measured in mosses collected over large area.
- 09:40 *Zbigniew Ziembik et al.* Application of gamma spectrometry and compositional data analysis in estimation of atmospheric deposition.
- 10:00 *Grzegorz Kosior et al. Pleurozium schreberi* (Brid.) Mitt. as a bioindicator of heavy metal pollution and radionuclides in selected Polish National Parks.
- 10:20 General discussion.

#### 10:30 – 11:00 Coffee/tea and poster viewing

Session 6: 11:00 – 12:30 (Two parallel sessions: Ozone and Moss survey)

#### Session 6a: Ozone: Global outreach activities - (2) Effects on carbon sequestration and

biodiversity Chair: Kent Burkey

- 11:00 *Mary Ramos* Ozone pollution in Central America.
- 11:20 Sheikh Saeed Ahmad Spatio-temporal analysis of atmospheric ozone based on GIS modelling in Rawalpindi/Islamabad, Pakistan.

11:40 Gina Mills et al. – Impact of ozone on carbon sequestration and biodiversity, field-based evidence of ozone impacts.

Discussing, including:

- What do we know? What do we need to know? Future activities.

#### **Session 6b:** Moss survey: future activities and opportunities

**Chair: Marina Frontasyeva** 

- 11:00 Luca Paoli et al. Do lichen bioaccumulation data tell the truth?
- Discussion on progress 2015/16 moss survey and future activities:
  - Preparations for report of 2015/16 moss survey;
  - Opportunities for monitoring air pollution in urban areas;
  - Opportunities for further enhancement participation EECCA coutries.

Lunch: 12:30 – 14.00

Session 7: 14:00 – 15:30 (Two parallel sessions: Ozone and Moss survey)

#### Session 7a: Ozone: mapping of ozone risks Chair: Gina Mills

- 14:00 *Harry Harmens* Mapping procedure within the Convention.
- 14:20 Gina Mills Mapping ecosystems at risk from ozone in the UK.
- 14:40 *Ignacio González Fernández* Mapping ecosystems at risk from ozone in Spain.
- 15:00 Discussion including:
  - How do national maps of risks of ozone impacts compare with those produced by EMEP?
  - Introducing a call for data within the ICP Vegetation Opportunities and limitation.

#### Session 7b: Moss survey in South-Eastern Europe Chair: Sébastien Leblond

- 14:00 *Trajce Stafilov et al.* Heavy metals air pollution study in mines environments. Case study Bregalnica river basin, Republic of Macedonia.
- 14:20 *Pranvera Lazo et al.* First Albanian moss biomonitoring survey and some future considerations.
- 14:40 Agnes Balint et al. Atmospheric deposition of heavy metals in "Óbuda" and "Margaret" Islands (Budapest, Hungary) tested by different mosses and ICP-OES.
- 15:00 Claudia Stihi et al. Moss survey 2010 in Romania. Results and perspectives.
- 15:20 Discussion.

#### 15:30 – 16:00 Coffee/tea and poster viewing

Session 8: 16:00 – 17:30 (Two parallel sessions: Ozone and Moss survey)

#### Session 8 a: Ozone: critical levels methodology Chair: Ignacio González Fernández

Current developments in methodology (Led by Gina Mills).

Focus on (semi-)natural vegetation (Led by Ignacio González Fernández).

Discussion on field-based evidence of ozone effects:

- What do we know? What do we need to know? Future activities.

#### **Session 8b:** Moss survey: outreach

Dinesh Saxena – Assessing airborne pollution by mosses as biomonitors - Long-

term integrated monitoring of atmospheric metals (2000-2010).

16:20 Discussion on further outreach opportunities.

19:00 Conference dinner at JINR House of Scientists.

#### Thursday 3<sup>rd</sup> March, 2016

16:00

#### **Session 9:** 09:00 – 10:30 **Plenary session**

**Chair: Harry Harmens** 

Chair: Mitja Skudnik

- Reporting back from ozone and moss sessions
- Medium-term work plan ICP Vegetation 2016 2018
- Decisions and recommendations of the 29<sup>th</sup> Task Force Meeting
- 30<sup>th</sup> ICP Vegetation Task Force Meeting
- Other business

#### 10:30 – 11:00 Coffee/tea, taking down posters

**Departure bus to airports for those leaving on Thursday.** Lunch will be provided for the journey on request.

Lunch: 12:00 – 13:00

Afternoon Workshop on moss survey for EECCA countries (in Russian) and option for others to visit JINR.

#### Friday 4th March, 2016

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.

#### **List of Abstracts of Oral Presentations**

#### General

<u>Harmens H.</u>, Mills G., Hayes F., Sharps K., and the participants of the ICP Vegetation. Overview of the achievements of the ICP vegetation in 2015 and future workplan (2016 – 2018). (17)

Seidling W. *ICP forests network – a monitoring and research platform* (18)

#### **Ozone**

Agathokleous E., Kanie S., Paoletti E., Manning W.J., Saitanis C.J., Satoh F., Koike T. *Growth, physiology and productivity of willow (Salix sachalinensis L.), an energy crop, exposed to ethylene di-urea under O* $_3$ -enriched free air. (21)

Ahmad, S.S. Spatio-temporal analysis of atmospheric ozone based on GIS modelling in Rawalpindi/Islamabad, Pakistan. (23)

<u>Bermejo V.</u>, González-Fernández I., Elvira S., Sanz J., Calvete-Sogo, H; García-González, H., Alonso R. *O*<sub>3</sub>-sensitivity of the Mediterranean Spanish bread wheat: from the old cultivars to the current market-dominant. Preliminary results. (24)

<u>Burkey K.O.,</u> Ray S.J., Pursley W.A., Zobel R.W. *Updates on studies of ozone-temperature interactions in the field.* (25)

González-Fernández I., Calatayud V., Elvira S., Calvo E., Aparicio P., Sanz J., Sánchez-Sánchez M., Alonso R., Bermejo V. *Ozone effects on the marketable biomass of leafy crops under Mediterranean conditions.* (26)

Mills, G., Karlsson, P.-E., Pleijel, H., Braun, S., Büker, P., González Fernández, I. and participants of the workshop. *Preparations for ozone critical level workshop, autumn 2016, Spain and report from the epidemiology workshop.* (28)

Mills G, Sharps K., Simpson D., Pleijel H., Broberg M., Harmens H., Hayes F., Emberson L., Buker P., Feng Zh., Dentener F. *Quantifying the threat to global wheat production and quality from ozone pollution.* (29)

Ramos Aruca M. Air pollution in Central America. (30)

<u>Sicard P.</u>, De Marco A., Dalstein-Richier L, Tagliaferro F., Renou C., Paoletti E. *An epidemiological assessment of stomatal ozone flux-based critical levels for visible ozone injury in Southern European forests.* (32)

#### Moss survey

<u>Alekseev A.</u> Spatial analysis of the area damaged by heavy metals released from smelter industrial plants: case study for Kola Peninsula, Murmansk region, Russia. (39)

<u>Bálint Á.</u>, Komlós L., Szaniszló A. Atmospheric deposition of heavy metals in "Óbuda" and "Margaret" islands (Budapest, Hungary) tested by different mosses and ICP-OES. (42)

<u>Frontasyeva M.V.</u>, Harmens H., Steinnes E. *Information on the moss survey in 2015: some preliminary results.* (51)

<u>Ilyin I.</u> Analysis of long-term trends of atmospheric heavy metal pollution in the EMEP countries based on moss survey data and modeling results. (59)

Koroleva Yu, Okhrimenko M., Revunkov V. Trace elements accumulation by mosses, lichens and mushrooms in South-Eastern Baltic. (60)

Kosior G., Frontasyeva M., Zincovscaia I., Ziembik Z., Dołhańczuk-Śródka A. *Pleurozium schreberi (brid.) Mitt. as a bioindicator of heavy metal pollution and radionuclides in selected polish national parks.* (61)

<u>Krmar M.</u>, Radnović D., Mesaros M., Hansman J., Medić Ž. Spatial distribution of some radionuclides measured in mosses collected over large area. (62)

<u>Lazo P.</u>, Qarri F., Bekteshi L., Allajbeu S., Frontasyeva M., Stafilov T. *First Albanian moss biomonitoring survey and some future considerations.* (63)

<u>Lequy E.</u>, Pascaud A., Sauvage S., Leblond S. Assessment of the uncertainty associated with heavy metal concentrations in mosses measured in France (1996 to 2011). (66)

<u>Nekhoroshkov P. S.</u>, Kravtsova A. V., Frontasyeva M. V. Atmospheric deposition of major and trace elements in the mountain Crimea studied by the moss biomonitoring technique. (69)

Paoli L., Vannini A., Monaci F., Loppi S. Do lichen bioaccumulation data tell the truth? (70)

<u>Šajn R.</u>, Alijagić J. Applicability of artificial neural networks for predicting concentrations of chemical elements in various environments. (75)

Saxena D. K. Assessing airborne pollution by mosses as biomonitors - long-term integrated monitoring of atmospheric metals (2000-2010). (76)

Skudnik M., Jeran Z., Batič F., Kastelec D. Spatial interpolation of N concentrations and  $\delta^{15}n$  values in the mosses collected within or outside the area of canopy drip line. (78)

<u>Stafilov T.</u>, Balabanova B., Šajn R. *Heavy metals air pollution study in mines environments.*Case study Bregalnica river basin, Republic of Macedonia. (80)

<u>Steinnes E.</u> Use of mosses for monitoring atmospheric deposition of radionuclides: possibilities and limitations. (81)

<u>Stihi C.</u>, Popescu I.V., Frontasyeva M., Radulescu C., Ene A<sup>3</sup>, Culicov O., Cucu-Man S., Todoran R., Zinicovscaia I. *Moss survey 2010 in Romania. Results and perspectives.* (82)

Thöni L. Reduction of the number of sampling sites in Switzerland for the survey 2015. (84)

<u>Ziembik Z.</u>, Dołhańczuk-Śródka A. *Application of gamma spectrometry and compositional data analysis in estimation of atmospheric deposition*. (86)

<u>Zinicovscaia I.,</u> Hramco C., Vergel K.N., Gundorina S.F., Culicov O.A., Frontasyeva M.V. Multi-element atmospheric deposition study in the Republic of Moldova. (87)

#### **List of Abstracts of Poster Presentations**

#### Ozone

Agathokleous E., Kita K., Paoletti E., Manning W.J., Saitanis C.J., Koike, T. Samplings of a hybrid larch F1 (Larix gmelinii var. japonica  $\times$  L. kaempferi) grown under elevated  $O_3$  levels and treated with ethylene di-urea: a free-air- $O_3$ -enrichment experiment in northern east Asia. (22)

<u>Madkour S. A.</u> Different bean (Phaseolus vulgaris 1.) Genotypes exhibit different modes of tolerance against ozone injury. (27)

Saitanis, C.J., <u>Agathokleous, E.</u>, Pallides, A., Papadimitriou, D., Karpouzis, E., Bilalis, D., Vougeleka, V., Mouzaki-Paxinou, A.C. *A study of the response of 14 Cyprian wheat cultivars to ozone.* (31)

<u>Sicard P.</u> and Rossello Ph. *Spatiotemporal trends of surface ozone concentrations and metrics in France.* (33)

#### Moss survey

Allajbeu Sh., Lazo P., Frontasyeva M. Moss biomonitoring and epithermal neutron activation analysis of trace element atmospheric deposition in Albania (2010/2014). (37)

<u>Aleksiayenak Yu.</u> V., Frontasyeva M.V. *Trace element atmospheric deposition study in Belarus.* (38)

Aničić Urošević M., Vuković G., Milićević T., Vergel K., Frontasyeva M., Tomašević M., Popović A. Moss bag biomonitoring of airborne toxic element decrease on a small scale: crossroad and two- and one-lane street study. (40)

<u>Baljinnyam N.,</u> Lkhagvajav P., Enkhjargal E., Frontasyeva M.V., Pavlov S.S, Gundorina S.F. *Preliminary results of trace element atmospheric deposition study in Mongolia.* (41)

Barandovski L., <u>Stafilov T.</u>, Balabanova B., Sajn R. *Study of nitrogen pollution in Macedonia by moss biomonitoring technique and Kjeldahl method.* (43)

Borowiak K., Kanclerz J., Lisiak M., Budka A., Mleczek M., Przemysław Niedzielski P. Rare earth elements and platinum group elements accumulation in Taraxacum officinale collected from Poznan city area. (44)

<u>Bukharina I.L.</u> About the species composition of microscopic fungi in soils and woody plant roots in urban environment. (45)

Cucu-Man S.M, <u>Culicov O.A.</u>, Frontasyeva M., Ene A., Steinnes E. *Challenges and opportunities in biomonitoring atmospheric trace element depositions: a case study in eastern Romania.* (46)

Doan Phan T.T., <u>Trinh Thi T.M.</u>, Le Hong K., Frontasyeva M.V. *Air pollution in Central and Southern Vietnam using moss technique and neutron activation analysis.* (47)

<u>Dołhańczuk-Śródka A.</u>, Zbigniew Ziembik Z., Tadeusz Majcherczyk T., Maria Wacławek M. *Comparison of radioisotopes content in moss and in surface soil layer.* (48)

<u>Dunaev A.M.</u>, Rumayantsev I.V., Grinevich V.I., Strelkova L.P., Frontasyeva M.V. *Assessment of air quality in the vicinity of Volgorechensk power station using moss biomonitoring.* (49)

Erenturk S., Haciyakupoglu S. Preliminary study on radioactivity and heavy metals on moss at ITU Energy Institute. (50)

Gecheva G., Yurukova L., Gribacheva N. Temporal trends in Bulgaria within the European moss surveys. (52)

Gluschenko V.N., Solodukhin V.P., Siloachev I., Lennik S., Omarova N.M., <u>Makhambet A.</u>, Chepurchenko O., Frontasyeva M.V. *First moss survey in Kazakhstan.* (53)

Godzik B., Stanek M., Szarek-Łukaszewska G., Łopata B., Kapusta P. Spatial and temporal changes in heavy metal concentration in Niepolomice Forest – a long-time moss monitoring with Pleurozium schreberi as bioindicator. (54)

<u>Gorelova S.V.</u>, Babicheva D., Ignatova T., Volkova E.M., Svetasheva T.Yu., Vergel K.N., Frontasyeva M.V. *Elemental content in different moss species in Tula Region, Russia.* (55)

<u>Haciyakupoglu S.</u>, Erenturk S. *Neutron activation analysis of some plant samples at Istanbul Technical University Energy Institute.* (56)

<u>Hristozova G.</u>, Marinova S., Strelkova L.P., Goryainova Z.I., Frontasyeva M.V., Stafilov T. *Trace elements atmospheric deposition study in the vicinity of Kardzhali lead-zinc plant in Bulgaria*. (587

Ibrahimov Z., Djabbarov N., Khalilova L., Nuguyeva Sh., Madadzada A., Strelkova L.P., <u>Mammadov E.</u>, Frontasyeva M.V. *First attempt of trace element atmosperic deposition study in Azerbaijan based on moss analysis.* (58)

<u>Lequy E.</u>, Pascaud A., Sauvage S., Leblond S. *Temporal trends and spatial distribution of trace metals in mosses over France (1996 - 2011): new approaches including uncertainties.* (65)

Maňkovská, B., Izakovičová, Z., Oszlányi, J.Frontasyeva, M.V., Ostrovnaya T.M. Temporal and spatial trends (1990–2010) of trace element atmospheric deposition in Slovakia: assessment based on moss analysis. (67)

Monaci F., Ancora S., Bianchi N., Paoli L., Loppi S. *Biomonitoring mercury contamination in the Mt. Amiata mining area (S Tuscany, Italy): a historical appraisal and future perspectives.* (68)

<u>Pavlíková I.,</u> Jančík, P.1, Lacková, E., Motyka, O., Brunčiaková, M., Strelkova, L.P., Frontasyeva M.V. *Preliminary results of moss survey in Czech Republic in 2015.* (71)

Qarri F., Bekteshi L., Allajbeu Sh., Kane S., Marku E., Stafilov T., Lazo P. *Moss biomonitoring in Albania: present and future.* (72)

<u>Radnovic D.</u>, Hansman J., Krmar M. *Influence of vegetation on atmospheric deposition of airborne radionuclides.* (73)

<u>Rumyantsev I.V.</u>, Dunaev A.M., Grinevich V.I *Investigation of air quality of Ilinskoe district* (*Ivanovo region, Russia*) by moss technique. (74)

<u>Shetekauri S.</u>, Chaligava O., Shetekauri T., Kvlividze A., Kirkesali E.I., Kalabegishvili T., Chepurchenko O.E., Frontasyeva M.V. *First moss survey in Georgia*. (77)

Špirić, Z., <u>Stafilov T.</u>, Vučković, I. *Study of lead pollution in Croatia by using moss biomonitoring and ICP-AES.* (79)

Trtić-Petrović T. Technology-critical elements – novel pollutants. (83)

<u>Vergel K.N.</u>, VikhrovaI.V., Frontasyeva M.V., Goryainova Z.I., Ostrovnaya T.M. *The moss technique and neutron activation analysis for trace element atmospheric deposition study in Tikhvin district, Leningradskaya oblast'*. (85)

### **GENERAL**

#### OVERVIEW OF THE ACHIEVEMENTS OF THE ICP VEGETATION IN 2015 AND FUTURE WORKPLAN (2016 – 2018)

<u>Harmens, H.</u><sup>1</sup>, Mills, G.<sup>1</sup>, Hayes, F.<sup>1</sup>, Sharps, K.<sup>1</sup>, and the participants of the ICP Vegetation

<sup>1</sup> ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, Gwynedd LL57 2UW, UK. hh@ceh.ac.uk

The ICP Vegetation is an international programme that reports on the effects of air pollutants on natural vegetation and crops [1]. It reports to the Working Group on Effects (WGE) of the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP). In particular, the ICP Vegetation focuses on the following air pollution problems: quantifying the risks to vegetation posed by ozone pollution and the atmospheric deposition of heavy metals, nitrogen and persistent organic pollutants (POPs) to vegetation. The ICP Vegetation also studies the impacts of pollutant mixtures (e.g. ozone and nitrogen), impacts on ecosystem services and biodiversity, and interactions between air pollutants and climate change.

