



**Centre for  
Ecology & Hydrology**

NATURAL ENVIRONMENT RESEARCH COUNCIL



## **32<sup>nd</sup> Task Force Meeting**

**18 - 21 February 2019**

**Targoviste, Romania**



*Valahia University of Targoviste*

# **Programme & Abstracts**



## **Organizers:**

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

*Dr. Harry Harmens, Dr. Felicity Hayes, Dr. Katrina Sharps*

## **Local organizers:**

*Valahia University of Targoviste*

*Assoc. Prof. Claudia Stihi, Prof. Cristiana Radulescu,  
Assoc. Prof. Calin D. Oros, Lect. Oana Catalina Bute,  
Dr. Ioana Daniela Dulama, Dr. Sorina Geanina Stanescu,  
Madalina Maria Oachesu, Ioan Alin Bucurica*

**Local financial support is provided by**



*Targoviste City Municipality*



*Valahia University of Targoviste*

## PROGRAMME

**Venue:** *International Conference Center - Valahia University of Targoviste, 39 Maior Ion Alexandrescu Street, 130021, Targoviste*

### **Monday 18<sup>th</sup> February, 2019**

**17:00** – Registration at International Conference Center

**18:30** – Welcome reception and putting up posters

### **Tuesday 19<sup>th</sup> February, 2019**

- *Plenary sessions in the red room*
- *Ozone sessions in the blue room*
- *Moss survey sessions in the green room*
- *Poster session (International Conference Center Hall)*

**08:00**            **Late registration and putting up posters**

**Session 1:**    **9:00 – 10:45**            **Plenary**            **Chair: Claudia Stihl**

09:00    Welcome address + presentation

*Cristinel Mortici* – Dean of Faculty of Sciences and Arts, Valahia University of Targoviste.

*Dorela Mirica* – Delegate of Environmental Protection Agency, Dambovită County.

09:20    *Harry Harmens et al.* – Achievements of the ICP Vegetation in 2018 and future workplan (2019-2021).

09:45    *Marina Frontasyeva et al.* – Merits and drawbacks of passive moss biomonitoring used to study atmospheric deposition: Results of moss survey 2015/16.

10:05    *Klaudia Borowiak et al.* – Air monitoring system in selected countries and possibilities to start air biomonitoring of ozone and heavy metals.

10.35    General discussion

**10:45 – 11:30 Coffee/tea and poster viewing (with authors at poster)**

**Session 2:**    **11:30 – 13:00**            (Two parallel sessions: **Ozone** and **Moss survey**)

**Session 2a:**    **Ozone - Ozone flux modelling and the role of soil moisture**  
**Chair: Rocio Alonso**

11:30        *David Simpson* – Modelling ozone fluxes with the EMEP MSC-W Model – Status and future development.

- 11:50 *Ignacio González Fernández et al.* – Modelling the influence of soil moisture on ozone dose under water-limited climatic conditions.
- 12:10 *Gina Mills, Katrina Sharps et al.* – Closing the global ozone yield gap: Quantification and co-benefits for multi-stress tolerance.
- 12:30 *Harry Harmens et al.* – Can deficit irrigation mitigate impacts of ozone on wheat yield?
- 12:50 General discussion

**Session 2b: Moss survey - Trends**

**Chair: Marina Frontasyeva**

- 11:30 *Konstantin Vergel et al.* – Moss biomonitoring in Russia: overview of the 2015/2016 moss survey.
- 11:50 *Gergana Hristozova et al.* – Atmospheric deposition trends in Bulgaria over a 20-year period of participation in the European moss survey programme (1995/6-2015/6).
- 12:10 *Pranvera Lazo et al.* – The metal atmospheric deposition in Albania (2010 – 2015 moss survey).
- 12:30 *Zaida Kosonen et al.* – Anthropogenic vs. geogenic origin of elements in Swiss moss samples between 1995 and 2015.
- 12:50 General discussion

**13:00 – 14:00 Lunch** (Hotel Nova Restaurant)

**Session 3: 14:00 – 15:30 (Two parallel sessions: Ozone and Moss survey)**

**Session 3a: Ozone – Impacts on food production**

**Chair: Katrina Sharps**

- 14:00 *Håkan Pleijel et al.* – Ozone impact on wheat in Europe, Asia and North America - a comparison.
- 14:20 *Jérôme Schneuwly et al.* – Estimation of ozone induced yield losses of wheat and potato in Switzerland using the DO<sub>3</sub>SE model.
- 14:40 *Felicity Hayes et al.* – Dose-response relationships for African crops.
- 15:00 Some short poster presentations and general discussion. For list of ozone poster presentations, see page 8.

**Session 3b: Moss survey – Biomonitoring with mosses and lichens**

**Chair: Cristiana Radulescu**

- 14:00 *Julian Aherne et al.* – Moss as a biomonitor of atmospheric microplastic deposition.
- 14:20 *Stefano Loppi* – Mosses and lichens as bioaccumulators of airborne elements: What do we really measure? In addition, are these biomonitors suitable in environmental forensics?
- 14:40 *Carmen Iacoban et al.* – Nitrogen deposition in Romania. Levels determined within ICP Vegetation and ICP Forests.

- 15:00 *Luca Paoli et al.* – Air pollution still limits epiphytic recolonization: Heavy metals and ecophysiological parameters in threatened forest macrolichens of Central Europe.
- 15:20 General discussion

### **15:30 – 16.00 Coffee/tea and poster viewing**

#### **Session 4: 16:00 – 17:30 (Two parallel sessions: **Ozone** and **Moss survey**)**

##### **Session 4a: **Ozone – Discussion session (1)** Chair: **Felicity Hayes****

- 16:00 Sabine Braun – Uncertainty analysis of ozone flux with phenological models.
- 16:20 General discussion on new developments, future ozone work and outreach activities including:
- Monitoring ozone impacts on vegetation, including contributions of EU Member States to National Emission Ceilings Directive;
  - Photosynthesis-based DO3SE model, incorporation of ozone impacts in crop growth models, damage functions for trees in terrestrial biosphere models;
  - New ozone research (e.g. pasture quality, impacts on pollination, ozone removal by vegetation in urban areas, BVOCs);
  - ICP Vegetation Asia;
  - Interactions with climate change.
- Some short poster presentations will be included here on relevant subjects mentioned above. For a list of ozone poster presentations, see page 8.

##### **Session 4b: **Moss survey – Results of recent surveys** Chair: **Hilde Uggerud****

- 16:00 *Inga Zinicovscaia et al.* – Moss biomonitoring of atmospheric deposition study of minor and trace elements in the Republic of Moldova.
- 16:20 *Omar Chaligava et al.* – Atmospheric deposition study of major and trace elements in Georgia based on moss analysis.
- 16:40 *Chrysoula Betsou et al.* – Mosses as biomonitors of trace elements in Greece.
- 17:00 *Petr Jancik* – Air pollution management projects using mathematical modelling and special monitoring methods.
- 17:20 General discussion.

### **Wednesday 20<sup>th</sup> February, 2019**

#### **Session 5: 08:30 – 10:30 (Two parallel sessions: **Ozone** and **Moss survey**)**

##### **Session 5a: **Ozone – Interactions with nitrogen** Chair: **Håkan Pleijel****

- 08:30 *Håkan Pleijel* – Introduction and progress with data collation literature?
- 08:40 *Yasutomo Hoshika et al.* – Nutritional availability changes ozone dose-response relationships in poplars.

- 09:00 *Rocio Alonso et al.* – Sensitivity of Mediterranean mountain top herbaceous communities to ozone and nitrogen deposition.
- 09:20 *Victoria Bermejo et al.* – Ozone and nitrogen effects on fungal wheat diseases.
- 09:40 General discussion on new chapters for Scientific Background Document B, further developments regarding ozone critical levels and potential contributions to review of empirical nitrogen critical loads (with ICP Modelling & Mapping).

**Session 5b: Mosses – Preparations 2020 survey** **Chair: Harry Harmens**

- 08:30 *Alexander Uzhinkiy et al.* – Is it possible to predict heavy metal atmospheric deposition and when it could be useful?
- 08:50 *Alexander Uzhinkiy et al.* – Mobile application for ICP Vegetation moss sampling sites management.
- 09:10 Discussion on above presentations and preparations for 2020 moss survey:
- Amendments to moss survey biomonitoring protocol;
  - Call for data, data submission and participation;
  - Monitoring in Eastern Europe and beyond (background sites, inclusion of nitrogen, confounding factors);
  - Schedule 2020 survey (learn from past experiences);
  - Depository of past data & data paper;
  - Reporting back decisions & recommendations, future workplan.

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

**Session 6: 11:00 – 13:00 (Two parallel sessions: Ozone and Moss survey)**

**Session 6a: Ozone – Discussion session (2)** **Chair: Felicity Hayes**

- 11:00 *Felix Leung et al.* – Ozone garden: An experiment to examine the harmful effects of urban air pollution on ecosystems in South China.
- 11:20 *Valda Araminiene et al.* – Trends and inter-relationships of ground-level ozone metrics and forest health in Lithuania.
- 11:40 Final general discussions (see session 4a) and feedback to plenary, including future workplan.

**Session 6b: Moss survey – Biomonitoring studies** **Chair: Julian Aherne**

- 11:00 *Guntis Tabors et al.* – Spatial distribution of heavy metal pollution in moss (*Pleurozium schreberi*) and in soil O horizon in Latvia
- 11:20 *Stefan Fränzle et al.* – Chitin adsorption in environmental monitoring: not an alternative to moss monitoring but a method providing (lots of) bonus material/information.
- 11:40 *Nikolina Gribacheva et al.* – Heavy metal deposition monitoring in a mountain area with local emitters: a case study from Bulgaria.

- 12:00 *Oldřich Motyka* – Proper imputation of sub-limit and missing values in biomonitoring studies.
- 12:20 *Fabrizio Monaci et al.* – Native and transplanted aquatic moss (*Platyhypnidium riparioides*) for assessing long-term metal(loid) impacts from abandoned mines.
- 12:40 General discussion and feedback to plenary.

**13:00 – 14:00 Lunch** (Hotel Nova Restaurant)

**Session 7: 14:00 – 15:30 Final plenary session** **Chair: Harry Harmens**

- Reporting back from ozone (Felicity Hayes) and moss survey sessions (Marina Frontasyeva): decisions and actions;
- Medium-term work plan ICP Vegetation 2019 – 2021 and beyond;
- Decisions and recommendations of the 32<sup>nd</sup> Task Force Meeting;
- 33<sup>rd</sup> ICP Vegetation Task Force Meeting;
- Other business.

**15:30 – 16:00 Coffee/tea and taking down posters**

- 16:00** Visit to Chindia Tower and the Royal Court of Targoviste (15 minutes' walk from the International Conference Center)
- 19:30** Conference Dinner at Hotel Nova Restaurant

**Thursday 21<sup>st</sup> February, 2019**

**Excursion** to Bran and Peles Castles in the Carpathians Mountains (Departure from Hotel Nova at 8:30; Arrival at Hotel Nova up to 20:00).

## LIST OF POSTERS

### OZONE

Author(s)	Title
Araminiene, V. et al.	Ozone impacts on insects
Ashworth, K. et al.	Ozone impacts on respiration and photosynthesis rates in three contrasting forest ecosystems
Calatayud, V. et al.	Project ELEMENTAL: Ozone fluxes in Mediterranean vegetation
Dell'Orso, A., Alonso, R. et al.	DNA integrity and ecophysiological responses of Spanish populations of <i>Ulmus glabra</i> to increasing ozone levels
Eghdami, H. et al.	Time series (1998-2015) of ozone flux on forest in Rhineland Palatinate (Germany)
Fusaro L., Salvatori E. et al.	Modelling ozone uptake by urban and peri-urban forest: A case-study in the Metropolitan city of Rome, Italy
Hayes, F. et al.	<i>Evidence of impacts of ozone on ecosystem services of grasslands</i>
Leung, F.P.K et al.	Quantifying the impact of present-day and future tropospheric ozone on crop productivity at global and regional scale using JULES-CROP
Neiryck, J. & Verstraeten, A.	Ozone deposition over a mixed suburban temperate forest
Paoletti, E., Hoshika, Y. et al.	Towards the definition of epidemiologically-based stomatal-flux critical levels for forest protection against ozone: the MOTTLES approach
Roberts, H.	Do biogenic VOCs protect plant productivity under multiple environmental stress?
Sharps, K. et al.	<i>Smart-phone app for recording incidences of ozone injury on vegetation</i>
Tai, A. et al.	<i>Estimating the impacts of ozone pollution and climate change on terrestrial ecosystem productivity using an offline ecophysiological model</i>

Short presentations were given for all posters in the ozone sessions except for those in italics.