At the 29<sup>th</sup> Task Force Meeting we will report on the achievements of the ICP Vegetation in 2015 [1], including:

- Implications of rising background ozone for vegetation in Europe [2];
- Interacting effects of co-occurring pollutants (ozone and nitrogen) and climatic stresses on vegetation [3];
- Update of Chapter 3 of the Modelling and Mapping Manual [4];
- Supporting evidence for ozone impacts on vegetation;
- Progress with the European moss survey 2015/2016;
- Contributions to common workplan items of the WGE.

We will also discuss the future workplan (2016 - 2018), such as progress made with items to be reported to the LRTAP Convention in 2016:

- Update report on field-based evidence of ozone impacts on vegetation;
- Report on ozone impacts on biodiversity;
- Ozone critical levels workshop (Spain, autumn), including preparations so far.

And other deliverables for the immediate future:

- Revised ozone risk assessments methods and further revision of Chapter 3 of the Modelling and Mapping Manual (2017);
- Report on the outcome of the European moss survey 2015/2016 (2018).

#### Acknowledgement

We thank the UK Department for Environment, Food and Rural Affairs (Defra) for funding the ICP Vegetation Programme Coordination Centre. Further financial support was provided by the UNECE and the UK Natural Environment Research Council (NERC).

#### References

- [1] http://icpvegetation.ceh.ac.uk/publications/documents/FinalICPVegetationannualreport2014-15.pdf
- [2] http://icpvegetation.ceh.ac.uk/publications/documents/Brochureozonetrends.pdf
- [3] http://icpvegetation.ceh.ac.uk/publications/documents/Brochureozonenitrogenandclimatechange.pdf
- [4] http://icpvegetation.ceh.ac.uk/publications/documents/Ch3-MapMan-2015-06.pdf

#### ICP FORESTS NETWORK – A MONITORING AND RESEARCH PLATFORM

Seidling W.

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Forests reveal complex interactions with environmental conditions and provide timber and various other benefits for human societies including climate change mitigation effects. Various aspects of forest condition and performance have, therefore, to be carefully monitored. Especially the longevity of its main element, the trees, and the therefore inevitably long rotation periods of commercial forests make careful planning indispensable. Therefore, impacts of air pollutants and adverse climatic conditions along with relevant biotic interactions need to be adequately monitored and reported. As monitoring continues, long time-series evolve, providing excellent opportunities for revising old hypotheses, once given cause to start with the monitoring activities. Besides the revision of old hypotheses on air pollutants and its effects on forests, new research questions have appeared, especially in connection with the climate change and the biodiversity debate. Answers for such questions often need new, not readily available data. Combining data from the monitoring with simulated or remotely sensed data might deliver opportunities to scrutinize upcoming hypotheses. In other cases new parameters have to be assessed. It seems more than reasonable to attach such new assessments to the existing physical infrastructure and use at the same time old data series from the same sites in order to gain higher momentum for explorative and inferential approaches or even mechanistic modeling [1]. Such assessments can not necessarily be provided by the institutions maintaining the monitoring and research infrastructure. Only collaboration with specialists can enable respective investigations. At national level, single ICP Forests plots are already part of various co-operations. At the continental scale, an attached mycorrhiza project has already gained new insights [2]. Similarly, projects should be linked to the ICP Forests possibly in the context of larger international research infrastructure efforts on terrestrial ecosystems.

- 1. Fischer R, Aas W, De Vries W, Clarke N, Cudlin P, Leaver D, Lundin L, Matteucci G, Matyssek R, Mikkelsen TN, Mirtl M, Öztürk Y, Papale D, Potočić N, Simpson D, Tuovinen JP, Vesala T, Wieser G, Paoletti E, 2011: Towards a transnational system of supersites for forest monitoring and research in Europe an overview on present state and future recommendations. iForest 4: 167-171
- 2. LM, Barsoum N, Benham S, Dietrich HP, Fetzer KD, Fischer R, García P, Gehrman J, Kristöfel F, Manninger M, Neagu S, Nicolas M, Oldenburger J, Raspe S, Sánchez G, Schröck HW, Schubert A, Verheyen K, Verstraeten A, Bidartondo MI, 2014: Environmental drivers of ectomycorrhizal communities in Europe's temperate oak forests. Molecular Ecology 23: 5628-5644

### **OZONE**

# GROWTH, PHYSIOLOGY AND PRODUCTIVITY OF WILLOW (Salix sachalinensis L.), AN ENERGY CROP, EXPOSED TO ETHYLENE DI-UREA UNDER O<sub>3</sub>-ENRICHED FREE AIR

<u>Agathokleous E.<sup>1</sup></u>, Kanie S.<sup>1</sup>, Paoletti E.<sup>2</sup>, Manning W.J.<sup>3</sup>, Saitanis C.J.<sup>4</sup>, Satoh F.<sup>5</sup>, Koike T.<sup>1</sup>

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During the daytime of growing seasons 2014 (> 2 months) and 2015 (> 4 months), willow cuttings were exposed to ambient O<sub>3</sub> (≈25 nmol mol<sup>-1</sup>, AOZ) or to elevated O<sub>3</sub> (≈80 nmol mol<sup>-1</sup>, EOZ) concentrations, in a free-air-O<sub>3</sub> fumigation system. Furthermore, during 2015 and every 9 days, they were sprayed with 0 or 400 mg L<sup>-1</sup> Ethylene di-urea (EDU0 and EDU400 respectively). Growth over time, photosynthesis and photosynthetic pigments content in O<sub>3</sub>-asymptomatic leaves in autumn 2015 and the final biomass production in late September 2015 were measured. There were no significant EOZ effects on tree height, average crown spread and stem diameter. However, EOZ suppressed, and EDU400 prevented reduction of, the photosynthetic assimilation (A<sub>380</sub>) and the maximum assimilation rate ( $A_{max}$ ). There was no impact of EOZ on stomatal conductance ( $g_{s380}$ ) of EDU0 leaves, but this variable was positively influenced the EDU400 treated plants. In addition, there was no effect of EOZ on Ci:Ca, maximum rates of carboxylation  $(V_{cmax})$ and electron transport  $(J_{max})$ . Asymptomatic leaves of EDU0×EOZ had lower total chlorophyll (TChl) and total carotenoids (TCar) contents and TChl/TCar ratio than those of EDU0×AOZ. EDU400 showed an unexpected trend towards decreased TChl and TCar contents. EOZ protected plants against insect grazing that was impressively significantly? high in AOZ plants. Therefore, plants of both EDU treatments in AOZ and plants of EDU0 in EOZ had similar biomass production. However, plants of EDU400 in EOZ showed higher biomass production than AOZ plants. From these results, it seems that (i) EDU protected the plants of this species against EOZ through a biochemical mode of action rather than by biophysical limitations and (ii) the effects of abiotic factors are hardly identified, or predicted, due to interactions with biotic factors, such as insect grazing.

# SAMPLINGS OF A HYBRID LARCH $F_1$ (Larix gmelinii var. japonica $\times$ L. kaempferi) GROWN UNDER ELEVATED $O_3$ LEVELS AND TREATED WITH ETHYLENE DI-UREA: A FREE-AIR- $O_3$ -ENRICHMENT EXPERIMENT IN NORTHERN EAST ASIA

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Near ground O<sub>3</sub> concentrations increased over the last decades, damaging, thus, plants. In order to study elevated O<sub>3</sub> effects on a hybrid larch F<sub>1</sub> (hereafter, F<sub>1</sub>), two-year-old seedlings were planted in 20 L pots and placed in the free-air-O<sub>3</sub> system of Sapporo Experimental Forest, in May 2014. The seedlings were exposed either to ambient (AO<sub>3</sub>) or to elevated (≈80 nmol mol<sup>-1</sup>; EO<sub>3</sub>,) O<sub>3</sub> concentration from mid-August to late October, in 2014 and from the end of April to the end of October, in 2015. In addition, 200 ml of 0 mg L<sup>-1</sup> (EDU0) or 400 mg L<sup>-1</sup> (EDU400) Ethylene di-urea (EDU) water solution was applied as a soil drench to each plant every 9 days, beginning 9 days before initiating the  $O_3$  fumigation in 2015. Tree height (h), canopy width (w) and basal stem diameter (d) were measured over time. There were no significant  $O_3$  effects on h and w, however,  $EO_3$ decreased d of EDU0 seedlings later in the  $2^{nd}$  growing season (2015). EDU400 protected the seedlings against EO<sub>3</sub>-induced decrease in d. Regarding photosynthesis of mature needles during late June 2015, EO<sub>3</sub> suppressed photosynthetic rate  $(A_{380})$ , stomatal conductance  $(g_{s380})$  and transpiration  $(E_{380})$ ; EDU400 did not prevent  $g_{s380}$  and  $E_{380}$ reduction caused by EO<sub>3</sub>. However, the  $A_{380}$  reduction was higher in EDU0 than in EDU400 treated plants. EO<sub>3</sub> did not affect the maximum rates of carboxylation  $(V_{cmax})$  and electron transport  $(J_{max})$ , however it did suppress  $A_{max}$ ; EDU400 did not prevent  $A_{max}$ suppression. At late July, there was a significant EO<sub>3</sub> impact on total chlorophyll content which was prevented by EDU400. The chlorophyll a to chlorophyll b ratio was not affected by EO<sub>3</sub>, and no phaeophytinization (as indicated by the OD435/OD415 index of phaeophytinization) was observed. Higher foliar O<sub>3</sub> injury and early abscission were observed in EDU0 plants. In conclusion, EDU protected F<sub>1</sub> seedlings from EO<sub>3</sub>, and its mode of action was not related to prevention of O<sub>3</sub> uptake by stomata.

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### SPATIO-TEMPORAL ANALYSIS OF ATMOSPHERIC OZONE BASED ON GIS MODELING IN RAWALPINDI/ISLAMABAD, PAKISTAN.

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Present study highlighted the application of Geographical information system (GIS) and emerging discipline of Eco-informatics which are very helpful in assessing air pollution and managing air quality system. Air pollution is considered as key threat to humans, animals and plants health globally. Pakistan is non-industrialized country, but also a victim of air pollution which is increasing day by day. Among all air pollutants, Ozone  $(O_3)$  has detrimental effects on biosphere's living organisms. In the present study, concentration of  $O_3$  is investigated by using ozone analyzer (Model 400E) in twin cities of Pakistan for two successive years i.e. 2009 and 2011. Results revealed that the annual average  $O_3$  concentration found in Rawalpindi/ Islamabad is  $18.2 \pm 1.24$  ppb respectively. Maximum concentration of  $O_3$  showed in months of summer and lower concentrations in months of winter resulting from the enhanced process of photolysis of  $NO_2$  that leads to  $O_3$  formation. While spatial interpolation by using ArcGIS showed variations graphically in  $O_3$  concentration level throughout different seasons (Fig. 1). Besides forecasting is done by mean of artificial neural network model trained with evolutionary approaches that is helpful in the simulation of air quality index with maximum performance.

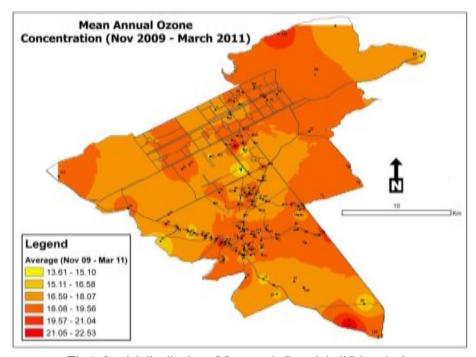


Fig.1. Spatial distribution of O<sub>3</sub> conc. in Rawalpindi/Islamabad.

### O<sub>3</sub>-SENSITIVITY OF THE MED SPANISH BREAD WHEAT: FROM THE OLD CULTIVARS TO THE CURRENT MARKET-DOMINANT. Preliminary results

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Wheat have been considered as the most sensitive cereal to the increasing levels of surface ozone (O<sub>3</sub>); accordingly the exposure and dose-response functions developed for this crop are currently uses for assessing the risk of O<sub>3</sub> effects on agricultural production at European scale [1]. However, the response functions are based on experiments developed under central and north-European climate and using cultivars adapted to these latitudes. However, high uncertainty exits about the application of these functions in the Southern European countries, with a Mediterranean climate profile and specific cultivars adapted to the water limited conditions characteristic of the area. In 2015, a new OTC experiment has been developed in the central Spain aiming to determine the relative sensitivity to O<sub>3</sub> of the most frequently wheat cultivars grew in Spain at the present, according with the agronomic statistics of the country, and to compare them with medium-age and old cultivars. A total of 15 cultivars have been tested, five from each of the three groups considered: old, medium and modern cultivars. Four O<sub>3</sub> treatments have been considered. Plants were exposed from the start of the anthesis until grain maturity. Biomass, yield and physiological parameters related to gas exchange and water stress tolerance have been measured in order to find the main traits related with O<sub>3</sub>-sensitivity. Preliminary results about biomass and yield effects are presented, and the effect is compared with the more northern wheat studies. This study is funded by projects NEREA (AGL2012-37815-C05). AgriSost (P2013/ABI-2717) and by the Agreement between CIEMAT and the Spanish Ministry of Agriculture, Food and Environment for stablishing critical levels and loads for vegetation.

1. CLRTAP, 2010. Chapter 3 of the CLRTAP Mapping Manual: Mapping Critical Levels for Vegetation. Available at: http://icpvegetation.ceh.ac.uk/manuals/mapping manual.html

### UPDATES ON STUDIES OF OZONE-TEMPERATURE INTERACTIONS IN THE FIELD

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Predicting the impacts of air pollution and climate change on vegetation requires understanding of the interactions between elevated air temperature and atmospheric gases such as ozone and carbon dioxide. Imposing elevated temperature treatments while manipulating gas concentrations remain a technological challenge for field studies. An air exclusion system (AES) for exposing plants to combinations of elevated temperature and ozone in field plots is being developed by our group. Each AES plot consists of two opentop chamber bottom panels placed in parallel to form a 3m x 10m treatment area. Modified open-top chamber fan boxes provide charcoal-filtered (CF) air that is heated to approximately +4°C above ambient conditions by a combination of electrical resistance heaters and solar heated water. Ambient air or heated air is then distributed within each plot through holes in the inner wall of the double-walled panels. To compensate for decreased relative humidity upon warming the air, the heated air is passed through a misting system prior to distribution within the elevated temperature plots. Elevated ozone treatments are imposed by adding ozone to the air stream before distribution in the plot. Soybean cultivar "Jake" was grown in the AES system during the 2015 growing season. Treatments were a CF air control, heated CF air (CF+H), elevated ozone (CF+O3), and the combination of heated CF air and elevated ozone (CF+O3+H). Ambient air (AA) plots were included in each experimental block. Drip irrigation was used to maintain soil moisture across plots because evapotranspiration demand differed between heat treatments. Elevated temperature had greater impact on seed yield than did elevated ozone for this cultivar-treatment combination. Yield declined by approximately 20% in both the CF+H and CF+O3+H heated plots relative to the unheated CF control (Table 1). Elevated ozone alone reduced vield by 6% in the CF+O3 treatment, but this decline was not statistically significant.

Table 1. Effects of elevated ozone and temperature on final seed yield of soybean grown in AES				
plots during 2015. Yields are plot means $\pm$ SE (n=3). Percentages indicate relative yield				
compared to CF. Seasonal values for the ozone 12-hour mean and AOT40 are shown.				

Treatment	Seed yield	12-hour mean	AOT40
	$(g m^{-2})$	(ppb)	(ppb-hours)
CF	$783 \pm 63 \ (100 \ \%)$	16	111
CF+O <sub>3</sub>	737 ± 66 (94 %)	62	33000
CF+H	618 ± 77 (79 %)	16	95
CF+O <sub>3</sub> +H	586 ± 34 (75 %)	60	31011
AA	715 ± 58 (91 %)	34	3602

### OZONE EFFECTS ON THE MARKETABLE BIOMASS OF LEAFY CROPS UNDER MEDITERRANEAN CONDITIONS

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Visible injury surveys have shown that the scale of the O<sub>3</sub> effects on horticultural crops can be wide enough to cover extensive areas of Europe and particularly in the Mediterranean area [1], one of the main regions for horticultural production in Europe. Yield data from fumigation experiments have been used to derive exposure- and doseresponse relationships for some horticultural crops and O<sub>3</sub> critical levels (CLe) have been established for a set of representative species for which the experimental dataset was considered of sufficient quality: potato and tomato (CLRTAP, 2010). However, it has been recognized that the species selected for the derivation of O<sub>3</sub> CLe may not be the most sensitive ones [2, 3] meaning that O<sub>3</sub> effects on horticultural production may be happening at O<sub>3</sub> levels below the current CLe. Leafy crops are important horticultural crops with a proven sensitivity to O<sub>3</sub>. In addition to O<sub>3</sub> induced reductions in biomass growth, the incidence of leaf visible injury can reduce the marketable yield of these crops even causing, under exceptional circumstances, a complete crop loss due to the effects on the aspect of the crop [1]. Furthermore, agronomic practices for these crops, providing a plentiful supply of water and nutrients during periods of high O<sub>3</sub> concentration, can favour the absorption of O3 through the stomata, which has been associated with increasing risks of O<sub>3</sub> effects [4]. For these reasons, leafy crops are probably more O<sub>3</sub> sensitive than tomato, the representative crop used for risk assessments of O<sub>3</sub> effects on horticultural production in Mediterranean areas. With the aim of extending the experimental database of O<sub>3</sub> effects on leafy crops, an O<sub>3</sub> fumigation study with cultivars of spinach and chard growing under Mediterranean conditions was established in two open-top chamber facilities from Spain. On average, the elevated O<sub>3</sub> treatments induced a reduction of the marketable yield of 16 and 7% compared to charcoal-filtered air controls in spinach and chard respectively. However, ambient O<sub>3</sub> concentrations did not induced a statistically significant effect. Differences between cultivars and site in the response to O<sub>3</sub> were identified. These results will be discussed in combination with other studies on O<sub>3</sub> effects in leafy crops in order to explore the experimental basis for establishing a common O<sub>3</sub> CLe for this type of crops.

- 1. Fumagalli et al., 2001. Atmos Env 35, 2583-2587.
- 2. CLRTAP, 2010. Chapter 3 of the CLRTAP Mapping Manual: Mapping Critical Levels for Vegetation. Available at: <a href="http://icpvegetation.ceh.ac.uk/manuals/mapping">http://icpvegetation.ceh.ac.uk/manuals/mapping</a> manual.html.
- 3. Bermejo et al., 2010. 23<sup>rd</sup> ICP-Vegetation TFM, Tervuren, Belgium, 1-3 February. Available at: <a href="http://icpvegetation.ceh.ac.uk/events/23rd\_tf">http://icpvegetation.ceh.ac.uk/events/23rd\_tf</a> programme.htm
- 4. Mills et al., 2011. Atmos Env 45, 5064-5068.

### DIFFERENT BEAN (PHASEOLUS VULGARIS L.) GENOTYPES EXHIBIT DIFFERENT MODES OF TOLERANCE AGAINST OZONE INJURY

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Different mechanisms of ozone tolerance were detected in 7 genotypes of *Phaseolus* vulgaris. Three-week-old plants were exposed to 80-120 ppb ozone for three days (7-8 hrs per day) in controlled environment chambers. Ozone sensitivity was assayed by recording the extent of visible injury and measuring physiological characters thought to mediate ozone response: the net photosynthetic rate (Pn), stomatal conductance (Gs), electrolyte leakage, specific activity and isozymes level of superoxide dismutase (SOD) and specific activity of glutathione reductase (GR) (two superoxide scavenging enzymes). None of the genotypes studied appeared to defend against ozone damage simply by blocking ozone entry through decreased stomatal conductances. Giza 3 the only Egyptian cultivar was found to be the most tolerant genotype and appeared to mitigate ozone damage through an effective stomatal closure coupled to the action of antioxidants. Two of the tested varieties exhibiting only mild visible symptoms and low stomatal conductances in response to ozone incurred the most serious membrane damage and were thought to lack an antioxidant defense mechanism. Damage in sensitive genotypes could not be linked to high stomatal conductances and extensive ozone absorbance into the leaf chamber. Injury to sensitive cultivars appeared to be caused by low level of antioxidant or insufficient protection from scavenging enzymes which leads to membrane peroxidation in spite of effective stomatal closure. One fact was eminently clear: in the two pairs of bean genotypes tested, high levels of oxiradicals generated by ozone stress resulted in high protein turnover, which lead to the induction of *de novo* enzyme synthesis (mainly SOD) to maintain a scavenging level sufficient for cell protection against oxidative damage. Tolerance could not be ascribed to levels of SOD only or GR only but that endogenous optimal levels of all SOD isozymes and GR should exist in a given genotype to induce tolerance. The results also pointed to the danger of ranking bean cultivars for ozone tolerance on the basis of visible injury. It also disputed the hypothesis that tolerance in common beans derives primarily from lowered stomatal conductances under ozone stress. The results suggest that different bean cultivars possess different modes of tolerance to ozone even when they belong to comparatively related genetic lines.

### PREPARATIONS FOR OZONE CRITICAL LEVEL WORKSHOP, AUTUMN 2016, SPAIN AND REPORT FROM THE EPIDEMIOLOGY WORKSHOP

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From 23–25 November, 2015, the ICP Vegetation organised two back-to-back works covering (i) Epidemiological evidence of effects of ozone pollution and (ii) Agreement of methodology to be applied in data analysis conducted in preparation for the next Ozone Critical Levels Workshop in the autumn, 2016, Spain. In the epidemiology workshop, the "state of the art" and the methodology (including mapping of variables and statistical methods) regarding epidemiological studies of air pollution impacts on forest growth were discussed. In the critical level workshop, there were a series of generic methodology discussions and group discussion regarding the methodology of particular relevance for crops, (semi-)natural vegetation and trees. Current status, future needs and new developments were discussed:

- Revision of the structure of Chapter 3 of the Modelling and Mapping Manual;
- Flux-based response functions and critical levels for integrated assessment modelling;
- Supporting observational and epidemiological evidence;
- Deriving parameterization of the stomatal ozone flux model (DO<sub>3</sub>SE);
- Establishing dose-response functions;
- Concentration-based critical levels.

At the 29<sup>th</sup> ICP Vegetation Task Force meeting we will discuss the outcome of the two workshops and further actions agreed in preparation for the Ozone Critical Levels Workshop in the autumn, 2016, Spain.

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### QUANTIFYING THE THREAT TO GLOBAL WHEAT PRODUCTION AND QUALITY FROM OZONE POLLUTION

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At the global scale, ozone  $(O_3)$  pollution has been predicted to pose as big a threat to food security as climate change by 2030. Several of the world's most important crops such as wheat, soybean, maize and rice respond to  $O_3$  pollution by decreasing vegetative growth, seed production and root growth leading to reductions in both quantity and quality of yield. Even though negative effects have been detected in the field under current ambient  $O_3$  concentrations,  $O_3$  is not currently included as a modifier of crop growth in global and regional crop modelling.

In this paper we describe a new development in quantifying losses from O<sub>3</sub> pollution for wheat on a global scale based on modelling the stomatal uptake of O<sub>3</sub>. Evidence from European chamber and field studies shows that the uptake of O<sub>3</sub> by stomata (flux) is a superior predictor of O<sub>3</sub> damage, compared to more conventional exceedance of O<sub>3</sub> threshold concentrations. This analysis presents a major step forwards from previous predictions of risk based on O<sub>3</sub> concentration as it includes the modifying effects of climate and soil moisture (including irrigation) on instantaneous O<sub>3</sub> uptake and subsequent effect. We discuss methods for quantifying uncertainty in the analysis and show how we can model the effects of different crop growth cycles or pollution scenarios. Our analysis showed that wheat crops in many areas of the world are being negatively impacted by the pollutant. The worst problems were identified for China, India and the USA. Globally, percentage effects were greater for the temperate climates of the northern rather than the southern hemisphere, in part reflecting the higher O<sub>3</sub> concentrations in the northern hemisphere. Effects were greatest in warm-temperate-dry areas of China and tropical-dry areas of India where irrigation is commonly used resulting in conditions that are highly conducive to O<sub>3</sub> uptake. Estimates based on stomatal uptake of O<sub>3</sub> were lower than those for commonly used concentration-based metrics such as the 7h mean and AOT40. This study has highlighted the spatial variability of global impacts of ozone pollution on wheat production. It also draws attention to the need to consider ozone pollution as a modifying factor in global crop production and food security modelling.

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#### AIR POLLUTION IN CENTRAL AMERICA

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The Central American countries have similar statistics regarding air quality: the six countries of the region show a deterioration of the atmosphere, due to high pollution levels, the result of several factors, including population growth, increasing vehicle fleet, habits agricultural burning and burning of solid waste. The difference between some countries and others are the measures taken to preserve the purity of the air we breath. Air pollution is at the third place among the most serious environmental problems in the area, although some countries have a higher priority. The main air pollutants are particulate matter (generated mainly by vehicles using diesel) and carbon monoxide (CO) and nitrogen dioxide (NO2) and ozone, but these two are issued to a lesser extent than before.

#### A STUDY OF THE RESPONSE OF 14 CYPRIAN WHEAT CULTIVARS TO OZONE

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Tropospheric ozone is considered one of the most widespread phytotoxic air pollutants across the globe. It is well documented that its levels in the atmosphere are continuously growing, threatening the natural and agricultural ecosystems and, thus, the food security. Wheat is one of the most important crops worldwide and several research have documented as among the most sensitive to ozone plant species. We investigated the response of 14 Cyprian wheat cultivars to ozone, namely: Aronas, Acheleia, Gavdos, Giolou, Ekavi, Iosifina, Karpasia, KKolina, Kyperounda, Macedonia, Malloura, Mesaorea, Urania, DW673. The experiment was conducted under laboratory conditions in controlled environment chambers (Photoperiod 14:10; T 28 °C; RH 65%). Seedling were exposed either to ozone (110 ppb X 80 days X 8 hours/day) or to charcoal filtered air (control group).

Ozone caused macroscopic visible injury consisted of chlorosis and necrotic (usually bifacial) spots (Fig. 1). Symptoms were mainly developed in the fully expanded and fully functioning leaves. In the young (still expanding) leaves the symptoms were observed as necrosis of the tips. Some cultivars exhibited higher visible injury scores than others. Those exhibited the highest visible injury scores were the cultivars Malloura (45%), DW673 (43%) Mesaorea (34.3%) and Iosifina (33.5%) while the less injured ones were Kyperounda (5.1%), Urania (6%), Macedonia (11.4%) and Aronas (12.5). The extend of visible injury was highly correlated with SPAD value and chlorophyll content. Stomatal conductance was reduced in the highly injured plants.



Fig.1 Typical ozone-induced symptoms (chlorosis and necrosis) in wheat.

However, the experience from previous experiments with other wheat cultivars suggests that there is a high variability in the response of wheat to ozone and that different cultivars may respond to ozone differently under field conditions. Thus, more experiments are required in order to safely order the cultivars according to their sensitivity to ozone.

# AN EPIDEMIOLOGICAL ASSESSMENT OF STOMATAL OZONE FLUX-BASED CRITICAL LEVELS FOR VISIBLE OZONE INJURY IN SOUTHERN EUROPEAN FORESTS

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Southern forests are at the highest ozone (O<sub>3</sub>) risk in Europe where ground-level O<sub>3</sub> is a pressing sanitary problem for ecosystem health. Exposure-based standards for protecting vegetation are not representative of actual field conditions. A biologically-sound stomatal flux-based standard has been proposed, although critical levels for protection still need to be validated. This innovative epidemiological assessment of forest responses to O<sub>3</sub> was carried out in 54 plots in Southeastern France and Northwestern Italy in 2012 and 2013. Three O<sub>3</sub> indices, namely the accumulated exposure AOT40, and the accumulated stomatal flux with and without an hourly threshold of uptake (POD1 and POD0) were compared. Stomatal O<sub>3</sub> fluxes were modelled (DO3SE) and correlated to measured forest-response indicators, i.e. crown defoliation, crown discoloration and visible foliar O<sub>3</sub> injury. Soil water content, a key variable affecting the severity of visible foliar O<sub>3</sub> injury, was included in DO3SE. Based on flux-effect relationships, we developed species-specific flux-based critical levels (CLef) for forest protection against visible O3 injury. For O3 sensitive conifers, CLef of 19 mmol m-2 for P. cembra (high O<sub>3</sub> sensitivity) and 32 mmol m-2 for P. halepensis (moderate O<sub>3</sub> sensitivity) were calculated. For broadleaved species, we obtained a CLef of 25 mmol m-2 for Fagus sylvatica (moderate O<sub>3</sub> sensitivity) and of 19 mmol m-2 for Fraxinus excelsior (high O<sub>3</sub> sensitivity). We showed that an assessment based on PODY and on real plant symptoms is more appropriated than the concentration-based method. Indeed, POD0 was better correlated with visible foliar O<sub>3</sub> injury than AOT40, whereas AOT40 was better correlated with crown discoloration and defoliation (aspecific indicators). To avoid an underestimation of the real O<sub>3</sub> uptake, we recommend the use of POD0 calculated for hours with a non-null global radiation over the 24-h O<sub>3</sub> accumulation window.

### SPATIOTEMPORAL TRENDS OF SURFACE OZONE CONCENTRATIONS AND METRICS IN FRANCE

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Ozone pollution appears as a major air quality issue in Europe. The calculation of a human health- or vegetation-relevant metrics across a measurement network or administrative-policy region provides a consistent method to predict the relative severity of human health- or vegetation-relevant O<sub>3</sub>. A few issues about O<sub>3</sub>, such as a better understanding of surface trends and a better assessment of O<sub>3</sub> impacts, are still challenging. The objectives of this work were to (i) quantify the spatiotemporal trends in ground-levels O<sub>3</sub> concentrations, associated with potential impacts on human health and vegetation, and to (ii) assess the impact of the changing precursor emission on the time trends. For the first time, a long-term spatiotemporal analysis of annual trends were performed in "61" rural, "92" suburban and "179" urban background stations in metropolitan France over the time period 1999-2012. In this study, we focused on annual surface O<sub>3</sub> metrics (mean concentrations, hourly maxima, median and 98<sup>th</sup> percentile), O<sub>3</sub> human health metrics (SOMO35, i.e. the annual Sum Of daily maximum 8-h Means Over 35 ppb and EU60, i.e. the number of exceedances of daily maximum 8-h values greater than 60 ppb) and O<sub>3</sub> vegetation impact metrics (AOT40, i.e. sum of the hourly exceedances above 40 ppb for daylight hours during the assumed growing season for sensitive crops and forests) at individual sites. Long-term analysis of hourly surface O<sub>3</sub> data from 332 background air pollution monitoring sites in France showed that annual mean concentrations significantly decreased by 0.12 ppb.year<sup>-1</sup> at rural sites. Suburban stations increased annual averages (+ 0.10 ppb.year<sup>-1</sup>) and at urban sites, mean concentrations significantly increased (+ 0.14 ppb.year<sup>-1</sup>) over time. In all station types, a significant reduction in the amplitude of peak ozone concentrations was found at more than 75% of stations. The peak reduction may largely be attributed to the reduction in NO<sub>x</sub> and VOC emissions within the European Union which started in the early 1990s. We demonstrated that the O<sub>3</sub> control measures are effective at rural sites, while O<sub>3</sub> concentrations are still increasing in the cities. The human health and vegetation impact metrics showed a downward trend at the national level for all station types, with the slowest decrease at urban stations. As an example, we obtained negative trends for SOMO35 (- 45 ppb.d.year<sup>-1</sup>), EU60 (- 1.0 days.year<sup>-1</sup>), AOT40c (- 287 ppb.h.year<sup>-1</sup>) and AOT40f (- 302 ppb.h.year<sup>-1</sup>) at rural sites between 1999 and 2012. The generation of realistic spatiotemporal O<sub>3</sub> maps, with sufficient spatial resolution, is a valuable tool for risk assessment, i.e. the assessment of harmful effects to human health or to ecological systems resulting from O<sub>3</sub> exposure. Spatial interpolation techniques, i.e. environmental modelling approaches for estimating the exposure of large populations, are based on geostatistical techniques to interpolate pollutant levels over unsampled areas by means of data measured at the monitoring stations, starting from monitoring station measurements. The approach, concatenating local regression and kriging of residuals obtained by crossvalidation, is an effective way and a valuable tool to provide spatiotemporal mapping of O<sub>3</sub> metrics. This method has been successfully applied, from 332 monitoring stations, over whole domain at 250 × 250 m resolution to perform O<sub>3</sub> metrics maps for a given period.

### **MOSS SURVEY**

### MOSS BIOMONITORING AND ENAA ANALYSIS OF MULTIELEMENT ATMOSPHERIC DEPOSITION IN ALBANIA (2010/2014)

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Moss biomonitoring technique using moss species Hypnum cupressiforme and Scleropodium purum and neutron activation analysis (NAA) were applied to study multielement atmospheric deposition in Albania. Moss samples were collected during the autumn 2010 and summer of 2011 at 44 sites distributed over the country. Sampling was performed in accordance with the Long-Range Transboundary Air Pollution (LRTAP) Convention - International Cooperative Programme (ICP) Vegetation protocol and sampling strategy of the European Programme on Biomonitoring of Heavy Metal Atmospheric Deposition. The presence of 29 (Sc, Ti, V, Cr, Mn, Ni, Co, Zn, Se, Sr, Zr, Mo, Ag, Sb, Cs, La, Ce, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, W, Au, Th, U) elements that was determined by instrumental epithermal neutron activation analysis are discussing in this presentation. The aim of this study was to investigate spatial trends of multielement deposition in Albania by using mosses as biomonitors. Statistical analysis of the concentration data and factor analyses with Varimax rotation helps to identify the emission source. The metal concentration in mosses reflected local and long-range emission sources. Coefficients of varation (CV%) for most of elements are moderate (25 -75 %), while for Au, Co, Ni, Cr, Eu, Gd, and Tm CV > 75 % are high. The skewness and kurtosis are greater then 2 for elements Ag, Au, Sb, Se, V, Cr, Mn, Eu, and Gd, indicating that the frequency distribution of these elements are strongly positively skewed. Most of elements under investigate show high correlation between them. Three factors (F1 to F3) were extracted from Factor Analysis (FA) (Fig. 1). F1 is associated with significant loads on V, Ti, Zr, Hf, Ta, W, Cs, Sc, La, Ce, Sm,

Gd, Tb, Tm, Yb, Th. The association of these elements suggest their lithogenic source. F2 is associated with significant loads on Co Ni and Cr that is probably attributed to their geogenic origin and industrial emission of metallurgy in Elbasan town. F3 is associated with elements Sb, Mo, Zn by suggesting their geogenic origin of sulphure minerals positioned mainly in central part and in north part of the country. Geographical distribution maps of the elements over the sampled territory were constructed using GIS technology, to point out the regions most affected by pollution and to relate this to the known sources of contamination. survey confirms that present biomonitoring and statistical data analysis are important tools in environmental study of atmospheric deposition of metals.