### MOSS SURVEY

Aleksiyenak, Y., Frontasyeva, M.V. et al.	Data interpretation from Belarussian moss surveys using different statistical approaches
Aničić Urošević, M. et al.	Assessment of anomalies in distribution of rare earth elements across Serbia using moss biomonitoring
Bekteshi, L., Lazo, P. et al.	Assesment of air quality in Albania based on atmospheric deposition of trace elements in coastal and inland areas
Budka A. et al.	Heavy metal accumulation in <i>Taraxacum officinale</i> L. at urban areas
Bukharina, I.L., Frontasyeva, M.V. et al.	Moss monitoring of trace elements in the Republic of Udmurtia, Russia
Dalelova A.M, Omarova N.M., Frontasyeva M.V.	Investigation atmospheric deposition of heavy metals in north and west region of the Republic of Kazakhstan using the method of moss-biomonitoring
El Shall, A., Bellini, E. et al.	Intracellular response to cadmium in the moss <i>Leptodictyum riparium</i>
Ene, A., Stihl, C. et al.	Nuclear and atomic techniques used for heavy metal pollution investigations in agroecosystems
Frontasyeva M.V., Abdusamadzoda, D. et al.	Air pollution study in different regions of Tajikistan using the moss biomonitoring techniques, NAA and AAS
Gorelova S.V., Frontasyeva M.V. et al.	Trends of atmospheric deposition in Central Russia: Tula region (2015-2016)
Koroleva, Y., Bakhriz, B. et al.	PAHs measurements in moss <i>Pleurozium schreberi</i> in Kaliningrad region
Krakovská, A. et al.	Identification of the pollution sources by moss biomonitoring in the Upper Silesia region
Madadzada, A., Frontasyeva, M.V. et al.	Atmospheric deposition of trace elements in Guba region (Azerbaijan)
Marku, E. & Nuro, A.	Preliminary study of some organic pollutants in moss and pine needles in Tirana region, Albania
Mehrabova, M.A. et al.	Biomonitoring of air pollution in Azerbaijan
Moraru, S.S., Ene, A. et al.	Relation between land use, industrial activity and metal accumulation in plants
Movsisyan N., Tepanosyan, G. et al.	Estimation of atmospheric fallout radionuclides activity using mosses: Armenia
Nuhuyeva, Sh.S. et al.	Biomonitoring of atmosphere air in important ecotourism regions of Azerbaijan
Qarri, F. et al.	Biomonitoring of toxic metal air pollution using mosses in Albania
Radulescu C. et al.	Microclimatic monitoring and environmental impact assessment on heritage materials of Tropaeum Traiani Monument, Adamclisi
Stihl, C. et al.	Moss biomonitoring in Romania as integrated in European surveys: continuity, extending and perspectives
Štrbová, K. et al.	Missing values in biomonitoring data: Example from biomonitoring survey in Belarus
Svozilik, V. et al.	Verification of the air pollution mathematical modelling results using special monitoring and analytical methods



# **PLENARY**



## AIR MONITORING SYSTEM IN SELECTED COUNTRIES AND POSSIBILITIES TO START AIR BIOMONITORING OF OZONE AND HEAVY METALS

Borowiak K., Cakaj A., Chen Y., Mbah J.T., Nchouwet Mefire S.A., Vashchuk A., Wang T., Yandem G., Lisiak M.

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Air monitoring system is well developed in many countries, however biomonitoring might play an important supplementary role in areas, which are difficult to monitor. On the other side, there is a lack of information about air pollution in many countries and biomonitoring can bring valuable information about potential level of the air pollution and its effects on vegetation. Hence, we would like to present information about air monitoring system in Cameroon, China, Kosovo, Poland, Syria and Ukraine, in relation to possibilities of creation the supplementary biomonitoring system of ozone and heavy metals. The information are based on sources such as: official websites of national environmental agencies, Report of Delegation of UE Commission to Syria, as well as received during personal contacts with air pollution experts etc.

Cameroon – air monitoring system is not conducted at the country scale. There are some monitoring sites provided by private companies, but the data are not publically available. Heavy metals biomonitoring is done by private companies, and there will be conducting lead biomonitoring at northern part of the country by scientists with the aid of lichens.

China – environmental monitoring information management system started relatively late. Users and system administrators can query the urban and enterprise pollution source parameters in real time through the website. In recent years, China has also carried out biological monitoring work to use plants for monitor air pollution.

Kosovo - air monitoring is conducted through automatic equipment in different cities throughout the country, eight of which are available online. Biomonitoring data are restricted and not publically available. Biomonitoring of ozone and heavy metals is possible to start due to many favorable bioindicator plant species.

Poland – there is well developed air monitoring system with automatic equipment. The data are continuously available at website. However, the number of monitoring station is still not suitable for evaluation of air pollution effect on human health and vegetation. Ozone and heavy metal biomonitoring is restricted to some areas and years.

Syria – annual environmental reporting on a country-wide level is unknown, and aggregated data are available for only a few environmental parameters. Some information also takes considerable time before it becomes publicly available. The overall picture therefore sometimes remains somewhat incomplete. There is no air biomonitoring at all.

Ukraine – there is air monitoring system program since 1998, however, it has to be improved.

The data are not available for public. Hence, the best solution is to create an Internet website with monitoring data available for everyone. Biomonitoring is restricted to some local scientific projects supported by international programmes.

Overall, air biomonitoring of ozone and heavy metals could help to assess the state of pollution, its impact on human health and the vegetation. Also, it would be more cost effective, more convenient as well as more credible as compared to the technical monitoring.

# MERITS AND DRAWBACKS OF PASSIVE MOSS BIOMONITORING USED TO STUDY ATMOSPHERIC DEPOSITION: RESULTS OF THE MOSS SURVEY 2015/16

Frontasyeva M.V.<sup>1</sup> and Steinnes E.<sup>2</sup>

<sup>1</sup>*Joint Institute for Nuclear Research, str. Joliot-Curie, 6, Dubna, 141980, Moscow Region, Russian Federation, E-mail: [marina@nf.jinr.ru](mailto:marina@nf.jinr.ru)*

<sup>2</sup>*Department of Chemistry, Norwegian University of Science and Technology, Trondheim, Norway. E-mail: [eliv.steinnes@ntnu.no](mailto:eliv.steinnes@ntnu.no)*

Although mosses have been used extensively to monitor atmospheric deposition of heavy metals and other trace constituents [1], evidence from multi-element moss surveys in general, and the international moss survey 2015/2016 in particular, calls for a discussion of the feasibility of this technique and a critical evaluation of factors that may lead to misinterpretation of results [2-4]. Special attention must be paid to contributions to the elemental composition of the moss from sources other than air pollution, such as marine influence, windblown soil dust, and uptake from soil via higher plants and subsequent transfer to the moss. Specific problems are evident from the use of mosses as biomonitors in arid areas.

## Reference

1. M. V. Frontasyeva, E. Steinnes and H. Harmens. Monitoring long-term and large-scale deposition of air pollutants based on moss analysis. Chapter in a book “Biomonitoring of Air Pollution Using Mosses and Lichens: Passive and Active Approach – State of the Art and Perspectives”, Edts. M. Aničić Urošević, G. Vuković, M. Tomašević, Nova Science Publishers, New-York, USA, 2016.
2. E. Steinnes. A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals. *Science of the Total Environment*, Vol. 160/161, 1995, p. 243-249.
3. J.R. Aboal, J.A. Fernández, T. Boquete, A. Carballeira. Is it possible to estimate atmospheric deposition of heavy metals by analysis of terrestrial mosses? *Science of the Total Environment*, Vol. 408, 2010, p. 6291–6297.
4. Z. Varela, J.A. Fernandez, C. Real, A. Carballeira, J.R. Aboa. Influence of the physicochemical characteristics of pollutants on their uptake in moss. *Atmospheric Environment*, Vol. 102, 2015, p. 130-135.

## ACHIEVEMENTS OF THE ICP VEGETATION IN 2018 AND FUTURE WORKPLAN (2019 – 2021)

Harmens, H.<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,  
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The ICP Vegetation is an international programme that reports on the effects of air pollutants on natural vegetation and crops. 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: i) Quantifying the risks to vegetation posed by ozone pollution and collating field-based evidence of ozone impacts; ii) The atmospheric deposition of heavy metals, nitrogen and persistent organic pollutants (POPs) to vegetation. The ICP Vegetation encourages outreach activities to other regions such as Asia, Africa and South America and has established an ICP Vegetation-Asia network.

At the 32<sup>nd</sup> Task Force Meeting we will report on the achievements of the ICP Vegetation in 2018, including:

- Further evidence of ozone impacts on vegetation, including developing regions, and interactions with nitrogen;
- Ozone risk assessments: new developments and additions to Scientific Background Documents A and B of the Modelling and Mapping Manual [1];
- Heavy metals, nitrogen and persistent organic pollutants (POPs): Progress with the report of 2015/2016 moss survey;
- Contributions to workplan items of the WGE and collaboration with the European Monitoring and Evaluation Programme (EMEP);
- Technical support provided to the revised EU National Emission Ceilings Directive (Directive 2016/2284).

We will also discuss the future workplan (2019 – 2021), including:

- Further outreach activities in developing countries;
- Evidence of ozone impacts on crops in developing countries;
- Large-scale risk assessment of ozone impacts in soil moisture limited areas (collaboration with EMEP/MSK-West);
- Preparations for the 2020 moss survey.

For further details, see our newly launched website <http://icpvegetation.ceh.ac.uk>

### **Acknowledgement:**

We thank the UK Department for Environment, Food and Rural Affairs (Defra, project AQ0846) for funding the ICP Vegetation Programme Coordination Centre. Further financial support was provided by the UNECE.

### **References:**

[1] <https://icpvegetation.ceh.ac.uk/get-involved/manuals/mapping-manual>



# **OZONE SESSIONS**





## SENSITIVITY OF MEDITERRANEAN MOUNTAIN TOP HERBACEOUS COMMUNITIES TO OZONE AND NITROGEN DEPOSITION

Ruiz-Checa, R., Bermejo, V., Elvira, S., García-Gómez, H., González-Fernández, I.,  
Alonso, R.

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The Sierra de Guadarrama mountain range, located north Madrid, in central Spain, includes highly valuable Mediterranean ecosystems following an altitude gradient, from evergreen deciduous forest at the foothills to perennial psicroxerophilous pastures at the highest altitudes. Some of these are protected under the Sierra de Guadarrama National Park and are home of various endemic and endangered vegetation species. Air pollution monitoring activities performed in this altitude gradient between Madrid and the mountain summits since 2004 show that ozone (O<sub>3</sub>) levels tend to increase with altitude and distance to the city (Alonso et al., 2009, VI Jornadas Científicas del Parque Natural de Peñalara; Elvira et al., 2016, Env. Monit. Assess. 188(10), 593). Three monitoring sites located at 2,262, 1,850, and 995 m a.s.l. show that the Sierra de Guadarrama ecosystems are chronically exposed to AOT40 values in excess of 26.6 ppm.h during the summer, when the vegetation is actively growing in mountain areas (Elvira et al., 2016). Furthermore, nitrogen deposition models also show that nitrogen deposition in mountain areas of Spain, including the Sierra de Guadarrama, may be exceeding empirical critical loads established for pasture, heathland or conifer forest ecosystems (García-Gómez et al., 2014, Sci. Tot. Env. 485-486, 450-460; García-Gómez et al., 2017, Ecosistemas 26(1), 55-65).

Air pollution risk assessments have been performed in the Sierra de Guadarrama using reference critical loads and levels developed within the Convention on Long-Range Transboundary Air Pollution. However, little is known about the actual sensitivity of the species to O<sub>3</sub> and N and their combination. In 2018 a new O<sub>3</sub> fumigation experiment was set up in open-top chambers to study the response of common Mediterranean perennial pasture species from mountain areas to O<sub>3</sub>: *Festuca curvifolia*, *Nardus stricta*, *Stipa giganteum*, *Agrostis castellana*, and one endangered endemic species: *Erodium paularense*. Plants were exposed to 0.5 x ambient, ambient, ambient + 10 ppb O<sub>3</sub> and ambient + 20 ppb O<sub>3</sub> concentrations between 8:00 and 16:00 local time over 2 months. Preliminary results show that *Festuca* and *Nardus* presented a trend towards a decreasing biomass growth with increasing O<sub>3</sub> exposure while *Stipa* and *Agrostis* were rather tolerant. Gas exchange measurements performed during the experiment found a trend of and O<sub>3</sub> effect on *Nardus* and *Agrostis*. Carbon and nitrogen content and C:N ratio showed increasing or decreasing trends depending on the species in *Stipa*, *Nardus*, *Agrostis* and *Erodium*. New analysis are being performed to study O<sub>3</sub> effects on other traits such as LMA, leaf stoichiometry and reproductive capacity. These results point to a complex pattern of species-specific responses showing that O<sub>3</sub> may be a relevant stress factor affecting the conservation of sensitive species in Mediterranean mountain top pasture communities. New experiments considering the interactions with nitrogen availability will be performed to confirm the preliminary results obtained in this study and eventually to develop critical loads and levels for risk assessment of effects in these areas.

With the support of: MITECO - Fundación Biodiversidad (<https://fundacion-biodiversidad.es/es>) and EDEN-Med projects (CGL2017-84687-C2-1-R)

## GROUND-LEVEL OZONE METRICS AND FOREST HEALTH IN LITHUANIA

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Tropospheric ozone (O<sub>3</sub>) is an important greenhouse gas, in the Northern Hemisphere, and the most harmful air pollutant for vegetation. Lithuania is representative of maritime to continental climate, no water limitation, and moderate O<sub>3</sub> pollution. The study discussed the trends of meteorological variables and O<sub>3</sub> and how these environmental conditions associate with tree health from 2001 onwards. The study aimed to assess the relationships between environmental conditions and forest-response indicators, namely crown defoliation and visible foliar O<sub>3</sub> injury of adult trees, under field conditions; to estimate trends in O<sub>3</sub> metrics and plant responses, and to assess the efficiency of PODY and AOT40 O<sub>3</sub> metrics in predicting O<sub>3</sub> injury, by a large-scale field investigation in Lithuania. For this study, 10 dominant tree species (*Acer platanoides*, *Alnus glutinosa*, *Alnus incana*, *Betula pendula*, *Betula pubescens*, *Fraxinus excelsior*, *Picea abies*, *Pinus sylvestris*, *Populus tremula*, *Quercus robur*) were assessed over the time period 2007-2017.

The study results showed that over this time period, mean O<sub>3</sub> concentrations (annual average of 30.6 ppb) were able to induce visible foliar O<sub>3</sub> injury, under local meteorological conditions. Between 2007 and 2014, surface O<sub>3</sub> annual mean (- 0.28 ppb decade<sup>-1</sup>) and AOT40 (- 2540 ppb.h decade<sup>-1</sup>) decreased, while POD0 increased (+ 0.40 mmol m<sup>-2</sup> decade<sup>-1</sup>) under a hotter (+ 0.27°C decade<sup>-1</sup>) and drier (rainfall, - 48 mm decade<sup>-1</sup>) climate. Between 2007 and 2014, crown defoliation decreased by 5.0% per decade while visible foliar O<sub>3</sub> injury increased by 0.17% per decade. Some species showed no visible foliar O<sub>3</sub> injury at all, whereas other species showed visible injury (< 0.5% of the leaf surface). Although the visible injuries were relatively low, *Sambucus racemosa* and *Alnus incana* were the most O<sub>3</sub>-sensitive shrub and tree species, respectively. The results suggest that moderate O<sub>3</sub> pollution (approximately 30 ppb as annual average) in Lithuania can affect forest vegetation, and, under the on-going climate change, the overall O<sub>3</sub> risk to forests remained elevated.

## OZONE AND NITROGEN EFFECTS ON FUNGAL WHEAT DISEASES

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The development of critical levels to conduct risk assessments of ozone effects on agricultural production has been primarily focused on impacts on yield and yield quality (Mills and Harmens, 2011). However, ozone effects on agricultural production and quality mediated by interactions with other stress factors or management practices such as reductions in fertilization efficiency (Bröberg et al., 2017, STotEnv 607-608, 876-880) or reduced water use efficiency (Wilkinson and Davis, 2009, Plant Cell Env., 32, 195-210) may be as important as direct effects on yield. Wheat pest and diseases have been estimated to reduce wheat yields in the range of 26-29% worldwide (Oerke, 2006, J. Agr. Sci., 144, 31-43), thus representing an important constraint to agricultural production in comparison with estimated ozone-induced yield reductions, in the range of 4-15% (Ainsworth, 2017, Plant J., 90, 886-897). However, little is known to quantify the potential interaction between these two factors. Ozone has been shown to interact with diseases infection and development, where the direction of the interaction (increase or decrease of disease incidence) depends on species-specific host-pest inter-relationship (Manning and Tiedemann, 1995, Env.Pol. 88, 219-245).

An experiment was developed to test the sensitivity of *Triticum aestivum* cv. Arthur Nick to combined ozone and N fertilization treatments. Wheat plants growing in 15 l pots were exposed to ozone in 12 Open Top Chambers (OTC) to each of 4 O<sub>3</sub> treatments: charcoal filtered air (FA), non-filtered air (NFA) reproducing ambient levels, non-filtered air supplemented with 10 nl l<sup>-1</sup> O<sub>3</sub> (NFA+) and non- filtered air supplemented with 20 nl l<sup>-1</sup> O<sub>3</sub> (NFA++). The plants were exposed to the different O<sub>3</sub> treatments from tillering growing stage until seed maturity. Four pots and two plants per pot per OTC received a nitrogen fertilization equivalent to 100 and 200 Kg N ha<sup>-1</sup> y<sup>-1</sup> in the form of NH<sub>4</sub>NO<sub>3</sub>. Different plant physiology and productivity variables were evaluated during the experiment, including photosynthesis and stomatal conductance measured with LiCOR 6400, chlorophyll content measured with SPAD, flag leaf N concentration, flag leaf infection by leaf rust, ear number and weight, seed number and weight, yield and harvest index.

Ozone exposure reduced leaf rust affection on flag leaves from FA to NFA+ but leaf rust tended to increase again under the highest O<sub>3</sub> exposure (NFA++). Nitrogen fertilization tended to increase leaf rust affection of wheat leaves but no interaction was found between the two factors. No direct effects of ozone or nitrogen were found on yield parameters but there are indications of a leaf-rust-mediated ozone effect on the harvest index, which tended to decrease. These are preliminary results that would need to be confirmed by targeted studies, where known disease strains are inoculated at different growing stages and disease progression is monitored intensively.

Further studies on ozone and crop diseases will be conducted in the coming years in the frame of the project OZOCAM, including ozone-disease interactions on horticultural crops of importance in the Mediterranean area. Project OZOCAM will bring together plant disease epidemiologists, plant breeders, air quality modelers and ozone effect experts and farmers to study ozone pollution-disease interactions and perform ozone risk assessments to agricultural production in the region of Madrid, in central Spain.

## AN O<sub>3</sub>-N-FACE SYSTEM FOR POPLAR PLANTATION ECOSYSTEM

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With the acceleration of industrialization and urbanization and the intensification of agriculture, surface ozone (O<sub>3</sub>) concentrations and atmospheric nitrogen (N) deposition fluxes have been increasing, which is a common environmental issue in most regions of China, further affecting the service functions of farmland and forest ecosystems surrounding the city. To clarify the ecological processes in response to elevated O<sub>3</sub> and N addition, an O<sub>3</sub>-N-FACE system for Poplar Plantation Ecosystem was built at suburb of Beijing, China, in 2017. There are two O<sub>3</sub> treatments (ambient air (AA), elevated O<sub>3</sub> with 50% elevation of AA (E-O<sub>3</sub>), two N deposition (N0, and 60 kg N/ha/y (N60)) in two Poplar clones. The size of each plot is 16m×16m, surrounded in 30m×30m, and 8 plots in total with four replicates in each O<sub>3</sub> and N treatment for each poplar clone. The objectives are: 1) to reveal the combined effects of enhanced N deposition and O<sub>3</sub> concentration on the key processes of carbon (C)-N coupling in forest ecosystems at soil, leaf, plant individual and stand scales; 2) to analyze the biological mechanism of the C-N coupling cycle and its complex response to enhanced N deposition and O<sub>3</sub> concentration; 3) to reveal the combined effect of N deposition and O<sub>3</sub> concentration on the key microbial functional groups of soil C-N conversion from aspects of the soil microbial community structure, functional succession and functional genes.

## MODELLING THE INFLUENCE OF SOIL MOISTURE ON OZONE DOSE UNDER WATER-LIMITED CLIMATIC CONDITIONS

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Field-based evidences show that soil moisture is currently one of the dominant drivers of ozone stomatal deposition to rainfed vegetation in water-limited regions of Europe such as the Mediterranean area (Alonso et al., 2008, *Env. Pol.*, 155, 473-480; Gerosa et al., 2009, *Env. Pol.*, 157, 1737-1744; González-Fernández et al., 2010, *Atmos. Env.*, 44, 2507-2517), as well as in other regions of Europe during dry years (Grünhage et al., 2012, *Env. Pol.*, 165, 147-157). Future climatic condition scenarios show that drought episodes may become more frequent in many areas of Europe (EEA, 2016, <https://www.eea.europa.eu/data-and-maps/figures/changes-in-summer-soil-moisture>), which will have further influence on ozone fluxes (Fuhrer et al., 2016, *Ecol. Evol.*, 6, 8785-8799). However, modelling soil moisture and its influence on ozone stomatal fluxes is still considered one of the challenges for applying flux-based ozone risk assessment methodologies at the European scale (Büker et al., 2012, *Atmos. Chem. Phys.*, 12, 5537-5562; Simpson et al., 2012, *Atmos. Chem. Phys.*, 12, 7825-7865; Simpson et al., 2018, EMEP Report 1/2018).

The EMEP MSC-W chemical transport model is one of the key tools for effect based ozone risk assessment methodologies applied within the Convention on Long-Range Transboundary Air Pollution, providing ozone stomatal fluxes to vegetation receptors at the European scale. The current version of the EMEP model (Simpson et al., 2012, 2018) includes the influence of soil moisture on dry deposition through a soil moisture index (SMI) dataset provided by the European Centre for Medium Range Weather Forecast (ECMWF) as part of the meteorological inputs to the model. The influence of SMI on stomatal conductance is modelled by using a default parameterization for all vegetation types. However, the suitability of the SMI and its parameterization for ozone flux based risk assessment at the field scale for different vegetation types has not been tested to date.

A joint ICP-Vegetation – EMEP collaborative exercise is being developed aiming at improving current flux-based ozone risk assessment applications for large scales (IAM), especially at soil moisture limited areas and other regions of Europe under future climate change scenarios. The EMEP MSC-W has provided modelled SMI data for comparison with site-specific soil moisture data. Six Mediterranean sites from Italy and Spain have been included at this stage, covering a range of land uses including forest (2 broadleaf evergreen and 1 deciduous sites), rainfed crop fields (3 sites) and grasslands (1 site). Soil moisture records at these sites go from about 6 months on annual crop fields up to more than 7 years in grassland and forest sites and up to 2 meters deep into the soil. Analyses will be presented with a view to testing the SMI index at these sites and discussing the next steps of the exercise.