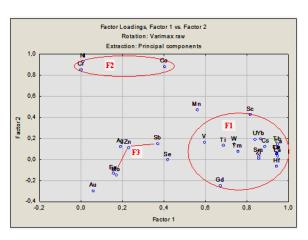


Fig. 1 Loading plots of F1 and F2

The most polluted location was found in the central part of the country, caused mainly by industrial emission of metallurgy, mining industry geogenic factors. The natural emission sources from wind blowing soil dust are also important in the level of concentration of these elements in moss.

#### TRACE ELEMENT ATMOSPHERIC DEPOSITION STUDY IN BELARUS

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For the third time since 2005 atmospheric deposition of trace elements in Belarus was monitored by the moss technique widely used in Europe for air pollution studies. Samples of moss species of *Hylocomium splendens* and *Pleurozium schreberi* were collected at 86 sites over the Gomel, Vitebsk and Minsk Regions in the summer of 2015. A total of 36 elements were determined by epithermal neutron activation analysis. Due to the results obtained in previous moss surveys in 2005/5 and 2010/11 [1], studying of the temporal trends in Belarus was undertaken. Comparison with the analogous data from the neighboring countries showed relatively low contamination levels in Belarus for the most heavy and toxic elements [2]. The results of survey 2010/11 showed that, except Cr and Zn, other element concentration reduced.

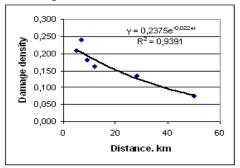
- 1. Yu. V. Aleksiayenak, M.V. Frontasyeva, T.M. Ostrovnaya, O. I. Okina. Moss biomonitoring technique, NAA and AAS in studying air pollution in Belarus. Problems of regional ecology, №4, 2015, p. 126-134 (in Russian).
- 2. Harmens H., Norris D., Mills G., and the participants of the moss survey (2013). Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe. ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK, 63 pp.

# SPATIAL ANALYSIS OF THE AREA DAMAGED BY HEAVY METALS RELEASED FROM SMELTER INDUSTIAL PLANTS: CASE STUDY FOR KOLA PENINSULA, MURMANSK REGION, RUSSIA.

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Spatial analysis of the area damaged by Pechenganickel smelter industrial plant located near borders of Russian Federation, Norway and Finland was done by combining of theoretical approach and field data on the conditions of vegetation cover. Content of nickel (Ni) was estimated in biomass of bilberry fruits as well as Scots pine tree stands state. The last was done by commonly used methodology of ICP-Forests monitoring program. It was theoretically obtained used enthropy approach that density of damage to vegetation cover decline exponetially with the distance from pollution source. Field data supports such a conclusion if also wind repetition is taken into account (see figure).



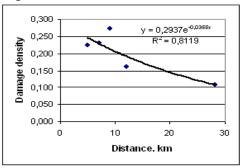


Fig. 1. Damage density of vegetation cover in relation with distance from smelter: left – damage density of Scots pine tree stands, right – damage density of bilberry fruits biomass.

Using exponential function and its parameters which are different according to wind repetition for 8 geographical gradients originated from the point of pollution source the damaged area was separated from undamaged one and subdivaded into 3 zones with different degree of damage for Scots pine tree stands. The damaged area according to nickel content in bilberry fruits biomass was determined using critical level of nickel content (maximum allowable level) which is equal 3.6 mg/kg of dry matter. Areas of zones was calculated, results are presented in the table. Special web-service was developed to facilitate spatial analysis of damaged territories.

Degree of damage for Scots pine tree	Area. km²				
stands	Total	Including territories			
		Norway	Finland		
Slight	3765.4	1431.1	468.3		
Medium	1248.3	455.5	-		
Severe	763.3	59.2	-		
Total	5776.0	1945.8	468.3		
Area with exceedance of Ni above 3.6 mg/kg in bilberry fruits biomass	6030.7	1633.7	194.0		

### MOSS BAG BIOMONITORING OF AIRBORNE TOXIC ELEMENT DECREASE ON A SMALL SCALE: CROSSROAD AND TWO- AND ONE-LANE STREET STUDY

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The use of "moss bag technique" has been developing in last several decades as a method of active monitoring of air pollutants. This method has been particularly useful for conducting a detailed survey of diversely polluted microenvironments within urban areas, where native mosses are usually absent because of predominantly paved and landscaped surfaces. In this study,  $Sphagnum\ girgensohnii$  moss bags were exposed at 48 crossroads, two-and one-lane streets across the city of Belgrade (Serbia) for 10 weeks during the summer of 2014. During the experimental period, traffic flows were estimated at each site by vehicles counting during the rush hours. The concentrations of 39 elements were determined in the moss samples by inductively coupled plasma – mass spectrometry (ICP-MS). For the majority of elements, the moss bags identified a common pattern of decrease in the element concentration from the crossroad to the one-lane street, especially for the most enriched elements – Sb, Cu, and Cr (Figure). A significant correlation (r = 0.65 - 0.70) between the moss concentration of Sb, Cu, and Cr, and traffic flows makes these elements reliable traffic tracers [1].

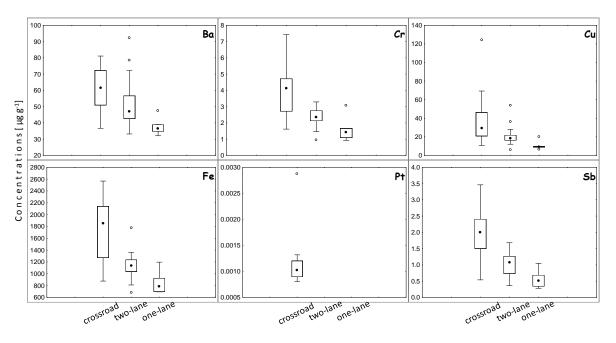


Figure. Element concentrations (µg g<sup>-1</sup>) in the *S. girgensohnii* moss bags; \* Pt was only detected at the crossroads

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### PRELIMINARY RESULTS OF TRACE ELEMENT ATMOSPHERIC DEPOSITION STUDY IN MONGOLIA

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The moss biomonitoring technique was applied to air pollution study in the city of Ulaanbaatar. The samples of the terrestrial mosses *Rhytidium rugosum* and *Entodon concinnus* were collected in the southern part of the city in September 2015 in accordance with the sampling strategy of the UNECE ICP Vegetation moss survey programme. A total of 42 elemental concentrations in these samples were determined by Instrumental Neutron Activation Analysis (INAA) using epithermal neutrons at the IBR-2M reactor, FLNP, JINR, and atomic absorption spectrometry at Central Geological Laboratory (CGL) of Mongolia. The mosses were used to access the atmospheric deposition patterns of heavy metals and other toxic elements in studied area. The results are compared to the data of previous study of atmospheric deposition in the city of Erdenet. Continuation of the moss survey in Mongolia in 2016 is discussed [1].

1. N. Baljinnyam, Sh. Gerbish, G. Ganbold, S. Lodoysamba, M.V. Frontasyeva. Heavy metals in the environmental objects of non-ferrous industrial region of Mongolia, the town of Erdenet. The 2nd International Conference on X-Ray Analysis, Proceeding of Conference, p. 185-193, Ulaanbaatar, Mongolia, 2009.

# ATMOSPHERIC DEPOSITION OF HEAVY METALS IN "ÓBUDA" AND "MARGARET" ISLANDS (BUDAPEST, HUNGARY) TESTED BY DIFFERENT MOSSES AND ICP-OES

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Nowadays, alarming amount of pollution enters into the environment due to anthropogenic activities, lessen of natural habitats. Because of the environmental pollution there is an increased attention on the potentially toxic elements and on the dangers related to heavy metals. Detailed and intensive examinations are necessary in order to avoid extensive contaminations. A lot of information is needed about different environmental elements to understand the fast changes in environment and to control the environmental laws. Therefore, it is important to evaluate different studies in the environment the deposition of heavy metals. Some plants, can be very useful as bioindicators in order to obtain information about heavy metal concentration data derived from the air pollution monitoring. For the investigations there were selected different type of moss, because they have a big surface and can adsorbed the deposition from the air. Particularly, the next moss species were selected: Neckera crispa, Campylium calcareum and Campylium stellatum. The sampling sites were in Budapest ("Margaret Island" and "Óbuda Island"), Hungary. Earlier in "Óbuda Island" were different factories with high heavy metal contaminations. Nowadays, this area is resting quarter. "Margaret Island" has always been a green space without industrial activity. This island is not far from Pest side, where was a great industrial area in street "Váci". Samples were digested by a MILESTONE 1200 Mega Microwave Digester. After the digestion procedure the concentrations of the following elements were measured by ICP-OES (Jobin-Yvon Activa M, France): Al, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Cd. From the results it could be concluded, that all measured heavy metal concentrations can be found in moss samples except Cd, whose concentration was under detection limit. Some of the heavy metal concentrations were higher in "Margaret Island". It needs further investigation to explore the reasons.

# STUDY OF NITROGEN POLLUTION IN MACEDONIA BY MOSS BIOMONITORING TECHNIQUE AND KJELDAHL METHOD

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During the summer of 2005 and 2010 moss samples were collected from 72 sampling sites evenly distributed over the territory of Macedonia Kjeldahl method was used to determine the nitrogen content in the samples. Descriptive statistics and distribution maps were prepared. Data obtained from these two surveys were compared, and additional comparison was done with data obtained from similar studies in other European countries. The median value of N content in the samples collected in 2006 is 1.21 % and varies from 0.70 % to 1.54 %. The content of N in samples collected in 2010 ranges between 0.68 % and 1.75 % with the lower median value of 1.06 %. High contents of N were found in the eastern, north-eastern and central parts of the country as a result of agricultural activities, industry and traffic.

## RARE EARTH ELEMENTS AND PLATINUM GROUP ELEMENTS CONTENT IN TARAXACUM OFFICINALE COLLECTED FROM POZNAN CITY AREA, POLAND

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Particulate matter is a donor of many compounds, which can accumulate in the environment, and furthermore negatively affect to living organisms. A numerous of air pollutants create in the urban areas, and elevated level of their accumulation in plant organs can be noted. There is a limited data about rare earth elements and platinum group elements accumulation in plant, while increasing emission from various sources was recently recorded.

The aim of presented study was to evaluate the level of rare earth elements (REE) and platinum group elements (PGE) content in leaves of *Taraxacum officinale*, collected from Poznan city area (Poland) in the spring of 2015. The city area was divided into 4 km² squares and the plant leaf samples were collected from each squares. The REEs include two groups Light Rare Earth Elements (LREE) and Heavy Rare Earth Elements (HREE). The following LREEs were here analysed: cerium (Ce), gadolinium (Gd), lanthanum (La), neodymium (Nd), samarium (Sm), while HREEs include terbium (Tb), thulium (Tm), yttrium (Y), ytterbium (Yb), erbium (Er). The analysed PGEs included: iridium (Ir), palladium (Pd), platinum (Pt) and rhodium (Rh). All elements were analysed by inductively coupled plasma optical emission spectrometry followed by microwave-assisted sample digestion by concentrated nitric acid. For graphical data presentation, GIS tools were used.

Results pointed at the higher levels of all groups of tested elements in the city in comparison to previous investigations in forest areas [1]. This confirms, that the city, as well as suburban area, can generate an elevated amount of these elements, which can be accumulated in living organism organs and finally influences on human health. The analysis of results includes also a land use structure, as well as the building height or road location. Authors conclude that on final accumulation several factors influenced, including land use of surroundings areas and wind directions.

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### ABOUT THE SPECIES COMPOSITION OF MICROSCOPIC FUNGI IN SOILS AND WOODY PLANT ROOTS IN URBAN ENVIRONMENT

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The high level of technogenic impact causes degradation and loss of tree plantations. In this regard, woody plants growing in the urban environment, especially in large industrial centers, are model plants, which allow studying the system of adaptive responses. The resistance to technogenic stress of woody plants is formed on different levels of organization: biochemical, physiological, organismic, ontogenetic, population as well as on the level of interaction with other organisms taxonomic groups. The role of the relationship of woody plants and fungi in the formation of adaptive and resistant mechanisms in plants to technogenic environment is less studied. The aim of our research was to study the species composition of mycorrhizal fungi in the root system of plants and soils of forests growing in the conditions of technogenic stress. The studies has been conducted in the major industrial center of the Ural region Russia - in Izhevsk - with developed industry, transport network and social infrastructure. The level of pollution in Izhevsk is that of the average pollution index of cities in the Urals, and it is evaluated as high. The objects of study are woody plants of the city. The studied species grew in various structural and functional types of plantations, which were growing in different levels of environmental pollution: plantations along highways (Udmurtskaya Street) and sanitary protective zone (SPZ) of the industrial enterprise, which is the main polluter of the city (the enterprise of "Izhstal") (high level of concentration of heavy metals in the soil); planting yards of a residential neighborhood "Sever" and plantation in sanitary protective zone of the industrial enterprise of "Keramblok" (medium level of concentration of heavy metals in the soil). The area of the largest urban park (The Central Park of Culture and Rest named after Kirov) with the area of 113 hectares with a compact undifferentiated configuration was selected as a zone of conventional control (low level of concentration of heavy metals in the soil). For each of study area we calculated the air pollution index in five major pollutants (carbon monoxide, nitrogen dioxide, formaldehyde, benz(a)pyrene, suspended substances). The results of soil analysis for heavy metals are presented in Table. 1.

Table 1: The content of total forms of heavy metals in soils of plantations of different ecological categories, mg/kg

Index	Kirov park	Residential area "Sever"	SPZ of enterprise "Keramblok"	SPZ of enterprise "Izstal"	Highway plantations Udmurtskaya Street
Cd	0.2±0.1	0.05±0.1	0.05±0.1	1.3±0.3	0.05±0.1
Mn	390.0±82.2	895.0±178.0	560.0±77.0	1822.0±547.0	891.0±187.0
Cu	3.8±1.1	28.4±8.5	20.3±4.5	114.0±34.0	85.0±1.2
As	< 0.05	< 0.05	< 0.05	7.4±2.2	< 0.05
Ni	13.6±4.0	$18.9 \pm 4.0$	15.9±4.0	46.4±9.8	27.8±5.6
Hg	< 0.05	$0.050\pm02$	$0.050\pm02$	0.11±0.03	$0.07 \pm 0.01$
Pb	11.6±2.4	15.2±4.5	13.2±2.4	103.0±22.0	43.6±2.0
Zn	34.6±7.3	51.9±10.9	49.9±8.9	274.0±82.0	94.0±28.0

The results showed that the highest species diversity of microscopic fungi was typical for soils in sanitary protective zone of enterprise "Izhstal". Arbuscular mycorrhizal fungi were also found in the roots and in soil samples taken around roots of *Acer negundo* and *Betula pendula*, growing in that plantations. The fact that endotrophic fungi in a relatively clean soil and roots of plants growing in the park haven't been found yet, can't be explained. This fact suggests the existence of the relationship between the resistance of woody plants to technogenic stress and the presence of symbiotic relationship with endotrophic fungi.

### CHALLENGES AND OPPORTUNITIES IN BIOMONITORING ATMOSPHERIC TRACE ELEMENT DEPOSITIONS. A CASE STUDY IN EASTERN ROMANIA

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In Eastern Romania, the moss-monitoring technique was introduced in 2000, to evaluate the atmospheric heavy metal deposition within the catchment of the Prut river, a transboundary river between Republic of Moldova, Romania, and Ukraine [1]. The occurrence of epigeic mosses in this area is limited by the climatic and geographical conditions. Therefore, the challenge appeared to find the appropriate moss species for biomonitoring and to achieve acceptable sampling densities. Among the ten different epiphytic moss species available in the area Hypnum cupresssiforme was the most abundant and it was selected for analysis. A comparative study between the epiphytic H. cupressiforme and Brachythecium salebrosum (second in abundance) indicated that the two species can be used interchangeably as biomonitors for 21 elements (Na, Mg, Al, Sc, V, Cr, Fe, Co, Ni, Cu, As, Se, Rb, Cs, La, Ce, Sm, Eu, Pb, Th, U) of a total of 29 determined elements. The suitability of epiphytic H. cupressiforme for biomonitoring was further assessed in a comparative study with its epigeic variety. Both varieties collected from 16 sampling sites were analyzed for V, Cr, Ni, Cu, Zn, As, Mo, Cd, In, Sn, Tl, Pb, and Bi. Significant correlations were obtained for V, Pb, Cu, Bi, Cr, Ni, As, Cd, and Tl, while a saturation effect for some essential elements, such as Mo (in the epiphytic moss) and Zn (in the epigeic moss) was observed. Element concentrations in both varieties are not significantly influenced by substratum and exposure to pollutants. The use of oak tree bark for monitoring purposes was tested compared with the epiphytic moss H. cupressiforme in order to find an alternative biomonitor in areas where there is a scarcity or lack of mosses [2]. The monitoring network in Eastern Romania started with 25 sampling sites in 2000 and has been continuously extended, to 44 sampling sites in 2002 [2] and over 70 sites in 2010 [3]. This researches started and continued within a Romanian-Russian-Norwegian collaboration, together with similar surveys in the other parts of Romania facilitated the integration of Romania in large-scale European moss survey programs [4].