## CAN DEFICIT IRRIGATION MITIGATE IMPACTS OF OZONE ON WHEAT YIELD?

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The ozone flux into leaves is dependent on stomatal conductance, which varies with environmental conditions, plant development and soil moisture. In crops, it might be possible to reduce ozone uptake during the ozone-sensitive flowering and grain/seed filling period by reducing soil moisture via reduced irrigation. In this study, an ozone-sensitive Kenyan wheat variety ('Korongo') was exposed to low (peak concentration of approximately 30 ppb) and elevated ozone concentrations (peak concentration of 80 ppb) in solardomes for 4 weeks during the flowering and grain-filling period. In addition, three watering regimes were applied: well-watered (WW - aim to maintain soil moisture >20%), frequent deficit irrigation (FD – daily watering reduced by approximately 30% compared to well-watered, mean daytime soil moisture 58% of WW) and infrequent deficit irrigation (ID - watering reduced by approximately 20% compared to well-watered by severely reducing the amount of watering every other day, mean soil moisture 53% of WW).

Whilst elevated ozone significantly reduced wheat yield (both total grain yield and 1000-grain weight), reduced watering did not significantly mitigate the reduction of total grain yield (i.e. there was no significant ozone x watering interaction). Despite a reduction in the ozone stomatal flux into the flag leaf of wheat (POD<sub>6</sub>SPEC) at reduced irrigation, the reduction was not large enough to cause a significant reduction in wheat yield compared to the well-watered treatment. However, reduced watering (both FD and ID) significantly stimulated individual grain weight. There was a tendency (but statistically not significant) towards a stimulation of wheat yield at reduced irrigation compared to well-watered plants. At elevated ozone, reduced watering (FD and ID) delayed the onset of ozone-induced leaf injury and reduction in photosynthesis of the flag leaf, hence delaying crop senescence and maintaining greenness for longer during the grain-filling period.

The experiment should be replicated in the field where it will be easier to control daily fluctuations in soil moisture compared to plants grown in pots. In a future climate, reduced watering might actually stimulate wheat yield when soil moisture is maintained at field capacity.

### **Acknowledgement**

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## DOSE-RESPONSE RELATIONSHIPS FOR AFRICAN CROPS

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Ozone pollution is a growing problem in Africa, and effects of ozone on subsistence agriculture crops are largely unknown. We exposed varieties of several crops to ozone in solardomes in 2017 and 2018, including bean, cowpea, finger millet, pearl millet, peanut, amaranth, sorghum and wheat. Peak ozone concentrations of approximately 30 to 110 ppb were used and ozone-induced visible leaf injury was observed on all species, including the leafy vegetable crop ‘amaranth’ (Figure 1).

The DO<sub>3</sub>SE model was parameterised for bean, cowpea, finger millet, pearl millet, amaranth, sorghum and Kenyan wheat, based on stomatal conductance measurements made during the growing season. Cowpea and bean showed a decrease in total yield with increasing ozone flux, due to a combination of a reduction in the number of peas per pod and the weight of individual beans. The varieties of cowpea with the highest stomatal conductance were more sensitive to ozone than those with lower stomatal conductance, however,  $g_{\max}$  did not explain sensitivity to ozone for bean. For African wheat, the reduction in total yield was due to a reduction in individual grain size. Flux-effect relationships for Kenyan wheat (using the Mediterranean wheat parameterisation) fit with those of the Mapping Manual, indicating that Kenyan wheat is as sensitive to ozone as European wheat.



**Figure 1:** Ozone-induced visible leaf injury on a) amaranth and b) peanut.

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## NUTRITIONAL AVAILABILITY CHANGES OZONE DOSE-RESPONSE RELATIONSHIPS IN POPLARS

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Assessing ozone (O<sub>3</sub>) risk to vegetation is crucial for informing policy making. The availability of nitrogen (N) and phosphorus (P) could influence photosynthesis and growth. However, our knowledge of plant responses to O<sub>3</sub> under various nutritional conditions is still limited. In this study, a sensitive poplar clone (Oxford) was subject to two N levels (N0, 0 kg N ha<sup>-1</sup>; N80, 80 kg N ha<sup>-1</sup>), three P levels (P0, 0 kg P ha<sup>-1</sup>; P40, 40 kg P ha<sup>-1</sup>; P80, 80 kg P ha<sup>-1</sup>) and three levels of O<sub>3</sub> exposure (ambient concentration, AA; 1.5×AA; 2.0×AA) for a whole growing season in an O<sub>3</sub> free air controlled exposure (FACE) facility in Florence, Italy (43° 48' 59" N, 11° 12' 01" E, 55 m a.s.l.), which is the first O<sub>3</sub> FACE facility in Mediterranean Europe. Ozone-induced biomass decline was greater at high N supply, while P alleviated such biomass losses, but not under high N supply. Ozone-induced loss of net photosynthetic rate was mitigated by N in medium O<sub>3</sub> exposure (1.5×AA). However, such a mitigation effect was not observed in the higher O<sub>3</sub> level (2.0×AA). Nitrogen addition exacerbated O<sub>3</sub>-induced increase of dark respiration rate suggesting an increased respiratory carbon loss in the presence of O<sub>3</sub> and N. This may result in a further reduction of the net carbon gain for poplars exposed to O<sub>3</sub>.



## OZONE GARDEN: AN EXPERIMENT TO EXAMINE THE HARMFUL EFFECTS OF URBAN AIR POLLUTION ON ECOSYSTEMS IN SOUTH CHINA

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Hong Kong is one of the most densely populated cities in the world, with millions of people living and working in close proximity to busy roads with severe air pollution. Among various air pollutants, surface ozone produced in situ from anthropogenic precursor gases is of particular concern due to its considerable harm to both human and ecosystem health.

We established a free-air experimental garden to monitor, quantify and understand the mechanisms of ozone damage on plants. In this experimental field, dubbed the “ozone garden”, we grew various genotypes of the French dwarf bean *Phaseolous vulgaris* with different ozone sensitivities as a bioindicator of the local air pollution impacts on ecosystems. Such a free-air ozone garden has been built at multiple locations in the US and Europe, but will be the first of its kind in South China. The data obtained from this garden are essential to not only demonstrate the impacts of air pollution on plants under locally specific environmental conditions, but also be used to derive important parameters of ecophysiology and biometeorology that can be used to build a regionally relevant ecosystem model for predictive purposes.

The ozone garden consists of a 10 m<sup>2</sup> of open space located at Chinese University of Hong Kong in “Gene garden” near CW Chu College. Twelve pots of resistant and sensitive genotype of *P. vulgaris* beans developed by Burkey et al., (2005) are grown in July 2018. We followed the growing protocol according to ICP Vegetation (2018). Two pots are grown indoor as a control. We monitored the ozone concentration and meteorology at the experiment site, gas exchange measurements and ozone visual damage analysis are also performed.

In this talk, we will present the challenges, observations and statistic analysis from the ozone garden biomonitoring project. Pilot study shows that sensitive beans developed around two weeks quicker than resistant genotypes but their survival rate and number of living leaves are lower. Sensitive beans produce more flowers than resistant beans but fewer pods are developed and the weight of the seeds is lighter than the resistant genotype.

The ozone garden project is still in continuation. The set of locally relevant ecophysiological and biometeorological data obtained will help identify particularly vulnerable periods and cultivars. The data will help to validate a computational ecosystem model developed in-house, namely, the Terrestrial Ecosystem Model in R (TEMIR), for simulating climate-chemistry-land interactions and predicting air quality under climate and land cover changes, with incorporation of more realistic and advanced treatment of urban morphology, plant physiology and biogeochemistry, and aerosol-radiation-cloud interactions.

## CLOSING THE GLOBAL OZONE YIELD GAP: QUANTIFICATION AND COBENEFITS FOR MULTISTRESS TOLERANCE.

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Whilst it is recognised that rapid breeding programmes will have an important role to play in adaptations of crops to a changing climate, the selection of traits for ozone tolerance is currently not included in such programmes. Furthermore, many crop yield models do not yet include the impacts of current or predicted future ozone pollution. The aim of our study was to build a case for improving crop yields by closing the ozone-induced yield gap. For the first time, we investigate how the spatial variation and severity of ground-level ozone effects on the yield of 4 staple food crops compares with other abiotic stresses on a global scale. Based on stomatal uptake of ozone (mean of 2010-2012), we estimate that the global yield was reduced annually by 12.4%, 7.1%, 6.1% and 4.4% for soybean, wheat, maize and rice respectively, with a total of 227 Tg of lost production due to ozone. Our modelling shows that the highest ozone-induced production losses for soybean were in North and South America whilst for wheat they were in India and China, for rice in parts of India, Bangladesh, China and Indonesia, and for maize in China and the United States. We show that the impact of ozone on crop yield is within the range of concern for other crop stressors. Also, areas with the highest production losses due to ozone were often at risk of high losses from pests and diseases, heat stress and to a lesser extent aridity and nutrient stress. In a solution-focussed analysis of these results, we define a crop ideotype with multi-stress tolerance (including ozone) and describe how ozone effects could be included in crop breeding programmes. We also discuss changes in crop management approaches that could be applied to reduce ozone impacts in the shorter term. This global study shows that ozone is an important crop stress, causing yield reductions of staple food crops and comparing in importance with other key stresses. We recommend increased attention to the benefits that could be gained by addressing the ozone yield gap.

For further information, see:

Mills, G., Sharps, K., Simpson, D., Pleijel, H., Frei, M., Burkey, K., Emberson, L., Uddling, J., Broberg, M., Feng, Z., Kobayashi, K. & Agrawal, M. (2018) Closing the global ozone yield gap: Quantification and co-benefits for multi-stress tolerance. *Global Change Biology*, **24**: 4869 – 4893. <https://doi.org/10.1111/gcb.14381>

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## OZONE IMPACT ON WHEAT IN EUROPE, ASIA AND NORTH AMERICA – A COMPARISON

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Data from experiments where field-grown wheat was exposed to ozone were collated in order to compare the effects in Europe, Asia and North America using dose-response regression. In addition to grain yield, average grain mass and harvest index were included to reflect the influence of ozone on the crop growth pattern. Also, these three variables were the most commonly reported in the experiments. In order to include as many experiments as possible, daytime average ozone concentration was used as the ozone exposure index, but AOT40, estimated from average ozone concentrations, was also used to compare the performance of the two exposure metrics. The response to ozone differed significantly between the continents only for grain yield when using AOT40 as the exposure index. North American wheat was less sensitive than European and Asian that responded similarly. The variation in responses across all three continents was smallest for harvest index, followed by grain mass and grain yield. The highly consistent effect on harvest index shows that not only effects on biomass accumulation, but also on the partitioning of biomass, are important for the ozone-induced grain yield loss in wheat. In general, AOT40 performed somewhat better than daytime average ozone. The average duration of daily ozone exposure was longer in European experiments compared to North American and Asian. It cannot be excluded that this contributed to the indicated higher ozone sensitivity in European wheat in relation to North American. The main conclusions from this study are that on the average the response of wheat to ozone was lower for the older North American experiments and that the ozone response of the growth pattern reflected by grain mass and harvest index did not differ between continents.

## ESTIMATION OF OZONE INDUCED YIELD LOSSES OF WHEAT AND POTATO IN SWITZERLAND USING THE DO<sub>3</sub>SE MODEL

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Elevated O<sub>3</sub> concentrations during the crop growing season can cause significant yield reductions. To assess the potential risk, plant stomatal O<sub>3</sub> uptake rates can be calculated with deposition models. The resulting phytotoxic ozone dose (POD) values over a flux threshold allow the estimation of O<sub>3</sub> induced yield losses. More than ten years ago, POD<sub>6</sub> had been modelled for wheat and grassland in Switzerland at a 2x2 km resolution with ODEM. However, that model was not further developed and specific dose response functions (DRF) are lacking. Therefore, we performed new POD calculations using the DO<sub>3</sub>SE model, for which necessary input data, model parameterizations and DRFs are available to estimate O<sub>3</sub> induced wheat and potato yield losses. Both, wheat and potato are among the most valuable and most widespread grown crops in Switzerland.

Because of major regional and annual differences in rainfall patterns as well as O<sub>3</sub> levels, we aimed to compare O<sub>3</sub> uptake rates and potential yield losses under different climatic conditions at different places in Switzerland.

For this purpose, O<sub>3</sub> uptake was modelled at 18 sites using measured O<sub>3</sub> concentrations combined with meteorological data from the closest weather station. The sites are located in the main crop growing areas or are situated in regions representing specific climatic conditions and O<sub>3</sub> patterns. The model was parameterized as proposed in the Mapping Manual for wheat and potato with some adjustments for Switzerland. The timing of wheat mid-anthesis was specified by a temperature sum of 1100°C days after 1 January, whereas for potatoes a common date of tuber initiation was derived from field trial data.