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# AIR POLLUTION IN CENTRAL AND SOUTHERN VIETNAM USING MOSS TECHNIQUE AND NEUTRON ACTIVATION ANALYSIS

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Atmospheric deposition of trace elements in the Central and Southern Vietnam was studied. Thirty-two moss samples of the *Barbula indica* species were collected in the autumn 2014 and subjected to neutron activation analysis at the pulsed fast reactor IBR-2, FLNP, JINR, Dubna. A total of twenty-eight elements were determined. Factor Analysis was applied to the obtained results to reveal possible pollution sources. Rotated factor loadings suggested five factors, that could explained more than 80% of variability. Additionally, factor scores were calculated, that confirmed the presence of pollution sources in the corresponding sites.

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# COMPARISON OF RADIOISOTOPES CONTENT IN MOSS AND IN SURFACE SOIL LAYER

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One of the species most frequently used in biomonitoring is moss. It accumulates substances deposited from air, among them the dust containing different contaminants.

Composition of a precipitate is determined both by distant emission sources and local secondary redeposition. It is highly desirable to differentiate between both deposition components. Distinction between them would be helpful in spatiotemporal characterization of pollution and estimation of its sources. Combustion of fossil fuels and some industrial activities produce large amounts of dust containing radioactive isotopes, which are then deposited on the ground surface. These include natural radioisotopes and their decay products as well as some artificial radioisotopes. The dust comprising radioisotopes can be transported in atmosphere in the long distances. When the dust is deposited on surface of earth it becomes an element of local environment. The aim of the studies was investigation of radioisotopes content in moss and in surface soil layer. It was expected that relationships between different radioisotopes content in plant and soil matrix will provide information about the deposited dust sources. Moss and its ground base samples were collected in Bory Stobrawskie forest, located in southwestern part of Poland. In samples activity concentrations of gamma-radioactive isotopes Cs-137, K-40, Bi-214 and Pb-210 were determined. Activity concentrations were recalculated to mass fractions (concentrations) of radioisotopes. An assessment of the structure presence in data was performed. To estimate groups formation in data, cluster analysis was performed. The dissimilarity matrix was Aitchison distances matrix. Covariability character of two components was deduced from variability of the components ratio. Some differences in relationships between the studied radioisotopes concentrations in moss and in surface soil layer were observed. Particularly, only in soil surface but not in moss, the <sup>137</sup>Cs and <sup>210</sup>Pb concentrations were proportional.

## ASSESSMENT OF AIR QUALITY OF THE VICINITY OF VOLGORECHENSK POWER STATION USING MOSS BIOMONITORING

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In the frame work of the moss survey 2015/2016 samples of moss and soil were collected in the vicinity of the town of Volgorechensk (Kostroma region, Russia). Volgorechensk power station is one of the most powerful in the region and has the highest chimney in Europe. Hence, the distribution of emission coves large territory. To investigate the influence from the power station in details is the aim of this work. Nine samples of moss and soils were collected at each sampling site distanced on 5 from the power station. Samples of mosses were collected according to the ICP Vegetation monitoring manual. A total of 40 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, In, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu, Hf, Ta, W) was determined by neutron activation analysis. To determine concentrations of Pb, Cd, and Cu flame atomic absorption spectrometry was used. To analyze the obtained data the statistical methods (descriptive statistics and factor analysis) were carried out. Maps of spatial distribution were created. The assessment of air quality confirmed the influence of power station and reveal additional source of air contamination - tube-rolling mill.

## PRELIMINARY STUDY ON RADIOACTIVITY AND HEAVY METALS ON MOSS AT ITU ENERGY INSTITUTE

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The overall aim of the preliminary study is to determine of radioactivity and chemical pollutants in soil and moss to assess the ecosystem impacts. Field study was performed in the Eastern Black Sea Region in Turkey due to affecting by metal mining activities in the area. For assessment of naturally occurring radionuclides (NOR), fission products and conventional chemical pollutants, soil from 6 sampling sites and mosses (*Hypnum cupressiforme*) from 3 sampling sites were collected. Radionuclide concentrations (<sup>137</sup>Cs, <sup>90</sup>Sr, <sup>238</sup>U, <sup>232</sup>Th, <sup>40</sup>K, <sup>226</sup>Ra and <sup>210</sup>Pb) in soil and moss samples was determined by standard methods using gamma-ray spectrometry. Elemental concentrations of soil and moss samples were determined using by XRF and ICP analysis, respectively. Transfer factor for natural uranium, thorium, <sup>40</sup>K, <sup>226</sup>Ra, <sup>210</sup>Pb, <sup>137</sup>Cs, <sup>90</sup>Sr and chemical pollutants between soil phases and moss was obtained. Contaminations from heavy metals in soils were classified as enrichment factor, geoaccumulation and ecological risk indexes.

#### INFORMATION ON THE MOSS SURVEY IN 2015: SOME PRELIMINARY RESULTS

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A brief historical review is given on the development and milestones of the moss biomonitoring technique used to study atmospheric deposition of trace elements, nitrogen, organic persistent pollutants (PAHs, PCBs, PBDEs, dioxins, PFOS, *etc.*) and radionuclides of technogenic origin in Europe. The relevance of these studies to the UN Convention on long-range transboundary air pollution (LRTAP) is enlightened.

History of moss biomonitoring surveys in Europe

1968: Moss technique was first proposed (Å. Rühling and G. Tyler, Lund University, Sweden)

1975: First nationwide survey in Sweden (Åke Rühling, coordinator)

1977: First nationwide survey in Norway (Eiliv Steinnes, coordinator)

1985: First joint Nordic Survey (Denmark, Finland, Norway, Sweden) (Åke Rühling, coordinator, supported by Nordic Council of Ministers)

1990: First European survey (Joint Nordic/Baltic survey) (Åke Rühling, coordinator)

1995: Second European survey, 28 countries (Åke Rühling and Eiliv Steinnes, coordinators)

2000: Third European survey, 28 countries (UNECE ICP Vegetation)

2005: Fourth European survey, 28 countries (UNECE ICP Vegetation)

2010: Fifth European survey, 27 countries (UNECE ICP Vegetation)

2015: Sixth European survey, 36 countries (UNECE ICP Vegetation) (Marina Frontasyeva, JINR, coordinator)

In agreement with the long-term strategy of the LRTAP Convention to enhance participation and improve air quality in Eastern Europe, the Caucasus, Central Asia and South Eastern Europe, efforts to extend the moss survey for former republics of the USSR were successfully undertaken in countries such as Azerbaijan, Georgia, Kazakhstan, and Moldova. Armenia and Uzbekistan most probably will join the moss survey in summer of 2016. Around 15 teams are formed in Russia to cover with moss sampling in Northern and Central Russia, Western Siberia, and Far East of Russia (Kamchatka and Sakhalin). JINR will continue support for the moss survey program in some of its member states: Bulgaria, Czech Republic, Mongolia, Poland, Romania, Slovakia, Vietnam, as well as in some non-member states: Albania, Croatia, Hungary, Thailand, South Korea, and China. Up-to-date 36 countries participate in the present moss survey. In spite of the growing interest in assessment of the deposition of persistent organic pollutants (PAHs, PCBs, PBDEs, dioxins, PFOS, etc.) using moss, only a limited number of the Western European countries intend to determine POPs. Radioecological laboratories in JINR (Dubna, Russia), Institute of Nuclear Physics (Almaty, Kazakhstan), University of Novi Sad (Serbia), Bratislava University (Slovakia) and Opole University (Poland) will be used to measure natural and man-made radionuclides (137Cs, 210Pb, etc.) under individual agreements with the interested countries. Some details are given on the newly established database for storage of information about the European and Asian moss survey, conducting and storing analytical results on heavy metals, nitrogen, persistent organic compounds, and radionuclides based on moss analysis. Potentialities of using moss planchettes for search of cosmic dust are also mentioned. Information obtained from the participants on the areas covered by the moss survey in 2015 is presented.

#### TEMPORAL TRENDS IN BULGARIA WITHIN THE EUROPEAN MOSS SURVEYS

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This study aims to review Bulgarian data (217 sites in the county net; 110 988 km²) from the last four European Moss Surveys (1995-2011). Elements Al, As, Cd, Cr, Cu, Fe, Ni, Pb, V and Zn were determined by ICP-AES. Atmospheric pollution trends, assessed by *Hypnum cupressiforme* revealed a serious decline for Pb (58%), Cu (53%), Cd (45%), V (37%), Fe (30%) and Zn (26%) between 1995 and 2010, while Ni and Cr had constant levels. Nevertheless, the highest Pb concentration for Europe was found in Bulgaria, although the median concentration declined. Despite reported Europe-wide dramatic decline in the concentrations of arsenic [1], the element tends to increase in Bulgaria (67% between 2000 and 2010). Both As and Pb concentrations could be associated with "hot spots" near non-ferrous metal industry, old mines or open way of mining, as well as secondary pollution by windblown dust. Higher heavy metal levels were constant in the western parts of Bulgaria for the study period. Current European moss survey 2015/2016 will be crucial to reveal atmospheric pollution models both on European and Bulgarian scale.

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#### FIRST MOSS SURVEY IN KAZAKHSTAN

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The method of moss biomonitoring of atmospheric deposition of trace elements was applied for the first time in the Mountains of Southeastern Kazakhstan and Akmola Region (around Astana, the capital of Kazakhstan) to assess the environmental situation in these areas. Forty four moss samples were collected in summer of 2014 and 2015 growth period. A total of 42 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As, Se, Br, Rb, Sr, Zr, Nb, Mo, Ag, Cd, Sb, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Hf, Ta, W, Au, Th, and U) were determined by epithermal neutron activation analysis at the reactor IBR-2, FLNP, JINR. Multivariate statistical analysis of the results obtained was used to reveal and characterize the pollution sources in the study areas. The work is in progress.

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# SPATIAL AND TEMPORAL CHANGES IN HEAVY METAL CONCENTRATION IN NIEPOŁOMICE FOREST – A LONG-TIME MOSS MONITORING WITH *PLEUROZIUM SCHREBERI* AS BIOINDICATOR

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The Niepołomice Forest is a large forest complex (110 km²) situated in southern Poland, 30 km from east border of Kraków agglomeration and large steelworks, which was built up in the end of 50. XX century. Due to prevailing westerly winds, the forest is affected by pollutants emitted by both the steelworks and the city. The level of heavy metal concentrations in the Niepołomice Forest was described using the common in Poland moss – *Pleurozium schreberi*. The first moss monitoring with this sensitive bioindicator for heavy metals in the Niepołomice Forest was conducted in 1975. Mean concentrations of heavy metals in mosses collected in this forest in 2014 were: Fe 392 mg/kg, Zn 144 mg/kg, Cu 7.4 mg/kg, Pb 9.7 mg/kg, Cd 0.23 mg/kg. Concentrations of heavy metals in *Pleurozium schreberi* decreased in time. Compared to last moss monitoring conducted in 1998, the concentrations of Pb, Cd, Fe and Cu in 2014 were lower, concentration of Zn was higher, while concentration of Mn was not change.

# ELEMENTAL CONTENT IN DIFFERENT MOSS SPECIES IN CENTRAL RUSSIA, TULA REGION

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The method of moss biomonitoring was used to study heavy metal atmospheric deposition in Central Russia (Tula Region) applying NAA and GIS technology. Tula, one of the ancient Russian cities, is located 180 km south of Moscow. The Tula Region is known for clustering of machine-building, metallurgical heavy industry, chemical and mining enterprises. In the study area there are three zones of plant biogeocenosis: mixed forests, deciduous forests, and steppe. Moss sampling was carried out in accordance with the sampling strategy adopted in European projects on biomonitoring atmospheric deposition. In addition to the moss biomonitors such as Pleurozium schreberi and different species of tipical deciduous and mixed forests of region Brachythecium rutabulum and B. salebrosum, Atrichum undulatum, Climacium dendroides, Plagiomnium undulatum, Sphagnum species and mosses of forest steppe of the region Cirriphyllum piliferum Oxyrrhynchium hians, Abietinella abietina. The method of epithermal neutron activation at IBR-2 reactor of FLNP JINR has made it possible to identify 43 elements, in the examined samples collected in the different part of Tula Region. Along with metals (Al, Sc, V, Cr, Mn, Fe, Co, Ni, Zn, Sr, Mo, Cd, W), halogens (Cl, Br, I), aniogenic elements (As, Se), rare-earth elements (Ce, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Lu), as well as U and Th were determined. The obtained data are used to construct colored maps of the distribution of elements over the investigated territory. An interspecies calibration of mosses carried out in the present study is discussed. The results obtained are compared with those from the moss survey in Tula Region in 2000 [1]. Studies have shown that the most similar to the biogeochemical characteristics accepted in sampling protocol are several species, including species of the genus Brachitecium.

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### NEUTRON ACTIVATION ANALYSIS OF SOME PLANT SAMPLES at ISTANBUL TECHNICAL UNIVERSITY ENERGY INSTITUTE

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The purpose of this study is optimisation of the experimental parameters for analysis of plant matrix by instrumental neutron activation analysis and quantitative determination of Ba, Br, Eu, Fe, K, La, Na, Rb, Sc, Sm and Zn in selected plant samples. Plant samples such as grass, paprika, chery laurel and rice are profficiency test samples provided by the International Atomic Energy Agency under a coordination project. Samples were irradiated in central irradiation tube of TRIGA MARK II Research Reactor of Istanbul Technical University and gamma spectroscopic measurements were evaluated by  $k_0$ -IAEA software. The performance of the applied method were evaluated by analysing standard reference materials. For selected elements, the statistical evaluation of the analysis results was carried out by z-score test. A good agreement between certified/reported and experimental values was obtained.

### ATMOSPHERIC DEPOSITION STUDY IN THE VICINITY OF KARDZHALI LEAD-ZINC PLANT IN BULGARIA BASED ON MOSS ANALYSIS

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For the first time the moss biomonitoring technique was utilized to assess the environmental situation in the area affected by one of the most hazardous enterprises in Bulgaria – the Kardzhali lead-zinc plant. 77 *Hypnum cupressiforme* moss samples were collected in the Kardzhali municipality in the summer and autumn of 2011. The concentrations of a total of 47 elements were determined by means of instrumental epithermal neutron activation analysis (ENAA), atomic absorption spectrometry (AAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Multivariate statistics was applied to characterize the sources of elements detected in the samples. Four groups of elements were found. Concentrations of the elements of industrial origin, averaged for the territory of Kardzhali (where the smelter chimney is located) were found to be much higher than corresponding values determined in the area outside of the town. GIS technology was used to produce element distribution maps illustrating deposition patterns of element pollutants. For the most toxic metals (Pb, Zn, Cd, As, Cu, In, Sb), median levels of the measured concentrations were extremely high in comparison to Bulgarian cross-country data from the 2010/2011 European moss survey.

## FIRST ATTEMPT OF 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. Moreover, in the territory of Azerbaijan over 400 mud volcanoes are present, making Azerbaijan top in the world in the number of mud volcanoes characterized by exceptionally high natural radioactivity. Those deposits in the Caucasus and Transcaspian are associated with large deposits of uranium and rare earth metals. 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).

# ANALYSIS OF LONG-TERM TRENDS OF ATMOSPHERIC HEAVY METAL POLLUTION IN THE EMEP COUNTRIES BASED ON MOSS SURVEY DATA AND MODELING RESULTS

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Long-term heavy metal pollution trends of lead (Pb), cadmium (Cd) and mercury (Hg) were evaluated on the base of modelling results and data from the EMEP monitoring network. For the period from 1990 to 2012 modelled total deposition of Pb, Cd and Hg in the EMEP region declined by 78, 53 and 23%, respectively. In particular countries long-term changes may significantly differ from EMEP-averaged values. There are about 20 EMEP monitoring stations providing measurement data on heavy metal pollution levels (wet deposition fluxes and concentrations in air) over most part of the 1990-2012 period. These stations are located mostly in the northern and western parts of Europe. Therefore, the analysis of trends over large areas of the EMEP region is mostly based on modelling information. Concentrations of heavy metals in terrestrial mosses, sampled in surveys of 1990, 1995, 2000, 2005 and 2010 were used as complementary data for analysis of long-term changes of the pollution levels over the last two decades. There are 10 countries which took part in all five moss surveys. Total reduction of lead, cadmium and mercury concentrations in mosses for 1990-2010 in this group of countries made up 82, 53 and 16%, respectively. The corresponding reduction of modelled deposition was 79, 56 and 14% (Fig.1 a-c). In a number of countries both deposition and concentrations in mosses decline at higher rate in the first half, and at smaller rate in the second half of the period. Factors responsible for long-term changes of the metal deposition in European countries were analysed.