Wheat POD<sub>6</sub>SPEC regularly exceeded critical levels (CL) in various regions, especially in humid years where soil moisture is only seldom limiting stomatal uptake. In contrast, dryer conditions generally led to lower POD<sub>6</sub>SPEC values. Model runs showed that O<sub>3</sub> induced yield reductions vary considerably between years and regions (min = 0%, max = 14.5%). POD<sub>6</sub>SPEC values for potatoes barely ever exceeded the CL of 3.8 mmol/m<sup>2</sup> PLA. Only in the south of Switzerland, where O<sub>3</sub> concentrations are comparably high and growing seasons with large amounts of rainfall are common, CL was regularly exceeded.

O<sub>3</sub> risk for wheat is highest in non-limiting soil water conditions, which depend on seasonal rainfall patterns and irrigation. Present day irrigated wheat area is negligible but might rise with increasing temperature and more pronounced drought events.

## MODELLING OZONE FLUXES WITH THE EMEP MSC-W MODEL - STATUS AND FUTURE DEVELOPMENT

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The EMEP MSC-W model (Simpson et al., 2007, 2012) has been used to calculate ozone fluxes for almost two decades now (e.g. Emberson et al., 2000, 2001, Mills et al., 2018), with the DO3SE model, EMEP model, and Mapping Manual formulations being developed in parallel to a large extent. There is a continuing need to update the EMEP model in several areas though, including use of the latest Mapping Manual settings, and reconsideration of various soil-water issues. On a global scale, many new ecosystem types (e.g. Tropical forests, savannah) need to be handled by the model. On all scales, the possibility of incorporating new methods such as photosynthesis-based gs-models or satellite data need to be considered.

This talk will briefly review the history and recent developments of the EMEP model, and discuss possible future developments. The aim is to encourage further cooperation with ICP Vegetation, and to outline some of the challenges involved in both fine and large-scale ozone flux modelling.

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# **MOSS SURVEY SESSIONS**





# MOSS AS A BIOMONITOR OF THE ATMOSPHERIC DEPOSITION OF MICROPLASTICS

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Microplastics, which are plastic particles < 5 mm, have been found throughout the environment; however, few studies have focused on their transport via atmospheric deposition. Bryophytes are widely used as biomonitors for the atmospheric deposition of trace elements, persistent organic pollutants and particulate matter, and may potentially be used to monitor the atmospheric deposition of microplastics.

During May 2018, *Hylocomium splendens* was collected from three ICP Waters lake catchments (Figure 1), following survey protocols recommended by ICP Vegetation. In the laboratory, moss samples were dried, digested and vacuum filtered onto glass fiber filters (Whatman 1.2  $\mu\text{m}$  pore sized). Each filter was visually inspected for the presence of microfibers to evaluate the use of moss as a biomonitor.

Microfibers were found in all moss samples, with an average of 23 mf g<sup>-1</sup> across sites. Average atmospheric deposition across the three lake catchments was estimated to be >45,000 mf/m<sup>2</sup>. Moss may be a useful biomonitor of the atmospheric deposition of microfibers and could potentially be incorporated into 2020 ICP Vegetation survey.



Figure 1: Location of moss sampling sites, i.e., three lake catchments monitored under ICP Waters.

## Acknowledgements

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## MOSSES AS BIOMONITORS OF TRACE ELEMENTS IN GREECE

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Mosses can be used for biomonitoring purposes. They are able to absorb and retain elements from wet and dry deposition. They have no rooting system, unlike the higher plants, and the elements are absorbed entirely by their surface (Harmens et al., 2008; Berg and Steinnes, 1997). There are a lot of advantages using moss method, such as the simplicity of the sample collection and the ease of the analysis. Also sampling can occur in remote areas easier and with lower costs than the sampling using the traditional methods.

Ninety-five samples of *Hypnum cupressiforme* Hedw. were collected in the region of Northern Greece during the end of summer 2016. Samples were collected from different altitudes (30 to 1450 m above the sea level). During the sampling all the requirements of the Protocol of the European Survey ICP Vegetation were strictly followed (Harmens et al, 2008). After sampling, mosses were analysed to the content of heavy metals using NAA. The chemical composition database of the moss samples was further used for the application of source apportionment by Positive Matrix Factorization (PMF), and specifically by the EPA PMF 5.0 model. In total 30 species were used for source apportionment (Na, Mg, Al, Si, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, As, Br, Rb, Sr, Mo, Cd, Sb, Cs, Ba, La, Ce, Tb, Hf, Ta and Th).

Finally, a high sampling density was achieved, providing information for the elemental deposition from the atmosphere to terrestrial systems over the North Greece. The source apportionment results revealed contribution from five sources: Soil Dust, Aged Sea Salt, Vehicular Traffic, Heavy Oil Combustion and Mining Activities, with Soil Dust displaying the highest contribution to the measured metal concentrations among all other sources.

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# ATMOSPHERIC DEPOSITION STUDY OF MAJOR AND TRACE ELEMENTS IN GEORGIA BASED ON MOSS ANALYSIS

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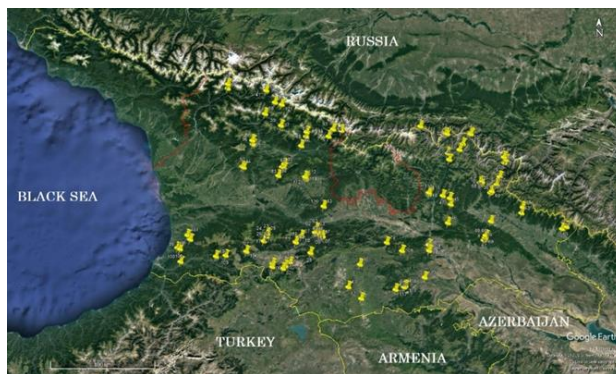
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The results of the 2014-2017 moss surveys of the levels of major and trace elements in Georgia are reported. The mosses *Pleurozium schreberi*, *Hypnum cupressiforme*, and *Hylocomium splendens* were used for this study. Overall, during these surveys, 122 moss samples were collected nearly over the whole territory of the country (Figure). In 2017 several samples were taken in the vicinity of the Chiatura mine complex, which is one of the largest manganese reserve in the world, and the other ones were taken near the Kazreti gold and copper mine.



**Figure.** The sampling map (yellow dots are the sampling sites)

The sampling was performed in compliance with the UNECE ICP Vegetation guidelines [1]. The determination of concentrations of 39 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Sr, Zr, Mo, Pb, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Hf, Ta, W, Au, Th, and U) in moss samples was carried out at the reactor IBR-2 of FLNP JINR by means of epithermal neutron activation analysis (ENAA), while concentrations of Cu, Cd and Pb were obtained by atomic absorption spectroscopy (AAS). Results obtained in this study were subjected to multivariate statistical analysis as in our previous publication [2]. Factor analysis revealed crust, industrial, and marine components. A comparison of median values of elements with corresponding data from the other Europe countries indicates that the concentrations of heavy metals in mosses collected in Georgia are mostly higher. For data visualization GIS technologies were used.

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# CHITIN ADSORPTION IN ENVIRONMENTAL MONITORING: NOT AN ALTERNATIVE TO MOSS MONITORING BUT A METHOD PROVIDING (LOTS OF) BONUS MATERIAL/INFORMATION

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We could show recently that chitin adsorption of environmental analytes allows to do something not feasible with studies of atmospheric deposition regardless which solid phase (moss, artificial filters) is used to intercept the latter: by chitin adsorption, establishment of chemical equilibria can be evaluated at water-sediment interfaces like in beaches, wells or at the bottom of some (natural or artificial) lake. Once the local relationship (in thermodynamic terms: water→sediment phase transfer energy of cations, complexes and oxoanions) is known for a multitude of elements co-existing at the site and analyzed in one run, **non-equilibrium effects** are readily identified. These non-equilibrium effects can be due to either

- input (“pollution”) via air or water from “above”,
- biological uptake of some trace element (e.g., Ni involved in methanogenesis, Mo in nitrate reduction) or
- (often biogenic) precipitation in the sediment or
- processing of entities which could/did form insoluble salts/mineral phases before (microbial reduction of sulfate dissolving minerals like coelestine or barite).

The focus rests with comparing adsorption from water ( $\text{pH} \geq 3$ ) and from sediment or other solid phases including (dead) wood, the process being completed in 10 min. Recent (2016 – 18) field work done especially in Mongolia (North, around Lake KhovsGöl) was combined with laboratory studies to understand chitin-metal ion or –metal complex interactions scaled to different chemical properties to some detail which in turn permits to evaluate equilibria in chitin adsorption from various phases connected to each other by matter exchange. In this setup, partition coefficients  $\text{chitin;sediment/chitin;water}$  for divalent ions normally behave accordingly to the Irving-Williams empirical rule of complex stabilities ( $\text{M}^{2+}$ , bidentate ligands: alkaline earths except of Be, Mg; Mn...Zn, Cd) and (also) those for trivalent ions (REEs, Cr, Al, Y, etc.) can be correlated to the inverse ion radius, such as  $\log \beta$  or  $\log P = a/r + b$ . Apart from effects from different ion radii in di- and trivalent Eu, Fe, tri- or tetravalent V, Ce, b depends on local redox potential. Then, of course, “deviations” of partition of Eu or Fe from expectations for trivalent ions of given radius (94.7 and 64 pm, respectively) can be attributed to thermo- (Fe) or photochemical (Eu, given presence of appropriate reaction partners) reduction.

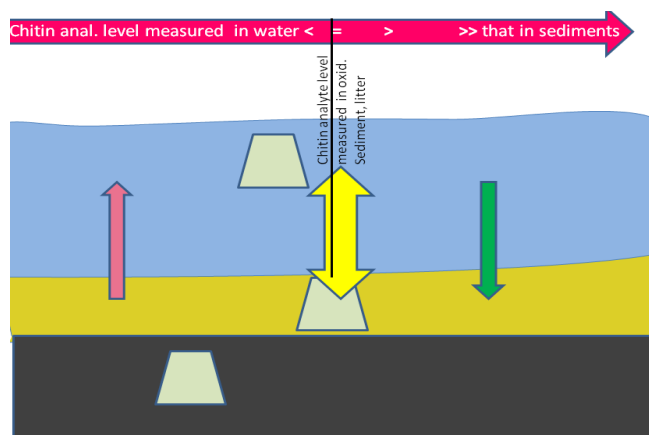


Fig.1a, 1b: Pathway of transport of analytes from both water and sediment to chitin. Equilibrium does not imply that concentrations on chitin plates exposed to either phase are equal, on the contrary.

After scaling by correlation with inverse ion radius, “exceptions” concerning elements undergoing either redox reactions in ambient conditions (Fe, Ce, V) or even catalyzing photochemical oxidations of organics, such as Eu(III) and uranium ( $\text{UO}_2^{2+}$ ) are identified, besides of pollution-related non-equilibrium (which is unlikely in rather abundant elements like Ba, Mn, Zn, Cr(III)). As a rule, both Eu(III) and  $\text{UO}_2^{2+}$  or their carbonatocomplexes are sufficiently abundant in natural waters including those from ombrotrophic bogs to be detected and quantified by chitin adsorption:  $< 1 \text{ nM}$  will do; the same threshold level holds for many other elements. After violet illumination Eu(III) will break C-H bonds to afford  $\text{Eu}^{2+}$  seen in electrochemical studies (cyclic voltammetry). When the sediment is somewhat oxidizing (i.e. sulfate, Fe(III) being present), Eu in sediment undergoes back-oxidation and is thus accumulated. This process stops and becomes inverted when ascending methane does reduce either potential reaction partner of  $\text{Eu}^{2+}$  in the sediment column. Thus the partition coefficient of Eu vs. other REEs, other trivalent M gives direct information on onset of methanogenesis even when  $\text{CH}_4$  still is intercepted in top layers of sediment rather than leaking to the atmosphere. Due to its redox-and photochemistry Eu does differ in partition from other REEs substantially; the latter (La, Ce, Yb, [Nd]) are used for scaling besides of Al, trivalent d-block metals.