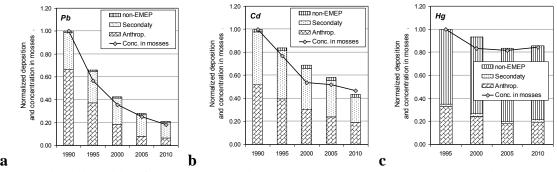


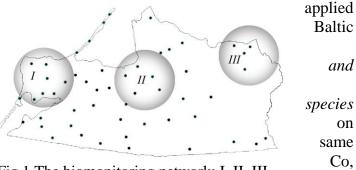
Fig. 1. Normalized deposition from anthropogenic, secondary and non-EMEP sources and concentrations in mosses of lead (a), cadmium (b) and mercury (c) in Europe in 1990-2010

# TRACE ELEMENTS ACCUMULATION BY MOSSES, LICHENS AND MUSHROOMS IN SOUTH-EASTERN BALTIC

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The biomonitoring technique was to pollution studies in South-Eastern (Kaliningrad region). Samples of the terrestrial moss *Pleurozium schreberi Hilocomium splendens, lichen Hypogimnia physodes and more than 30 of wild mushrooms* have been collected regular network of 10x10 km at the time. Metals such as Pb, Cd, Ag, Cr, Ni, Cu, Fe, Mn were determined by technique (by flame – Mn, Fe; ETA – others).



AAS

Fig.1 The biomonitoring network; I, II, III - sites where mushrooms were sampled. Zone 1 - Sambia peninsula.

Table 1 - Mean values for mass fraction of trace elements in mosses, lichen and mushrooms in region (mg/kg DW)

	Fe	Mn	Cu	Ni	Pb	Cr	Co	Cd	Ag
Mosses	216,9	345,8	4,46	1,198	2,507	2,161	0,119	0,109	0,044
Lichen	445,7	200,1	7,63	1,295	6,412	ı	ı	0,199	0,043
Mushrooms	193,1	23,64	36,7	7,050	0,555	1,488	0,202	1,309	1,302

Table 2 – Mean values for mass fraction of trace elements in mosses, lichen and mushrooms in Sambia peninsula (mg/kg DW)

	Fe	Mn	Cu	Ni	Pb	Cr	Co	Ag	Cd
Mosses	291,5	422,8	7,29	1,377	2,220	3,425	0,1193	0,0442	0,225
Lichen	722,6	320,4	7,58	2,191	6,295	-	-	0,0398	0,199
Mushrooms	157,8	12,09	34,5	10,61	0,556	1,075	0,0889	1,2619	2,014

There are no a clear relationship between the concentration of some metals in the most species of wild mushrooms and the level of antropogenic impact. But it is obviously, the concentration of cadmium and copper in fruit fungi bodies are higher on Sambian peninsula - the territory with high level of antropogenic (industrial) load.

The results of chemical analyses were interpreted by cartography method. The maps of trace metals content in mosses and lichens were created. Cartography analysis revealed spatial patterns of metals distribution. There are highest levels of metals in moss and lichens in the west part of region (Sambia peninsula) and elevated levels in the North, North-East and South-West parts.

# PLEUROZIUM SCHREBERI (BRID.) MITT. AS A BIOINDICATOR OF HEAVY METAL POLLUTION AND RADIONUCLIDES IN SELECTED POLISH NATIONAL PARKS.

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In Poland national park is a protected area because of its advantages, mainly outstanding natural value for the environmental, scientific, social, cultural and educational reasons. Natural resources of the national parks is one of the Polish strategic natural resources. The main objective of the present study is to test the ability of the P. schreberi to bioaccumulate atmospheric trace elements and radionuclides from Polish National Parks (NP) and compare the results between lowland and mountains parks. To compare the results with earlier data from Poland and neighboring countries. Our study thus examines the view that special care should be taken in regional comparisons of bryophyte concentrations of trace elements and radioactive elements. Samples of moss P. schreberi were collected from 4 lowland parks: Bory Tucholskie NP, Wielkopolski NP, Kampinoski NP, Roztoczański NP and from 5 upland and mountainous parks: Karkonoski NP, Gór Stołowych NP, Ojcowski NP, Babiogórski NP and Świętokrzyski NP. The concentration of elements in the moss P. schreberi samples was determined by a multielement instrumental neutron activation analysis using epithermal neutrons (ENAA) at the IBR-2 reactor, FLNP JINR, Dubna. The total content of Cd, Cu and Pb was determined by ASS method. The samples were analyzed for radionuclides using stationary semiconductor spectrometer gamma, equipped with a germanium coaxial detector with high resolution capacity. Concentration of all elements were higher in mosses collected from upland and mountainous parks than in lowland parks except Mn, while level of I was the same in two groups. To estimate covariability of elements concentrations the VR coefficients of all pairs of variables were calculated. In most cases the lowest VR value in the complete data was found for pairs of elements released into the environment primarily from anthropogenic sources. Low values of VR suppose proportionality of the listed element concentrations. This trend is confirmed by linear covariability between their concentrations. There were negative covariabilities (increase-decrease) in concentrations were observed also. In most cases for pairs of elements, where one of the variables was Mn. Contamination of NP in Poland by heavy metals as determined using mosses corresponds with the distribution of emission sources in the country. The southern, most industrialized part of the country e.g. Silesia Basin, Black Triangle that is subjected to the highest dust deposition, additionally receiving dusts from long transboundary transport. The evident decrease over 39 years of biomonitoring studies (1975-2014) was also observed.

## SPATIAL DISTRIBUTION OF SOME RADIONUCLIDES MEASURED IN MOSSES COLLECTED OVER LARGE AREA

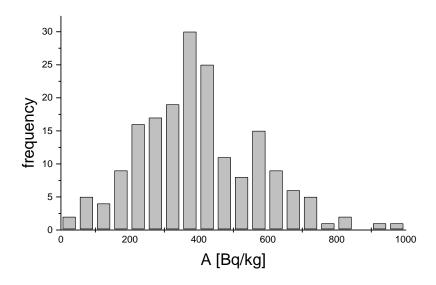
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The activities of natural occurring radionuclides were measured in samples of terrestrial mosses collected in Serbia. Almost complete area of country was covered by 197 moss samples. Measurements were performed by 9" x 9" NaI anti-Compton detector used as well counter. The most important objective of measurement was to check uniformity of deposition of airborne radionuclides over the large area. In all spectra measurable amount of <sup>7</sup>Be and <sup>210</sup>Pb was observed. In number of them presence of 137Cs is detected. Gamma lines of <sup>214</sup>Bi and <sup>40</sup>K can be seen in spectra too. In preliminary analysis of data is obtained that activity of <sup>7</sup>Be in collected moss samples is spread in the very large region. The highest activity concentration is almost 30 times higher than the lowest one. Distribution of obtained values of 7be activity is presented in Figure below. Maps showing the spatial distribution of <sup>7</sup>Be were created using geostatistical methods.



# FIRST ALBANIAN MOSS BIOMONITORING SURVEY AND SOME FUTURE CONSIDERATIONS

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The data of most toxic trace metal (As, Cd, Cr, Co, Cu, Hg, Ni, Pb and Zn) from the first Albanian moss biomonitoring survey (Hypnum cupresiforme and Pseudoschleropodim purum sp., 2010/2014) are presented. 44 moss samples more or less with homogenous distribution in the whole territory of the country were used in this study. High variations on spatial distribution patterns indicating their complex origins and controlling factors of atmospheric deposition. The contamination factor, pollution loads index and potential ecological index was used to asses the pollution level of atmospheric deposition. The values of CFs indicate that the elements are associated with the C3 to C5 contamination scale; the moderately to severely contamination scale. Beside it, the zone pollution index (PLIzone = 7.2 > 5) indicates that the whole territory under investigation is extremely polluted. The RI data indicate the central part of Albania as an area at high ecological risk. The Box-Cox transformation is used smoothing the variability of the data. Pearson correlation and factor analysis are used to identify the most significant association of the elements and the probable sources of these elements. Three dominant factors were extracted that represent the long-range atmospheric deposition associated with Cd, Cu, Pb, Hg and Zn; mineral and industrial local emission sources particularly associated with Cr, Ni and Co, and less with Cd, Cu, Pb, Hg and Zn; and the use of pesticides and herbicides in agriculture, particularly in the south part of the country.

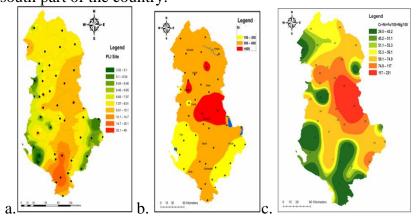


Fig. 1 GIS maps of PLI (a), RI (b) and (Cr+Ni+Fe/100+Mg/100) (c)

Certain local emitters were identified like, Fe-Cr metallurgy, cement industry, oil refinery, mining industry, and transport. The pollution problems are mainly related to the pollution by industry and less to the transport sector or urban waste incineration. Geogenic origin of wingblowing dust is another important factor of air pollution. The anomaly of (Cr+Ni+Fe/100+Mg/100) (Fig.1c) is a efficient indicator of ultrabasic rocks and ofiolitic formation that is a strong geological characteristic of Greece, Albania, Kosovo, Macedonia and Serbia and associated with high content of Mg, Cr, Ni, Fe and Co. Due to the space sampling sites in the north, the geogenic factor coming from sulfide mineralization in the central and northern part of the country is not clearly reflected in this study.

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In addition, the natural sources, from the accumulation of these metals in mosses caused by metalenriched soil, associated with wind blowing soils dust particularly in Southeast direction of the country, was pointed as another possibility of local emitting factors. A significant influence of Adriatic and Ionian Sea were reflected on geographical distributions of the elements at moss samples of the coastal area. The depletion process in moss is probably attributed to competition of the elements from sea-salt cations and lower anthropogenic inputs compare to the inland areas. High variability onto the concentration data of the elements require a denser sampling scheme and the minimum number of sampling sites is better to be calculated in future monitoring study of the area and air quality assessments. It may increase the reliability of the data coming from not normal distribution of the results. The results of this study are valuable to the policy makers and regulators taking proper decisions that may protect the environment.

# TEMPORAL TRENDS AND SPATIAL DISTRIBUTION OF TRACE METALS IN MOSSES OVER FRANCE (1996 - 2011): NEW APPROACHES INCLUDING UNCERTAINTIES

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Moss surveys are convenient tools to monitor the exposition of ecosystems to local or longdistance pollution. Concentration trends of Cd, Pb, and Hg in mosses have already been successfully analyzed at the European scale<sup>1</sup>. Combining such analyses with uncertainties associated with the sampling protocol would make them more robust. Here, we show our first attempt to describe and explain the temporal and spatial variations of moss concentrations after taking account the uncertainties estimated for a set of trace metals. We statistically analyzed the temporal variations over the 4 sampling campaigns, by taking into account uncertainties estimated beforehand for various trace metal concentrations in mosses. We were also able to propose Ambient Background Concentrations (ABC) for the four campaigns, as intervals of concentrations, including the protocol uncertainties as well. We then used kriging to interpolate moss concentrations over France to better visualize the spatial distribution of elements. We propose to analyze spatial distributions of elements by (i) defining areas fitting in the ABC, and (ii) highlighting sites and regions exceeding these ABC. Preliminary results indicate a clear decreasing trend for Pb over the 4 campaigns, while trends are not as clear for other elements, although no major increase was noticed. Large areas of France had concentrations fitting in the ABCs. Other zones with higher concentrations were found in regions with heavy industries or a history of mining, such as the North of France or the Rhone valley. Other factors such as possible local industries or Saharan plumes could also explain zones with higher concentrations. These results must be refined to produce clearer trends. Further investigations will also be conducted to explore potential relationships between moss concentrations and atmospheric deposition or soil composition and provide a better understanding of the significance of moss concentrations in France.

<sup>1.</sup> Harmens, H. *et al.* Heavy metal and nitrogen concentrations in mosses are declining across Europe whilst some 'hotspots' remain in 2010. *Environ. Pollut.* 200, 93–104 (2015).

# ASSESSMENT OF THE UNCERTAINTY ASSOCIATED WITH HEAVY METAL CONCENTRATIONS IN MOSSES MEASURED IN FRANCE (1996 TO 2011)

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Moss surveys have been conducted all over Europe with success as several interesting results have already been found out, especially regarding trends. However, the uncertainty associated with moss concentrations has never been assessed, even for chemical elements specifically required by the ICP-Vegetation. This study is the first one conducted in France, with the aim to ease and improve comparisons between countries and the study of temporal tendencies over Europe. Here, we propose to follow the Eurachem guidelines and the methodology of Sirois and Vet (1994)<sup>1</sup> to determine the uncertainty associated with the moss concentrations for various trace metals and nitrogen in four sampling campaigns over France between 1996 and 2011. We combined a bottom-up and a top-down approaches, the former and the latter respectively decomposing and integrating the different steps of the protocol (the chemical analysis, the sample homogeneity, the fraction of the moss chosen for the analysis, the sampling period, and the moss collector). We also studied the uncertainty associated to the moss species.

Uncertainties were expressed as percentages for all concentrations and for 14 elements and ranged from 14 to 61% for nitrogen and chromium respectively, with a median of 38% for all the elements, between 2000 and 2011. Uncertainties were generally larger in 1996, due to some differences in the protocol compared to the following campaigns. This study indicated a good performance and reproducibility of the sampling protocol. The chemical analysis generally contributed for a small part to the total uncertainty. On the contrary, the sampling period as well as the collector were largely involved for most of the studied elements. The moss species induced a supplementary uncertainty only for calcium, cadmium, copper, and iron.

This first estimation gives a magnitude of the uncertainties associated with the ICP-Vegetation guidelines. Extra care should be taken when sampling on common study sites between campaigns, in terms of site location and sampling period. This study needs further investigation in France and we also advise that countries participating to the ICP-Vegetation contribute to this uncertainty assessment.

<sup>1.</sup> Sirois, A. & Vet, R. J. in *EMEP Workshop on the Accuracy of Measurements. Passau*, 1993 EMEP CCC report 2/94, 67–85 (T. Berg and J. Schaug, 1994).

# TEMPORAL AND SPATIAL TRENDS (1990–2010) OF TRACE ELEMENT ATMOSPHERIC DEPOSITION IN SLOVAKIA: ASSESSMENT BASED ON MOSS ANALYSIS

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The results of moss analysis by two complementary analytical techniques – neutron activation analysis and atomic absorption spectrometry – from the consequent moss surveys in 1990, 1995, 1996, 1997, 2000, 2005, and 2010 undertaken in the framework of the UNECE ICP Vegetation programme are reported. A total of 39 elements (Ag, Al, As, Au, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Fe, Hf, I, In, K, La, Mg, Mn, Mo, Na, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn, and Zr) were determined by instrumental neutron activation analysis (INAA). Elemental analysis was applied to determine the concentration of S (LECO SC 132) and N (LECO SC 228). Atomic absorption spectrometry (VARIAN SPECTRA A-300 and mercury analyser AMA-254) for Cd, Cu, Pb and Hg was carried out in FRI Zvolen. Temporal and spatial trends of atmospheric deposition of some selected trace elements are discussed. It was determined on the basis of bryomonitoring performed in 3year old segments of *Pleurozium schreberi*, *Hylocomium splendens* and *Dicranum* sp., on 10 sites in the Slovakia that:

- we found concentration of elements more than 50 times higher: site Báb (Hf), Pol'ana (Hf, Sb); Vysoké Tatry (Hf); Slovenský raj (Hf, Sb); Vel'ká Fatra (Hf); Central Spiš (Ag, Hf, Pb, Sb Ta Tb, Yb); Žiar basin (F) and site Morské oko (Al, Hf, Sc, Sb, Ta, Tb, Th, Yb) in comparison to the Norway values;
- coefficient of loading by air pollutants K<sub>F</sub> move from 4.2 -Nízke Tatry; 6.2 -Žiar basin;
   6.7 -Vysoké Tatry; 7.6 -Veľká Fatra; Báb -8.8; 11.8 -Slovenský raj; 19 -Poľana; 44 Morské oko and 45 -Central Spiš;
- the obtained data can be useful as a reference level for comparison with the future measurements of air pollution in the examined area and also for biodiversity study. The significance of transboundary atmospheric transport in this region remains to be studied in the future.

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# BIOMONITORING MERCURY CONTAMINATION IN THE MT. AMIATA MINING AREA (S TUSCANY, ITALY): A HISTORICAL APPRAISAL AND FUTURE PERSPECTIVES

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Mt. Amiata (1738 m asl), in southern Tuscany, Italy, is known for its extensive deposits of cinnabar (HgS). Since 1850 up to mid-1980s, Abbadia San Salvatore, the main urban center on the eastern slope of the mountain, has been one of the largest Hg mining and smelting district in the world, and has released to the atmosphere more than 10.000 t of Hg (ca. 10% of its overall production). The cessation of the mining activity has left abandoned mining structures and contaminated soils (some with more than 1.000 µg g-1 Hg). A distinctive feature of Mt. Amiata is also its widespread geothermal activity. The industrial exploitation of this resource for electric power generation started at the end of 1970s when the decline of the mining industry prompted for the search of new opportunities of economic development. There are now power plants in Bagnore and Piancastagnaio, west and south of Abbadia San Salvatore respectively, exploiting a vast and deep (ca. 3.500 m) geothermal reservoir. The environmental impact of geothermal power generation is still a matter of debate, since with the geothermal vapors also Hg and other elements (i.e. As, B, Sb ) are released to the atmosphere. Atmospheric Hg measurements in the Mt. Amiata area are scanty and associated with a great uncertainty, primarily due to instrumental constraints (i.e. high costs of instrumentation, power requirements) that limit spatial and temporal coverage of the surveys. Historically, monitoring by living organisms, especially plants has offset the lack of instrumental, data providing spatially-distributed monitoring of Hg deposition. For example, early works by Bargagli et al. [1] in the late 1980s, demonstrated the applicability of Hg monitoring by the lichen Xanthoria parietina for identifying and mapping Hg sources in the Mt. Amiata area. More recently, Loppi and Bonini [2] using the lichen Parmelia sulcata and the moss Hypnum cupressiforme identified the contribution of thermal springs and fumarole activity to environmental levels of Hg and other elements. Here, we aim to demonstrate that the current state-of-the-art in Hg monitoring by lichens has advanced in recent years, to the point that routine estimation of Hg concentrations in the air should be possible, and may support source characterization. Based on our previously published data [3] on X. parietina collected from 9 sites in the Mt. Amiata area, and following the accumulation kinetics reported by Vannini et al. [4] we provide an estimation of average yearly concentration of atmospheric Hg from differently impacted areas of the region: near geothermal power plants (2-8 ng/m<sup>3</sup>), within small villages (2-8 ng/m<sup>3</sup>) and in direct proximity of the abandoned mines of Abbadia San Salvatore (70 ng/m<sup>3</sup>) and Aiuole (14 ng/m<sup>3</sup>). Our estimated minimum values are in agreement with the typical range found in the Northern hemisphere (1.3-1.7 ng/m<sup>3</sup>), while according to Ferrara et al [5], Hg background values for Mt. Amiata are in the range 3-5 ng/m<sup>3</sup>. Further research is currently in progress in the area to improve the reliability of the relationship between Hg concentration in the atmosphere and in lichen thalli.