Ligand effects on retention of metals to chitin are small, while chitin can be dissolved by adding Li salts in carboxamide- or lactam solvents (DMF, DMA, N-methyl pyrrolidinone), enabling both simple workup of environmental samples and electrochemical studies of both metal binding capacity to chitin strands (about  $40 \mu\text{M/g}$ ) and ligand-exchange in solutions kept at different redox potentials. In turn, given one knows the landcover, it is possible to understand partition of metals on chitin vs. the ion radius for trivalent ions and thus infer “deviations” by reduction, oxidation (Cr, Ce, V) or photochemistry (Eu).

Moss analysis has its big merits but more can be understood when combining studies on isolated chitin (from crab peeling not living arthropods in terms of an active biomonitoring!) with it, especially when considering ecotones. Perhaps chitin was used to extract essential trace elements from sediment rather than forming carapaces and mouthpieces for half of the time it does exist in Earth’s biosphere..., that is, the first 500 mio. years?

# HEAVY METAL DEPOSITION MONITORING IN A MOUNTAIN AREA WITH LOCAL EMITTERS: A CASE STUDY FROM BULGARIA

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The current monitoring study was applied in a mountain region (Bulgaria) with 3 background and 2 impacted sites in the range of altitudes from 425 m to 1430 m. Ten elements (Al, As, Cd, Cr, Cu, Fe, Ni, Pb, V and Zn) were analysed in mosses (*Hypnum cupressiforme* and *Homalothecium lutescens*) by ICP-OES and ICP-MS. Samples were taken in a 5-year period: in 2014, 2015 and 2018 in order to reveal the frequency of sampling in mountain region with local emission sources. The results showed that mosses respond rapidly to decreasing/increasing atmospheric pollution and annual sampling is suggested in territories which were not studied before, in mountain regions, especially those with local emission sources in order to assess correctly tendencies and average pollution levels. Significant variance was found between the 3 sampling periods for 4 sites ( $R^2$  between 0.941 and 0.703;  $p < 0.05$ ). The results reflected that green parts of mosses represent the last two or three years of growth and consequently the pollutant levels for that time period. Based on the above, if the research aims to assess variance in pollutant levels, sampling should be carried out in 3 years.

Keywords: *Hypnum cupressiforme*, *Homalothecium lutescens*, mountain region, Bulgaria

ATMOSPHERIC DEPOSITION TRENDS IN BULGARIA  
OVER A 20-YEAR PERIOD OF PARTICIPATION  
IN THE EUROPEAN MOSS SURVEY PROGRAMME (1995/6-2015/6)

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In 2015, for the fifth consecutive time Bulgaria participated in the moss survey carried out in the framework of the UNECE ICP Vegetation. Over the years, different moss species were collected in the country – predominantly *Hypnum cupressiforme*, but also *Pleurozium schreberi*, *Pseudoscleropodium purum*, *Rhytidium rugosum*, and *Abietinella abietina*. Throughout the survey, the areas studied and the number of samples, as well as the sampling networks and density, were inconsistent. All samples were collected in accordance with the ICP Vegetation sampling protocol, which justifies the comparison of the results from the surveys. However, optimization of the sampling network is necessary. An overview of the available data was made to reveal temporal and spacial deposition trends for the investigated metals and metalloids during the 20-year period of participation. In 2010, an observation was made that, in general, the concentrations of atmospheric pollutants deposited onto the moss biomonitors in Bulgaria had decreased by about 30%. The most recent moss survey data does not show continuation of that trend.

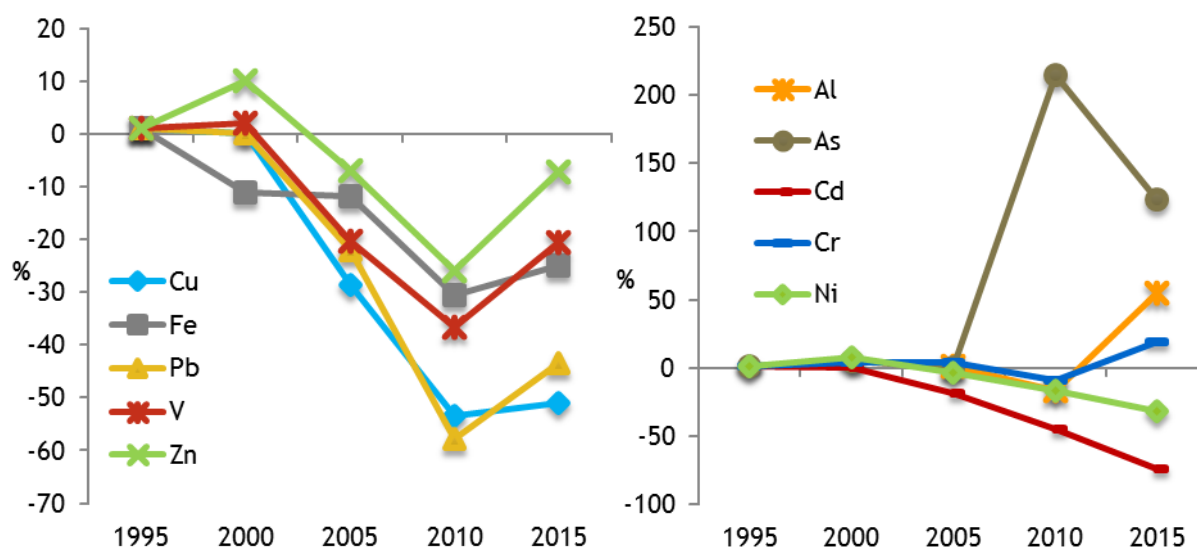


Fig. 1. Magnitude of change relative to the median concentrations in 1995 (Bulgaria).  
Number of sites over the years: 1995 (N=215), 2000 (N=217), 2005 (N=213), 2010 (N=129),  
2015 (N=115)



# NITROGEN DEPOSITION IN ROMANIA. LEVELS DETERMINED WITHIN ICP VEGETATION AND ICP FORESTS

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As a part of the moss biomonitoring survey, aiming to estimate the heavy metals pollution in the framework of ICP Vegetation, beginning with 2005 nitrogen concentrations were also measured and considered as important for evaluation the trends of nitrogen deposition in Europe. In Romania, the campaign from 2015/2016 was the first for which nitrogen was included in moss monitoring.

The mean concentration of nitrogen in mosses collected in Romania was more than 1,5% and represent a high value, according to the results reported in 2005 and 2010, when comparable concentrations were registered only for Slovakia and Slovenia. For all the other 13 countries, including Bulgaria, the content of nitrogen was lower than 1,5% (Harmens et al, 2013).

In the framework of ICP Forests, nitrogen depositions were monitored in Romania since 1998, by measuring the concentrations of oxidised and reduced nitrogen in bulk deposition. For four level II plots, for the period 2013-2015, the mean nitrogen depositions were low (<4 kg ha<sup>-1</sup>a<sup>-1</sup>) and medium (between 4 and 8 kg ha<sup>-1</sup>a<sup>-1</sup>). The highest value (12,8 kg ha<sup>-1</sup>a<sup>-1</sup>) was determined at Ștefănești, a plot located close to Bucarest, the capital of the country.

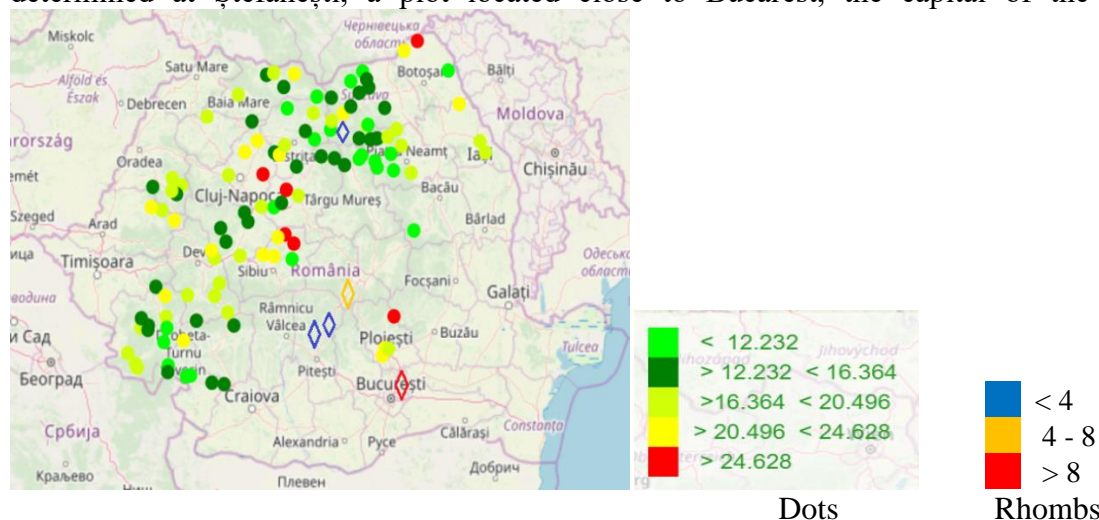


Figure 1. Concentrations of nitrogen in mosses ( $\mu\text{g g}^{-1}$ ) for 43 ICP Vegetation plots and nitrogen mean deposition for the period 2013-2015 at 5 level II ICP Forests plots

Further researches and measurements for the same plots would contribute to reveal the correlation between nitrogen concentrations in mosses and nitrogen deposition levels in Romania.



## ANTHROPOGENIC VS. GEOGENIC ORIGIN OF ELEMENTS IN SWISS MOSS SAMPLES BETWEEN 1995 AND 2015

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Switzerland started participating in the moss monitoring program of the ICP vegetation 1990 and has since then collected samples every five years up to 2015. The sample sites have been distributed as equally as possible over the whole country while taking the different biogeographical regions into account. During the whole study period it was aimed to collect data for as many elements as possible, resulting in a large dataset of concentration data, allowing the analysis of development over time using over 70 consequently sampled sites.

To approximate the source of metal deposition as geogenic or anthropogenic, lithogenic elements (Ti, Zr, Al, Rb) are often used as reference elements. Aluminium especially is an often-chosen reference element as a proxy for geogenic origin as it is expected not to be emitted by anthropogenic activity. On the other hand, Sb can be used as a reference element for anthropogenic activity as it is mostly not being of geogenic origin.

In this present study we used our moss samples from 1995 and 2015 to find out, if there has been a change in the main origin for some pollutants from anthropogenic sources to geogenic origin or vice versa. Thus, we compared the concentration of Al or Sb respectively to concentrations of some metals of interest in order to estimate how well these concentrations correlate. The preliminary regression analyses show that the pollution sources for Pb, As, Tl and V seem to have changed from anthropogenic sources in 1995 to be mainly of geogenic origin in the samples of 2015.

For Pb this change is further supported by the finding, that the Pb isotope ratios of 2015 moss samples are much closer to the natural Swiss Pb isotope ratios than the Pb isotope ratios found in moss samples collected in 1995. These results show that the reduction of Pb deposition originating from anthropogenic activity is measurable with different methodological approaches and highlight the importance of the efforts for emission reduction taken in the past.

In contrast to Pb, As, Tl and V, many other metals analysed do not show a change in the pollution origin.