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### ATMOSPHERIC DEPOSITION OF MAJOR AND TRACE ELEMENTS IN THE MOUNTAIN CRIMEA STUDIED BY THE MOSS BIOMONITORING TECHNIQUE

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For the first time the moss biomonitoring technique was applied to major and trace element atmospheric deposition study in the Mountain Crimea, the Black Sea region of Russia. A total of 30 samples of the terrestrial mosses *Pleurosium* sp. and *Hylocomium splendens* were collected in summer of 2015. The concentrations of 40 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Tm, Yb, Hf, Ta, W, Au, Th and U) were determined by means of neutron activation analysis performed at the pulsed fast reactor IBR-2, FLNP JINR [1]. Mg, K, Ca, Zn, Se, Br, Sr, Sb, and I were relatively evenly distributed in mosses of the studied region, while the highest and minimal values of Mo and Au differed by a factor of 20. Br and I tended to accumulate in mosses sampled in the coastal areas that reflects the marine origin of halogens [2]. The concentrations of the majority of elements determined in our study were lower than the values reported for mosses from the industrial regions of Bulgaria and Macedonia, but 1.5-2 times higher compared to mosses from relatively pristine areas of Norway [3]. The peculiarities of elemental distribution reflect the absence of obvious sources of anthropogenic pollution except for some outliers.

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#### DO LICHEN BIOACCUMULATION DATA TELL THE TRUTH?

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Lichens are known as reliable bioaccumulators of inorganic and organic atmospheric pollutants. They are especially effective in trapping trace elements from the surrounding environment, and it has been demonstrated that the concentrations of trace elements in lichen thalli are correlated with the environmental levels of these elements. Heavy metals may occur as particles adsorbed on the cortex or within intercellular spaces, as ions bound to extracellular and intracellular exchange sites, as soluble intracellular ions. The lichen thallus is characterized by cation exchange properties and the uptake of soluble cations may occur by means of passive reversible binding to anionic sites. The contemporary supply of positively charged elements may displace the original cations from their extracellular exchange sites, depending on chemical affinities and available concentrations. In this context, the nature of the elements and their different competitive capacities for exchange binding sites might mask their real environmental load of some elements. Hence bioaccumulation data might result in an underestimation of some elemental levels measured in biomonitoring studies. Here we report the preliminary results of experiments carried out in order to assess the competitive behaviour of heavy metals (Cd, Cr, Pb, Zn) during element uptake in lichen thalli. To this purpose, thalli of the foliose lichen Xanthoria parietina, that is commonly used in bioaccumulation studies, were collected from a remote area and treated with solutions containing 10 or 100 µM CdCl<sub>2</sub>, CuCl<sub>2</sub>, PbCl<sub>2</sub> and ZnCl<sub>2</sub>, firstly tested individually and then in combination (Cd+Cu+Pb+Zn). In general, Pb is an element with a strong affinity for cell wall ligands, whereas Zn, Cu, Cd may penetrate the plasmalemma, assuming an intermediate distribution. Divalent elements with high atomic mass have higher binding affinity to negatively charged exchange sites in the cell wall. Mineral uptake and release in lichen thalli are reversible processes influenced by thallus morphology and age, physiological status, exposure duration, microclimatic conditions and the presence and type of pollutants in the environment. Examples will be given on the application of lichens to witness the worsening and improving of environmental conditions under the influence of heavy metal depositions. Monitoring around air pollution sources and environmental gradients offered the opportunity to outline potentialities, limits, critical aspects and needs for future development of bioaccumulation techniques with lichens.

## CHARACTERISATION OF THE AIR POLLUTION IN THE MORAVIAN SILESIAN REGION USING NUCLEAR ANALYTICAL TECHNIQUES AND GIS TECHNOLOGY

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The research is focused on the characterization of the origin of particulate matter air pollution in the Moravian-Silesian region - one of the most polluted regions of the Czech Republic. Air pollution is assessed using the unmanned airship monitoring system, the moss survey and mathematical modelling. The sampling area comprises the most polluted part of the region at the both sides of the Czech-Polish border (3844 km<sup>2</sup>) [1]. A total of 43 moss samples (*Hypnum* cupressiforme, Brachythecium rutabulum, and Pleurozium schreberi) was collected within two first weeks of October 2015. Samples were analyzed by atomic absorption spectroscopy, instrumental neutron activation analysis and elemental analysis for content of Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, Fe, Zn, As, Br, Rb, Mo, Cd, I, Sb, Ba, La, Sm, W, Au, U, and N. Geographic information system (GIS) and statistical analysis are used to interpret the results obtained from this moss survey performed in such a small scale. Together with mathematical modelling it allows to understand the pollution distribution in the area and to characterize the origin of particulate matter air pollution as done previously on large scales [2, 3]. A comparison with available data from previous survey in the Czech Republic was made [4]. Additionally, the modified sequential elution technique was applied on the part of the collected moss material in order to determine the distribution of the particular elements in the moss thalli. So the information on the bioavailability of contaminants is provided too.

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#### MOSS BIOMONITORING IN ALBANIA: PRESENT AND FUTURE

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The use of mosses as biomonitors of atmospheric deposition of heavy metals started five years ago in connection with the development and problems of the industrial complexes in Albania. The results were presented in "Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe." The active moss biomonitoring (moss bags technique) was used to study air pollution in streets of the important cities of Tirana, Vlora and Elbasan. The PhD students of University of Tirana, Faculty of Natural Sciences, Dept. of Chemistry were involved in sampling campaigns and in the analysis of Hg via CVAAS method. The ICP/AES analysis of 19 elements (Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) were performed by the Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Republic of Macedonia. The rest of elements (39 elements included rare earth elements like Sc and lanthanides), were determined by Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research Dubna, Russian Federation. Geographical distribution maps of the elements over the sampled territory were constructed using Geographic Information System (GIS) technology. The atmospheric deposition of heavy metals in Albania was investigated by using a carpet-forming moss species (Hypnum cupressiforme) as bioindicator. Two different sampling schemes were conducted: a random sampling scheme with 62 sampling sites distributed over the whole territory of Albania and systematic sampling scheme with 44 sampling sites distributed over the same territory. The results of sampling schemes are compared with the results of other European countries. The results are generally expressed as pollution gradients. The second moss survey in Albania took place in August and September 2015 when 44 samples of the terrestrial mosses Hypnum cupressiforme were collected over the whole territory of the country using the same sampling network grid as for the previous survey in 2010. Using neutron activation analysis (NAA), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and atomic absorption spectrometry (AAS), a total of 47 elements (Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Hf, Hg, I, In, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn, and Zr) will be determined. Distribution maps will be prepared to point out the regions most affected by pollution and related to known sources of contamination. A comparison of the results that will be obtained in 2016 with the results of 2011 survey will be carried out to examine temporal trends in the elemental depositions.

### INFLUENCE OF VEGETATION ON ATMOSPHERIC DEPOSITION OF AIRBORNE RADIONUCLIDES

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Activity of airborne radionuclides <sup>7</sup>Be μ <sup>210</sup>Pb<sub>us</sub> (unsupported <sup>210</sup>Pb) were measured in moss samples taken on ten different locations and seventeen sampling points. The objective was to estimate influence of the forest vegetation on atmospheric deposition of airborne radionuclides attached to aerosols. Mosses were collected at two close sampling points (not more than couple of hundred meters between them) taking care that one of them was from area that is not covered by high vegetation and another sampling point was in the forest under crowns of trees. Samples were taken in the spring season, right before trees come into leaf and in the fall season, right before trees drop their leaves. As a result of this measurement it is obtained that high vegetation can postponed aerosol deposition and that mean activities of <sup>7</sup>Be measured in samples collected at open field can be 2.5 higher than activities measured in samples collected in forest.

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### INVESTIGATION OF AIR QUALITY OF ILINSKOE DISTRICT (IVANOVO REGION, RUSSIA) BY MOSS TECHNIQUE

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The increased anthropogenic impact was established for the territory of Ilinskoe district (Ivanovo region, Russia) during preparation to the Moss survey 2010/2011 in the framework of eco-monitoring study of air and soil quality of Ivanovo region. The influence of transboundary air pollution from neighboring Yaroslavl, Valdimir and Kostroma regions was hypothesized in account of absence of local emission sources. Different industrial centers of the metalworking, chemical, petrochemical and varnishes industries, as well as different objects of the heat power industry are located in the border area of these regions. To check this assumption the additional detailed investigation of air and soil quality by using the different methods of environmental monitoring and modern procedures of the physical and chemical analysis in the framework moss survey 2015/2016 was performed. Sampling grid consisted of 9 points with 5 km distance. Samples of moss, snow, and soils were collected at each sampling site. Samples of mosses were picked up according to the ICP Vegetation monitoring manual. Sampling of soil was made by standard techniques. The concentrations of 8 heavy metals (Cu, Zn, Pb, Cd, Co, Ni, Mn, Fe) were determined by flame atomic absorption spectrometry (AAS). The obtained data were undergone statistical analysis. Descriptive statistics and factor analysis (principal component method) were performed. To reveal potential sources of the pollutants the maps of spatial distribution were created. The assessment of air quality was carried out by comparison of element content in mosses and snow with the ones obtained previously for Ivanovo region (background sites and territories of natural preserve) and neighboring regions. The main conclusion of the present study is the justification of the suggested hypothesis.

# APPLICABILITY OF ARTIFICIAL NEURAL NETWORKS FOR PREDICTING CONCENTRATIONS OF CHEMICAL ELEMENTS IN VARIOUS ENVIRONMENTS

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Some interpretation methods in geochemistry using an artificial neural networks technology are presented. Due to study complexity such as the anthropogenic, geogenic, morphological impact or some sampling restriction, as well as high cost and time consuming nature of sampling and analytical treatment, research in developing methods for the creation of such maps are becoming increasingly important. Development of nonlinear prediction method that use secondary attributes sourced from the DEM, land use, and remote sensing in combination with sparse and expensive soil measurements has been sharpening focus of research. Consequently, the potential for using such information to soil mapping at the within field extent is greater than ever before. The state-of-the-art modelling techniques help us in reconstruction of both natural and anthropogenic influences simultaneously, that influenced the entire study area. Validation and applicability of this prediction method has been demonstrated within various geologically and morphologically complex study areas but also within various sampling materials (such as soil and moss) sensitive to anthropogenic and geogenic impact. In this study, the comparison between two prediction methods the Artificial Neural Network - Multilayer Perceptron and Universal Kriging are demonstrated. Examples of some case studies in Slovenia, Bosnia and Herzegovina, Kosovo and Macedonia illustrate the efficiency of these linear and non-linear state-of-the-art methods.

### ASSESSING AIRBORNE POLLUTION BY MOSSES AS BIOMONITORS—LONG-TERM INTEGRATED MONITORING OF ATMOSPHERIC METALS (2000-2010).

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Atmospheric contamination is one of the most pressing problems facing the world at present. Instrumental techniques used to evaluate atmospheric levels of the main contaminants are accurate but (i) provide data of short period, (ii) and very costly as there is need of man power and number of instruments to run simultaneously to monitor at many place is again expansive. It also requires power to run instruments which is not possible in remote areas. On the contrary, bryophytes (mosses) are an ideal biomonitoring agent [1] as (i) it does not require power to run instrument, (ii) thus enabling intensive surveys to be carried out at large number of different monitoring sites simultaneously, (iii) Bryophyte reactions to environmental changes is quicker and more direct than those of the majority of vascular plants [2] and (iv) The morphological constitution makes them an excellent tools to monitor the deposition of airborne pollutants [3]. In present study, moss species have been identified most clearly from metro-towns of undertaken states in the India's in longest running metal monitoring programme. For this tolerant (validated by using PEA) and widely distributed moss species were calibrated (interspecies calibration) and were transplanted on annual basis during 2000-2010 and were sampled end of each year for metal analysis from Garhwal, Himanchal, Jammu & Kashmir, Karnataka, Kumaon, Maharastra, Uttar Pradesh and from west Bengal. Analysis of annually exposed moss transplants showed presence of Pb, Cd, Mn, Cu, Zn, Cr, Ni, Fe and Al in harvested moss exposed each year. Lead values were highest in Dehradun during 2000 and 2010 and lowest in Manesar (Jammu). Cd, Cu, Zn, Ni and As values were maximum in Moradabad during both periods. However Mn values were highest from Bhowali, Fe was high in moss from Nainital, and Al in moss samples of Cherrapunji. Values of Cd, Zn, Mn, and Fe were lowest in moss samples from Mysoore while Pb and Cu values were low in moss samples from Manesar. Low values for As and Al were from Ranikhet and from Mysoore while Ni values were lowest in moss samples of Moradabad. Most of metals in atmosphere crossed FEPA(1991) and WHO (2001) threshold limiting values except from Mysoor and Dhanolti. Results showed their levels varied from element to element and from location to location. Present study reports widespread exceedance of the critical load for lead, copper, cadmium, nickel, iron, and zinc from the study regions.

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### FIRST MOSS SURVEY IN GEOGIA

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Georgian industries and agricultural sector provide considerable anthropogenic impact on the environment of the Caucasus and Georgia as a country with different relief and climate. The first attempt to study atmospheric deposition of major and trace elements in the Greater and Lesser Caucasus Mountains by the moss technique and neutron activation analysis was undertaken in 2014 [1]. The performed preliminary investigation showed that the moss biomonitoring of atmospheric deposition of heavy metals is an efficient technique to study the environmental situation in the Georgian mountainous regions characterized by mining and metallurgical enterprises. The experience of this study then successfully was used in the other regions of the Caucasus. In 2015 summer growth period 36 moss samples (Pleurosium schreberi – 8, Hylocomium splendens – 13, Hypnum cupressiforme – 15) were collected along altitudinal gradients in the range of altitudes from 160 m to 2200 m for prolongation of the moss survey in Georgia. Concentrations of 25 elements Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, Fe, Zn, As, Br, Rb, Mo, Cd, I, Sb, Ba, La, Sm, W, Au, Th, and U determined by neutron activation analysis in the moss samples are reported. A comparison with the data for moss collected in Norway (pristine area) was carried out. Multivariate statistical analysis of the results was used for assessment pollution sources in the studied part of the Caucasus. The increase in concentrations of most of elements with rising altitude due to gradually disappearing vegetation cover and wind erosion of soil was also observed. A comparison with the available data for moss collected in the Alps [2] at the same altitude (~ 2500 m) was performed.

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# SPATIAL INTERPOLATION OF N CONCENTRATIONS AND $\delta^{15}$ N VALUES IN THE MOSSES COLLECTED WITHIN OR OUTSIDE THE AREA OF CANOPY DRIP LINE

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Pollution maps are often used as a decision tools to develop emission control policies since the pollution maps are easy to interpret, and the information on pollutants of interest is available for the entire area and not only for the monitored locations. Different interpolation techniques are used to construct this type of pollution map. The techniques share a common aim, namely to predict the quantity of the pollutant in a nonsampled area based on the concentrations measured in the sampled areas. The accuracy of those maps is dependent on the sampling design, sample preparation, measurement error of the chemical analysis, the method used for mapping and finally also on the quality of the interpolation. The aim of presentation was to explore a different techniques for the spatial interpolation of N concentrations and  $\delta^{15}$ N values in the mosses that were collected within or outside the area of the canopy drip line. For this purpose the samples of Hypnum cupressiforme Hedw. were collected in 2010 at 103 locations in the forests of Slovenia. At each location, moss samples were collected from two types of site: a) under the tree canopies (inside the area of the canopy drip line) and b) in adjacent forest openings (outside the area of the canopy drip line). The mosses that were collected outside the area of canopy drip line ( $N_{open}$  and  $\delta^{15}N_{open}$ ) were expected to estimate the N deposited on the forest overstory or clearings, whereas the mosses that were collected inside the area of canopy drip line ( $N_{canopy}$  and  $\delta^{15}N_{canopy}$ ) were expected to estimate the N deposited onto the forest floor beneath the tree canopies. Results showed that spatial correlation was found only for N<sub>open</sub>, and therefore, ordinary kriging was used. For the other parameters (N<sub>canopy</sub>,  $\delta^{15}N_{open}$  and  $\delta^{15}N_{canopy}$ ), spatial correlations were not found. However, the regression models showed that certain environmental characteristics explained the variation of N and  $\delta^{15}$ N in the moss tissues. Using the maps of selected environmental characteristics, the spatial prediction with the regression model and the inverse distance weighted interpolations of residuals was applied to the  $N_{canopy}$  and  $\delta^{15}N_{open}$  and in a comparison of the two spatial interpolation techniques, also to  $N_{open}$ . In general, maps for Nopen created with ordinary kriging or with regression prediction, identified similar locations with increased N concentrations. Additionally, the map of the N<sub>canopy</sub>, with the exception of some areas in which the pattern was mirrored by the wind velocity map or the elevation map, the high concentrations of N around urbanized areas were consistent with the Nopen map. Moreover, some local emitters of NO<sub>x</sub> also emerged in this map, which were not observed on the N<sub>open</sub> map.

Skudnik, M., Jeran, Z., Batič, F., Kastelec, D., 2016. Spatial interpolation of N concentrations and  $\delta^{15}$ N values in the moss *Hypnum cupressiforme* collected in the forests of Slovenia. Ecological Indicators 61, 366-377.

### STUDY OF LEAD POLLUTION IN CROATIA BY USING MOSS BIOMONITORING AND ICP-AES

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Moss biomonitoring technique was used for the first time in Croatia for studying the air pollution in 2006 in the framework of International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops under the auspices of the United Nations Economic Commission for Europe (UNECE-ICP Vegetation) [1, 2]. This survey was repeated in 2010 when moss samples from different species (*Hypnum cupressiforme, Pleurozium schreberi, Homalothecium sericeum, Brachythecium rutabulum*) were collected during the summer and autumn from 121 locations evenly distributed over the territory of Croatia. Moss samples were digested in microwave digestion system and then analysed by using atomic emission spectrometry with inductively coupled plasma (ICP-AES). Data obtained from these two surveys were compared, and additional comparison was done with data obtained from similar studies in neighbouring countries and Norway as a clean area. The lead content ranges between 1.11 mg kg-1 and 36.64 mg kg-1 with the median value of 3.21 mg kg-1. Compared to the study performed in 2006, highest content of lead decreased for 2.25 times [1, 2]. High levels of lead were found in moss samples collected near industrial areas, northwest coast and Podravina region as a result of anthropogenic pollution but also in the region of south-west coast of Adriatic Sea as a result of geological origin.

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# HEAVY METALS AIR POLLUTION STUDY IN MINES ENVIRONMENTS. CASE STUDY BREGALNICA RIVER BASIN, REPUBLIC OF MACEDONIA

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Application of several moss species and attic dust for monitoring of anthropogenic impact on heavy metals air pollution in Bregalnica River Basin, Republic of Macedonia, was studied. Moss samples were reviewed for their potential to reflect heavy metals air pollution. The attention was focused on their quantification ability, underlying the metal accumulation within moss plant tissue and attic dust "historical archiving". Potential "hot spots" were selected in areas of copper mine (Bučim mine) and lead and zinc mines (Zletovo mine and Sasa mine) as main metal pollution sources in the Eastern part of the Republic of Macedonia. Continuously, dust distribution from ore and flotation tailings occurs. This results with air-introduction and deposition of higher contents of certain metals. Several moss species (Hypnum cupressiforme, Homalothecium lutescens and Scleropodium purum) were used as plant sampling media. Determination of chemical elements was conducted by using both instrumental techniques: atomic emission spectrometry with inductively coupled plasma (ICP-AES) and mass spectrometry with inductively coupled plasma (ICP-MS). Combination of multivariate techniques (PCA, FA and CA) was applied for data processing and identification of elements association with lithogenic or anthropogenic origin. Spatial distribution maps were constructed for determination and localizing of narrower areas with higher contents of certain anthropogenic elements. In this way influences of selected human activities in local (small scale) air pollution can be determined. Summarized data reveal real quantification of the elements distribution not only in order determination of hazardously elements distribution, but also present complete characterization for elements deposition in mines environs.

# USE OF MOSSES FOR MONITORING ATMOSPHERIC DEPOSITION OF RADIONUCLIDES: POSSIBILITIES AND LIMITATIONS

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Samples of naturally growing moss have been extensively used in Europe over the last 40 years for large-scale monitoring of atmospheric deposition of trace metals. As radioactive isotopes of an element behave the same way as the corresponding stable isotopes under equilibrium conditions there is no reason why moss sampling could not be used for monitoring of radionuclides as well, provided that the moss technique works for the corresponding stable elements. There have been some reports in the literature on the use of this approach for the study of radionuclides in natural (<sup>7</sup>Be, <sup>210</sup>Pb, <sup>210</sup>Po ) as well as anthropogenic processes (<sup>131</sup>I, <sup>137</sup>Cs, <sup>90</sup>Sr, <sup>95</sup>Zr-<sup>95</sup>Nb, <sup>140</sup>Ba-<sup>140</sup>La, <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>241</sup>Am), but most of these efforts have been limited in time and space, and very few of them have considered in detail the mechanisms involved in the fixation of the radionuclides to the moss surface and the character and strength of the binding. From studies of trace element deposition it is known that metals may be fixed to the moss surface bound to particles as well as attached to the moss surface in free state by electrostatic or chemical bonds, and the feasibility of the moss monitoring technique for an element depends on the chemical property of the elements and its physical or chemical association with other substances in the atmosphere. These facts have not always been considered critically in monitoring studies employing moss samples for mapping deposition of radionuclides. Several investigations have been reported on geographic distribution of 137Cs in moss, but most frequently without considering the interaction of Cs with the moss. It has been shown that the Cs ion is transported in the moss plant from the older to the younger annual growth increment [1, 2]. This was clearly indicated in a study from Belarus where the original atmospheric deposition pattern from the Chernobyl accident was evident in moss samples collected over 20 years after the accident [3]. The present talk will briefly review the literature on monitoring of radionuclides in air using mosses and discuss some of the possible problems based on general experience with this technique applied to stable forms of trace elements.

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### MOSS SURVEY 2010 IN ROMANIA. RESULTS AND PERSPECTIVES

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Large-scale monitoring using the moss technique was carried out in Romania in the frame of the European moss survey 2010/2011. A total of 330 moss samples, *Pleurozium schreberi*, Hylocomium splendens, Hypnum cupressiforme and other species were collected during August and September 2010 according to the European moss surveys standardised protocol. The elemental concentrations of moss samples were determined in 2011/2012 using two complementary methods: instrumental epithermal neutron activation analysis (ENAA) at the IBR-2 reactor in the Joint Institute for Nuclear Research in Dubna, Russian Federation, and furnace/flame atomic absorption spectrometry (GFAAS graphite /FAAS) Multidisciplinary Research Institute for Science and Technologies from Valahia University of Targoviste, Romania. The obtained data were statistically processed and spatial distribution maps for each specific element were prepared for interpretation of the obtained results. Median values for some heavy metals in mosses collected in Romania, such as Cd and Pb are rather high compared to other European countries. The results revealed that the atmospheric deposition of these metals is a considerable problem in the northern and north-western parts of Romania, most probably, because of the lead smelter presence and not full abolishment of the leaded petrol at that time. To monitor the future trends in heavy metal deposition Romania continues to participate in the UNECE ICP Vegetation program (moss surveys).

### TECHNOLOGY-CRITICAL ELEMENTS - NOVEL POLUTANTS

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The aim of this abstract is to pay attention on needs for determination of novel group of elements so called Technology-Critical Elements (TCEs). TCEs include Ga, Ge, In, Te, Nb, Ta, Tl, the platinum group elements and most of the rare-earth elements. Contrary to well-known heavy metals which have been treated as significant pollutants, TCEs were considered as laboratory curiosities. However, in modern technology development TCEs represent essential components in a variety of applications such as information and telecommunications technology, semiconductors, electronic displays, optic/photonic or energy related technologies. Application of TCEs rapidly increases, and their presents in the environment also increase. For most of these elements, the present understanding of their concentrations, transformation and transport in the different environmental compartments is scarce and/or contradictory. The current significant gaps in the knowledge on TCEs, from their environmental levels and fate to their potential ecotoxicological impact due to their typical ultratrace concentrations and the absence of any significant industrial role (apart some biomedical applications) prior to their massive use in the increasing demand of new technological applications. Analytical methods, from sampling to analysis, possess a number of critical steps that may cause errors and misinterpretation of the results. Although, numerous analytical methods have been developed and exploited for determination of metal ions, determination of many of TCEs are still not routine due to their typical ultratrace concentrations which making their analytical determination extremely difficult and/or timeconsuming. The increasing use of TCEs and their environmental and biological impact is associated with need for accurate analytical methods for their determination in ultratrace level. With regard to lack of information about contamination of environment with TCE, as well as their species and fate, development of chemical instrumental methods such as ICP/MS and electochemical for determination is hindered. We propose the analyses of TCEs in environmental samples (water, soil, deep see sand) by Instrumental Neutron Activation Analysis. We expect that results obtained by NAA could be the base for further development analytical methods (ICP-MS and electrochemical) for determination TCEs.

### REDUCTION OF THE NUMBER OF SAMPLING SITES IN SWITZERLAND FOR THE SURVEY 2015

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In 1990, Switzerland started analysing heavy metals in mosses using 235 sampling sites. In the following surveys the site number was reduced several times: 1995 to 201 sites, 2000/2005/2010 to 142 sites. For the survey in 2015 a reduction was again necessary in order to get funds for analysing POPs at 22 sites. The requirement was to reduce the number of sites by half to about 70 sites. How to reduce the number of sites such that the data are still representative? A pragmatic approach was used: (i) Excluding sites that do not conform to the guidelines of the monitoring manual anymore, (ii) Preferring sites where the sample could be collected at the same or a very similar place, (iii) Preferring sites where in the last 5 surveys the same moss species could be collected, (iv) Preferring sites where other monitoring studies have been done, e.g. N and PAH analysis 2010, or soil and air measurements, (v) Distributing the sites evenly throughout Switzerland, (vi) Making sure that each geographical region – Jura (J), Plateau (M), Northern (NA), Central (ZA), Southern (SA) Alps – has at least 12 sites. All these requirements were met with 73 sites. The result is comparable to that with 142 sites (Fig. 1). Even with this additional reduction, the sample density in Switzerland is, with 1.7 moss samples/1000km², still within the demanded range defined in the monitoring manual.

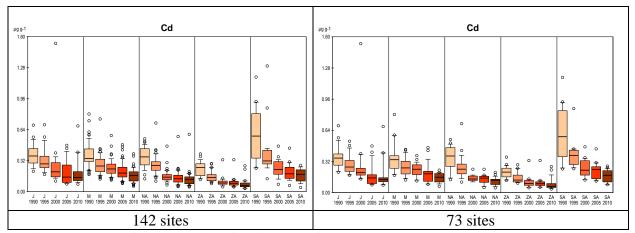


Fig. 1: Boxplots of concentration of Cd in moss of the 5 surveys – 1990, 1995, 2000, 2005, 2010 - and 5 regions. Left 142 sites, right 73 sites

# THE MOSS TECHNIQUE AND NEUTRON ACTIVATION ANALYSIS FOR TRACE ELEMENT ATMOSPHERIC DEPOSITION STUDY IN TIKHVIN DISTRICT, LENINGRADSKAYA OBLAST'

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For the first time the moss biomonitoring technique was used to study trace element atmospheric deposition in the area affected by a ferroalloy (Fe-Cr) plant in the town of Tikhvin, Leningradskaya Oblast', to apportion its deposition patterns and to reveal previously unknown pollution sources located in and within the sampled territory. Moss samples were collected in the summer of 2011 from 36 sites evenly distributed over the Tikhvin District in accordance with the guidelines of the UNECE ICP Vegetation. A total of 35 elements were determined by means of epithermal neutron activation analysis at the reactor IBR-2 FLNP, JINR, Dubna. Multivariate statistical analysis was applied to characterize the sources of determined elements over the examined territory. Contamination factors (CF) for selected elements and ecological risk index were calculated using their concentrations for the Tverskaya Oblast' considered as a relatively unpolluted territory. The results obtained are compared to the data of the atmospheric deposition of trace elements in Central Russia and in some countries of Eastern Europe. Distribution maps of most hazardous element-pollutants over the surveyed territory created using GIS technologies are demonstrated. These maps show that the main source of contamination in the investigated area is Tikhvin ferroalloy plant. In the close vicinity of Tikhvin was observed the highest content of Al, As, Co, Fe, Cr, Ni and V in moss samples. Factor analysis revealed that high content of these elements had one source. In 10 km zone around Tikhvin CF is 2 times higher than on the rest of investigated territory. Maximum value of CF for Cr was determined in the vicinity of Tikhvin ferroalloy plant and is considered as extremal. The main source of contamination in the sampling area is the metallurgic plant in Tikhvin. Another source is located close military airdrome and metallurgic waste dump in the north of the investigated tirritory. In general the investigated area is quite clean in comparison with other Russian regions as well as European countries.

### APPLICATION OF GAMMA SPECTROMETRY AND COMPOSITIONAL DATA ANALYSIS IN ESTIMATION OF ATMOSPHERIC DEPOSITION

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A dust transported in the atmosphere is released from natural and artificial sources. Composition of an atmospheric precipitate is determined both by distant emission sources and local secondary redeposition. Combustion of fossil fuels and some industrial activities produce large amounts of dust containing radioactive isotopes, which are then deposited on the ground surface. These include natural radioisotopes and their decay products as well as some artificial radioisotopes. Some radioisotopes form decay chain as a result of parent – daughter relationship between them. In the closed system, after an appropriate period, radiochemical balance occurs between isotopes in decay series. In environment radioisotopic composition of its components can be changed in time. It is a result, for example, of radioactive matter deposition, washing or leaching. A change in radioisotope concentration leads to break in radioactive equilibrium in fragment of decay series. The way of changes is related to the disturbance temporal character. In natural decay series approx. 34 unique radioisotopes representing 10 chemical elements occur. Determination of their concentrations in components of the environment can provide valuable information. Analysis of joined data comprising chemical properties of an element, half-life time of radioisotope, and characteristic features of environmental component, deliver a base for studies of matter sources and transport routes, fate of deposited dust in ground and chemical compounds circulation between components of environment. Activity concentration of some radioisotopes can be determined using gamma spectrometry. Unfortunately, concentration of only limited number of radioisotopes in decay series can be determined with this method. To assess characteristic features of radioisotopic composition in a sample, the activity concentrations should be recalculated to mass concentrations. In the results exploration the methods designed for the compositional data analysis should be used.

# MULTI-ELEMENT ATMOSPHERIC DEPOSITION STUDY IN THE REPUBLIC OF MOLDOVA

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For the first time the moss biomonitoring technique and two complementary analytical techniques, neutron activation analyses and atomic absorption spectrometry, were applied to study multielement atmospheric deposition in the Republic of Moldova on a large scale. Moss samples were collected during the spring 2015 at 34 sites evenly distributed over the country. Sampling was performed in accordance with the LRTAP Convention - ICP Vegetation protocol and sampling strategy of the European Programme on Biomonitoring of Heavy Metal Atmospheric Deposition. A total of 45 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Cd, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Hf, Ta, W, Hg, Au, Pb, Th, and U) were determined by instrumental epithermal neutron activation analysis at the reactor IBR-2 of FLNP JINR and atomic absorption spectrometry. Principal component analysis was used to identify and characterize different pollution sources. Distributional maps were prepared to point out the regions most affected by pollution and to characterize the deposition patterns of pollutants. The median values of the elements requested by the European programme were compared with the data reported in the "Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and longtemporal trends in Europe" [1]. The concentrations of Al, Cr, V, Ni, and Fe in moss samples collected in the Republic of Moldova were higher compared to those for other European countries and lower for Cd, Cu, Ni, and Zn, but very similar to the data reported for Romania. This study was performed in order to identify the local pollution sources in the Republic of Moldova and to assess long-range transboundary air pollution from the neighboring countries.

1. H. Harmens, D. Norris, G. Mills, J. Aboal Viñas, R. Alber, Y. Aleksiayenak, K. Baceva, L. Barandovski, T. Berg, O. Blum, A. Carballeira Ocaña, A. Chilian, S.-M. Cucu-Man, O. A. Culicov, M. Dam, H. Danielsson, A. M. Dunaev, D. Elustondo, A. Ene, J.Á. Fernández Escribano, M.V. Frontasyeva, A. Gheboianu, B. Godzik, Z. I. Goryainova, A. Hanus, K. Hoydal, M. Infante Olarte, S. Izquieta, Z. Jeran, P. Kapusta, J. Karhu, E. Kubin, X. Laffray, P. Lazo, N.A. Lebedeva, S. Leblond, S. Liiv, S. Magnússon, B. Mankovska, J. Martínez-Abaigar, A. Maxhuni, E. Núñez-Olivera, J. G. Pihl Karlsson, J. Piispanen, J. Poikolainen, I. V. Popescu, F. Qarri, C. Radulescu, A. Riss, A. Ruttens, J. M. Santamaría, M. Skudnik, Z. Spiric, T. Stafilov, E. Steinnes, C. Stihi, I. Suchara, J. Sucharová, L. De Temmerman, H. Thelle Uggerud, L. Thöni, R. Todoran, R. Tomás-LasHeras, K.N. Vergel, I. V. Vikhrova, N. Waegeneers, L. Yurukova, H.G. Zechmeister, I. Zinicovscaia, Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe, H. Harmens, D. Norris, G. Mills (Eds.), ICP Vegetation Programme Coordination Centre Centre for Ecology and Hydrology Environment Centre Wales, Bangor, UK, March 2013, 63 pp.; ISBN 978-1-906698-38-6. http://icpvegetation.ceh.ac.uk/publications/documents/Finalmossreport2010-11forweb

# Plan of Dubna