## THE METAL ATMOSPHERIC DEPOSITION IN ALBANIA (2010 – 2015 MOSS SURVEY)

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Air quality in Albania was assessed by moss biomonitoring. *Hypnum cupressiforme* (Hedw) sps. was collected during August and September 2015 and October 2010 at 55 and 48 sampling sites more or less homogeneously distributed over the entire territory. Sampling and sample preparation was done by following the European moss network manual (Frontasyeva and Harmens, 2015). The spatial distribution and temporal trend of metal atmospheric deposition was studied through the determination of twenty elements determined by ICP-AES, AAS (As and Cd) and CV AAS (Hg) analysis. The concentration data show significant differences in spatial distribution of the elements derived from different emission sources. The distribution trend of trace metals was studied by comparing the data of 2015 moss survey with similar study of 2010. Compared to 2010, the 2015 data of Cr, Ni, Cu, As, Zn and Na were increased, while Ba, K, Mg and Hg moss data were declined. Other elements remained mostly at the same level. The differences in the deposition fluxes of the pollutants in different time or between different monitoring sites may be due to the differences on their atmospheric concentrations and their scavenging ratios from atmosphere to terrestrial ecosystems, and may partly affected by the variations on meteorology, such as dispersion and atmospheric conditions. From this point of view, to avoid the effect of meteorological variations on deposition rates of pollutants during wet and dry deposition, the sampling should be performed on similar atmospheric conditions. High levels of Al, Fe, Cr, Ni and V were found in Albania on 2010 (Lazo et al. 2018, Harmens et al. 2015). The contamination levels evaluated by the contamination factor (CF) of each element provided similar results for 2015 and 2010 moss surveys. Factor analysis (FA) was applied to identify the possible sources of elements in moss samples. Five dominant factors were extracted that represent long-range and local atmospheric transport of wind blowing soil dust particles (F1); local emission from chromium industry and of wind blowing mineral dust particles (F2); anthropogenic sources of traffic emission and wind blowing fine mineral dust particles derived from geogenic factors (F3); natural transport from marine environment (F4); and long-range atmospheric deposition (F5). These approaches reflect the important role of bioindicators and moss biomonitoring that in combination with data analysis and the inventory of emission sources are important tools for interpreting moss concentration data and to assess air quality of the studied area.

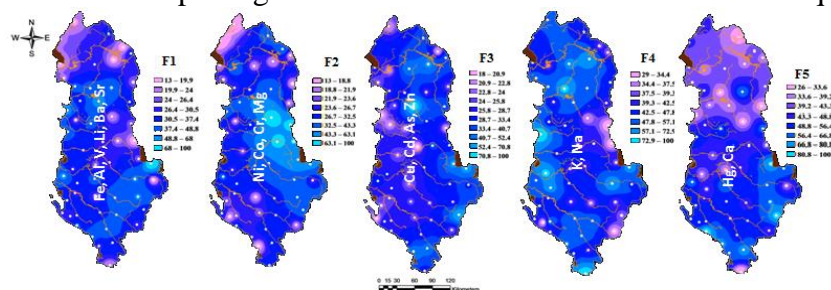


Fig. 1 Maps of Factor loads

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MOSSES AND LICHENS AS BIOACCUMULATORS OF AIRBORNE ELEMENTS:  
WHAT DO WE REALLY MEASURE? IN ADDITION, ARE THESE BIOMONITORS  
SUITABLE IN ENVIRONMENTAL FORENSICS?

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Mosses and lichens are efficient bioaccumulators of airborne elements and hence are widely used as biomonitors of atmospheric pollution. Owing to the lack of cuticle and stomata, as well as to their large surface:volume ratio, mosses and lichens may readily accumulate airborne chemical elements, mostly as trapped particles onto their surface or as ions bound extracellularly to cell wall sites. There are, however, some issues that need careful evaluation. First of all the identification of the moss/lichen species to be sampled requires a good degree of systematic expertise, otherwise the variability of the results may be greater than the variability in the phenomenon to be investigated, and all tentative species-specific coefficients to convert biological data into concentration/deposition data may be useless.

Second, the information that can be obtained from these organisms is not always much the same and sometimes is not even very clear. Not only contrasting results may emerge between lichens and mosses, but also within different species of the same organism, and sometimes also from a single species. Standardization procedure, especially in the expression of the results, are thus critically important.

Third, speaking of atmospheric pollution, ideally, a good biomonitor should have a linear correlation between the environmental concentration of a pollutant to be observed and the content accumulated inside the organism. However, there is enough evidence that mosses and lichens do reflect bulk (wet and dry) atmospheric deposition rather than average atmospheric concentrations over a certain time span.

Last, biomonitoring studies are now increasingly used in environmental forensics to trace the footprint of polluting sources and to depict different pollution zones serving as basis for case-control epidemiological studies. However, this requires that the overall uncertainty of the whole biomonitoring study is evaluated and clearly put forward, thing that is seldom done.

NATIVE AND TRANSPLANTED AQUATIC MOSS (*PLATYHYPNIDIUM  
RIPARIOIDES*) FOR ASSESSING LONG-TERM METAL(LOID) IMPACTS FROM  
ABANDONED MINES

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Aquatic mosses are efficient accumulators of trace metals and ideal indicators of contamination in freshwater ecosystems. *Platyhypnidium riparioides* is among the most common species in biomonitoring studies and it has been proven effective in assessing river quality. In this study, *P. riparioides* was used to quantitatively assess the impact from potentially toxic elements in the river Merse, flowing in the area of *Colline Metallifere* (Tuscany, Central Italy) a major Italian mining district for centuries known for its large pyrite (FeS<sub>2</sub>) deposits and veins bearing Ag, Cu, Pb, Zn and other ores. By comparing data from different sampling campaigns carried out with native moss specimens collected at 8 sites along the river in 2004, 2009 and 2015, this research aimed at assessing temporal trends in trace element contamination and, indirectly, the efficacy of the adopted water management strategies. To offset the lack of information in the most polluted stretches of the stream near the mine sites, due to the absence of autochthonous specimens, the moss bag technique was implemented in a small-scale investigation of calibrated sampling density and intensity which was aimed at source characterization.

Native moss samples showed statistically significant higher concentrations of As, Cd, Hg, Co, Cu and Zn near abandoned mining sites in the upper course of the river than in the lower course. Cu was the metal showing the greatest variability (range: 17.9-843 µg g<sup>-1</sup>) with the lowest Cu concentration in the lowland sampling sites. Temporal trends traced by native moss specimens collected at the same sampling sites in the watercourse highlighted a decrease in contamination (e.g. up to 50% for As) as a consequence of clean-up technologies put in place at a mining site to minimize Acid Mine Drainage production.

In May 2015 the moss bags deployed for 3 weeks in the stretch of the stream within the mining district showed limited As and Cu contamination from the mine tributary to the investigated riverine system. Rather, huge masses of slags and reddish roasting (waste heaps) accumulated on the left river banks since more than 100 years ago, were found to still represent a major source of contamination for As, Cd, Cu, Fe, Pb, Zn. These wastes are subject to erosion and, over time, may be flushed to the stream by storm runoff causing an intermittent emission into the river systems

The results of this study demonstrated the benefits of combining native and transplanted specimens of *Platyhypnidium riparioides* to identify hotspots of bioavailable elements that are likely to cause negative impacts to biological receptors of the river and thus prompt for an urgent completion of the environmental reclamation to reduce toxic metal loads to the aquatic and riparian environment.

## PROPER IMPUTATION OF SUB-LIMIT AND MISSING VALUES IN BIOMONITORING STUDIES

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Three mechanisms of missingness in data exist: Missing completely at random (MCAR), missing at random (MAR) and not missing at random. While MCAR data are almost never encountered in environmental datasets, MCAR and MAR are rather common and pose a considerable challenge for the data analysis and results interpretation. Random missingness of the data is caused by a factor irrelevant to the measured variables, e.g. accidental destruction of the sample or equipment malfunction and are commonly expressed as Not Available (NA) data. Conversely, non-random missingness is closely related to the variable of interest, in the case of biomonitoring studies NMAR data are caused by the sub-limit concentration of a chemical in the assessed matrix and are usually expressed as zeros.

Since multivariate methods such as Principal component analysis (PCA) are the most common ways of statistical analysis of the biomonitoring data, NA values are of great concern – their presence violates the assumptions of the analyses. Prevalent – yet inappropriate – way of dealing with MAR data is a deletion, either listwise (deleting all the rows with NA value) or pairwise (utilising correlation matrix). Both methods have their drawbacks – the former discards a portion of the data acquired, and the latter expects the data to be MCAR which is rarely the case. Substituting the NA value by the variable median is also sometimes applied, yet it is still far from ideal and only suitable when relatively few values are missing in the dataset. Two types of zeros exist in the quantitative compositional environmental datasets: seldom encountered structural (real) zeros and rounded zeros which are NMAR – they represent an unknown yet non-zero value below the detection limit of the measurement apparatus. The latter are commonly substituted by an arbitrarily chosen small sub-limit value, typically 65% of the detection limit, this approach, however, leads to spurious correlations between the variables with such zeros.

In either case of missingness, it has to be taken into consideration that the biomonitoring data are compositional. Hence, not only an appropriate transformation has to be applied prior to the analyses, but the compositional nature of the data has to be reflected in the imputation mechanism chosen. For the MAR data, the appropriate way of imputation seems to be a k-nearest neighbours (defined via the Aitchison distance) algorithm as proposed by Hron et al. (2010). For the sub-limit values, the possible imputation methods are additive log-ratio expectation-maximisation (alr-EM) algorithm or isometric log-ratio expectation-maximisation (ilr-EM) algorithm (Martín Fernández et al., 2012). The former assumes at least one variable with no zeros (which may present a problem) and utilises alr coordinates which are, however, not isometric and invariant to permutation. Both problems can be taken care of by using the ilr-EM algorithm which is, thus, hereby recommended.

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# AIR POLLUTION STILL LIMITS EPIPHYTIC RECOLONIZATION: HEAVY METALS AND ECOPHYSIOLOGICAL PARAMETERS IN THREATENED FOREST MACROLICHENS OF CENTRAL EUROPE

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Air pollution and intensive forest management may heavily affect epiphytic organisms and limit habitat recolonization. The macrolichen *Lobaria pulmonaria* (L.) Hoffm was used to assess to what extent recent atmospheric pollution limits the survival of threatened forest epiphytes in Central Europe, by means of a transplant experiment (May 2016 – May 2017) of thalli saved from logged trees. The species was selected being an endangered forest lichen very sensitive to air pollution. It is considered as a "flag" indicator species of forest ecosystems with long ecological continuity worthy of conservation, often used as a model species, red-listed and legally protected in several European countries. The experiment was run in the Western Carpathians (Slovakia) where the species was spread over the country at the beginning of 20<sup>th</sup> century, while currently it is confined to remote areas of mountain ranges, due to air pollution and forest management. Forest sites (chiefly dominated by *Fagus*) were carefully selected with regard to the occurrence in the past (SW Slovakia) and to prevent the contact with local populations of *L. pulmonaria* thus limiting or excluding at all the potential erosion of local genetic diversity. The bioaccumulation of trace elements (Al, As, Cd, Cr, Cu, Mn, Ni, Pb, S, Sb, Zn) and the photosynthetic efficiency (expressed as chlorophyll *a* fluorescence emission) were used as respective proxies of the intensity of pollution and the vitality of lichen transplants before and after the exposure on the bark of *Fagus* trunks. Exposed to Control (EC) ratios were used to interpret the accumulation of heavy metals after the exposure period. A strong accumulation (EC>2) was locally reported for As, Mn, Pb, Sb and Zn. In such cases, lichen thalli also showed a partial alteration of their vitality. Relevant depositions of Sb were attributed to traffic from the main urban areas and Mn from local mining activities and geological outcrops. In general, a higher pollution load index – PLI (about 2.4) calculated accounting all investigated elements characterised those sites where the model species also showed a worse vitality, whereas a lower PLI (about 1.5) corresponded to the thalli with higher vitality. In this latter case, transplants developed new propagules and attached by themselves to the substrate. Using *L. pulmonaria* as a model species, the study suggested atmospheric pollution as one of the factors limiting the recolonization of threatened forest macrolichens in historically previously colonized habitats. The role of microclimatic features and other abiotic factors is currently under investigation.

## SPATIAL DISTRIBUTION OF HEAVY METAL POLLUTION IN MOSS (*PLEUROZIUM SCHREBERI*) AND IN SOIL O HORIZON IN LATVIA

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Various sorbents, including moss and soil, are used to mapping the spatial distribution of atmospheric pollution. Moss typically describes the dispersal of pollution over the past three years, while soil – in a prolonged period. At the same time, using both sorbents allow to assess changes in pollution over a long period of time. To determine changes of concentrations of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, Zn and V) and spatial distribution of heavy metals in the whole territory of Latvia (101 plots in pine forest type) we are using *Pleurozium schreberi* moss and soil O horizon. Moss and soil sampling was realized in 2015. In the moss, the order of the median concentration of heavy metals was following: Fe > Zn > Cu > Pb > V > Ni > Cr > Cd, but in soil O horizon: Fe > Zn > Pb > Cu > V > Ni > Cr > Cd (Table 1). The only element whose location differs in this ranking was Pb, which indicates that currently the environmental atmospheric pollution level in Latvia has decreased significantly (Tabors et al., 2017), while historical pollution in the soil has remained. The overall trends of our study show that higher concentrations of metals in moss and soil are in the western part of Latvia, relating to cross-border pollution transfer from Western Europe and Liepāja city (local metallurgical, boiler house source), and at the Lithuanian border due to impact of Naujoji Akmenė cement factory and Mažeikiai oil refinery.

Table 1. Median values of heavy metals' (mg/kg) concentrations in *Pleurozium schreberi* moss and in soil O horizon in Latvia. \* Pearson Correlation is significant at the  $p < 0.05$  level

	V	Cr	Ni	Cd	Pb	Zn	Cu	Fe
Moss	0.49	0.33	0.48	0.10	1.26	33.13	5.17	133.02
Soil	4.18	1.86	2.24	0.41	21.78	41.00	4.52	1213.64
Pearson Correlation	0.48*	0.20	0.49*	0.34*	0.09	0.38*	0.46*	0.13

When calculating Pearson's correlation between the metals' concentrations in the moss and the soil O horizon, no significant correlation for the Pb, Fe and Cr concentrations between soil and moss (Table 1) were found. Changes of concentrations of Pb and Cr are associated with a significant decrease in pollution level in Latvia and the good sorption capacity of these elements in soil. The content of Fe in the soil O horizon relates significantly with the soil composition. There is a relatively close correlation between the other elements, where the highest correlation is between V and Ni concentrations in moss and soil. It is determined by the long-running Mažeikiai oil refinery, from which pollution was distributed in a broad area of Latvia. This study showed that at the same time moss and soils can be used as sorbents, not only to clarify the spatial distribution of pollution in the atmosphere, but also to determine temporal changes.

### Reference:

Tabors G., Nikodemus O., Dobkeviča L., Kļaviņa L., Ajanoviča A., Viligurs K., Krūze I. 2017. Assessment of atmospheric pollution with heavy metals and nitrogen using *Pleurozium schreberi* mosses as bioindicator in Latvia: spatial and temporal aspects. *Environmental and Experimental Biology*. 15: 143–150.



# MOSS TRACE ELEMENT CONTENTS AND SPATIAL DISTRIBUTION PECULIARITIES IN ARMENIA

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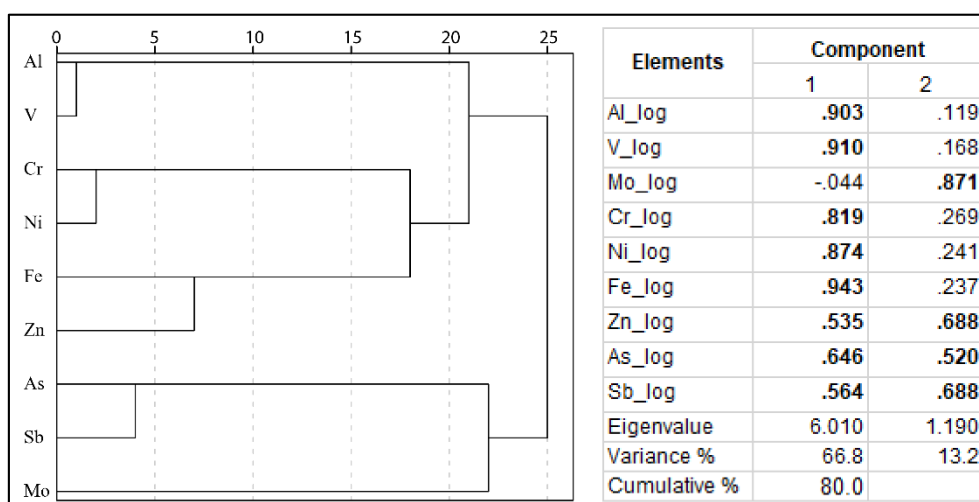
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Moss biomonitoring technique was applied to study the spatial patterns of chemical elements atmospheric deposition in the territory of the Republic of Armenia. Totally, 76 moss samples were collected and the contents of Al, As, Cr, Fe, Ni, Sb, V, Zn and Mo were determined by instrumental epithermal neutron activation analysis. In order to study the relationship between Al, As, Cr, Fe, Ni, Sb, V, Zn and Mo and identify their possible sources principal component analysis (PCA) and cluster analysis (CA) performed. To illustrate spatial distribution pattern of studied elements colour maps were created by ArcGIS 10.3.

The results showed that according to the Shapiro-Wilk test Al, Cr, Ni, V, Sb and Fe has lognormal whereas As, Zn and Mo abnormal distribution. Fig.1 illustrate the results of CA and PCA. It is evident that in the case of PCA two groups have been identified. First group included Al, V, Cr, Ni and Fe with high loading and Zn, As and Sb with moderate loading. In the case of second group high loading observed for Mo and moderate loading for Zn, As and Sb. The presence of Zn, As and Sb in both groups indicates the presence of different sources of origin of these elements. The result of CA verified PCA. The detailed inspection of spatial distribution maps of studied elements showed that Al, Cr, Fe, Ni, V and Sb has similar patterns of spatial distribution. The high values of As and Zn have been identified in the northern part of Armenia where a copper smelter is operating. The spatial distribution of Mo differs from other studied elements. The high values (>95%) of Mo have been identified in the southern part of Armenia where the Zangezur copper-molybdenum combine is operating and near the capital city of Yerevan where the “Plant of Pure Iron” is operating on the base of molybdenum concentrate (containing 50% of molybdenum) received from Kajaran.

Overall, the combination of multivariate statistical methods and geospatial mapping techniques allows to reveal the spatial pattern of studied elements contents in mosses and identify their potential sources.



**Fig.1.** CA (left) and factor loadings for varimax rotated PCA (right) of studied elements in moss samples.



## IS IT POSSIBLE TO PREDICT HEAVY METAL ATMOSPHERIC DEPOSITION AND WHEN IT COULD BE USEFUL?

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An approach to predict heavy metals atmospheric deposition by statistical models and machine learning algorithms is presented. The source of the field deposition data is ICP Vegetation Data Management System (DMS). The source of the satellite images is Google Earth Engine platform (GEE). The data from GEE together with sampling data from DMS are used to train deep neural models. Then trained neural net together with only data from GEE is used to predict atmospheric deposition of some heavy metals. More information can be found in [1].

A connection between heavy metal atmospheric deposition and indexes from satellite images for some metals at some regions are presented. Some statistical models and results of modelling are considered. Perspectives and potentialities of the suggested approach to atmospheric deposition prediction are shown.

1. Alexander Uzhinskiy, Gennady Ososkov, Pavel Goncharov, Marina Frontasyeva, Combining satellite imagery and machine learning to predict atmospheric heavy metal contamination // Proceedings of the 8th International Conference Distributed Computing and Grid-technologies in Science and Education, CEUR Workshop Proceedings, Vol-2267, ISSN 1613-0073

## MOBILE APPLICATION FOR ICP VEGETATION MOSS SAMPLING SITES MANAGEMENT

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A mobile application that allows filling in required by the UNECE ICP Vegetation manual information about sampling sites is presented. The application automatically sets longitude and latitude of the sampling site, controls correctness of the input data and allows capturing photos of the moss samples. Application integrated with the DMS (moss.jinr.ru) and all information about sampling sites can be imported to the DMS.

We demonstrate:

- How to work with the application.
- How to import information about sampling sites.
- How get xls-file with sampling sites from DMS to fill in concentrations.
- How to work with DMS to get statistics, analysis and maps.

## MOSS BIOMONITORING IN RUSSIA: OVERVIEW OF THE 2015/2016 MOSS SURVEY

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The moss biomonitoring technique was applied to air pollution studies in the Russian Federation in the framework of the UNECE ICP Vegetation Programme. In the 2011–2015 period, samples of the terrestrial mosses *Pleurozium Shreberi* and *Hylocomium splendens* were collected at the evenly distributed 150 sites over the territory of the Moscovskaya, Tverskaya, Leningradskaya, Braynskaya and Ryazanskaya regions in accordance with the sampling strategy of the European moss survey protocol. Two complementary analytical techniques: epithermal neutron activation analysis and atomic absorption spectrometry (Pb, Cd, Cu) were applied to determine up to 40 elements. Multivariate statistical analysis (factor analysis) was used to identify and characterize different pollution sources. Distributional maps of atmospheric deposition of the determined elements were created to point out the areas most affected by air pollution and to associate these data with the known sources of contamination. Median values of the elements were compared with those obtained in the previous surveys and for the other regions in Russia. The dominant anthropogenic impact of air pollutants of heavy metals and other element-pollutants is explained by industrial activity and transport.

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## MOSS BIOMONITORING OF ATMOSPHERIC DEPOSITION STUDY OF MINOR AND TRACE ELEMENTS IN THE REPUBLIC OF MOLDOVA

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In the framework of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops (UNECE ICP Vegetation), the moss biomonitoring technique was applied for the first time to air pollution studies in the Republic of Moldova. In May 2015, 33 samples of the terrestrial moss samples were collected over the whole territory of the country. Using neutron activation analysis and atomic absorption spectrometry, a total of 41 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, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, W, Pb, Th, and U) were determined. Distributional maps for all elements were prepared to point out the regions most affected by anthropogenic activities. Three different indices used to quantify the degree of contamination pointed out a moderate to severe industrial pollution localized around main urban and industrial centres: the municipalities of Chisinau and Balti. Analysis of the spatial distribution of the first three principal factors points towards thermoelectric plants as main factor, while the use of leaded gasoline and industrial activity accounts for secondary and tertiary sources of airborne contamination.

## **OZONE POSTERS**



## OZONE IMPACTS ON INSECTS

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Present mean ambient tropospheric ozone (O<sub>3</sub>) concentrations are from two to five times higher than in the last century. In cities, the annual O<sub>3</sub> mean concentrations increased by 0.16 ppb per year on average, across the globe over the time period 1995–2014. Ground-level O<sub>3</sub> is a serious air pollutant which induces oxidative stress in plants with a negative impact on the nutritional quality of leaves for insects. Moreover, reactive O<sub>3</sub> molecules can modify or degrade volatile organic compounds (VOCs), and this may impair the communication between plants and their pollinators by affecting the olfactory system of pollinators or imbedding insects to trace host plants.

Pollination by insects is a key ecosystem service not only in natural but also in managed terrestrial ecosystems. Bees are among the most important pollinators. Global cultivation of insect-pollinated crops has expanded since the 1960s, leading to about a 300% increase in the demand for pollination services. In 2005, the global economic value of pollination service was estimated to be about 189 billion Euro or 9.5% of global food production value, and, in 2009, the global economic value of insect pollination is suggested to be 153 billion Euro per year.

Recent studies showed complex impact of global change and O<sub>3</sub> on plants and insects. Nevertheless, there is just a little knowledge about the O<sub>3</sub> impacts on the interaction between plants and pollinators and other types of insects. The aim of this study is to review the effect of O<sub>3</sub> on the relationships between plants and insects (including herbivores and pollinators) and on insect behaviour and other services based on the current literature.

# OZONE IMPACTS ON RESPIRATION AND PHOTOSYNTHESIS RATES IN THREE CONTRASTING FOREST ECOSYSTEMS

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Dry deposition is the dominant sink for tropospheric ozone and removal rates by vegetated surfaces are several times higher than bare ground. Ozone is a powerful phytotoxin and uptake through the stomata leads to oxidative stress, impairing many physiological processes. This damage reduces photosynthesis and carbon assimilation, induces early senescence and disrupts stomatal functioning. However, the net effect of these various impacts on plant health and growth, and on stomatal control are not well understood. We apply the FORCAsT (FORest Canopy-Atmosphere Transfer) one-dimensional canopy model to investigate the effects of ozone uptake on canopy stomatal conductance, evaporative fluxes and photosynthesis. We implement three widely-used photosynthesis and stomatal conductance models (Jarvis, Ball-Woodrow-Berry and Medlyn) within the FORCAsT framework, and evaluate the ability of the model to reproduce observed evapo-transpiration and Gross Primary Productivity (GPP) at three evergreen forest sites with differing reported sensitivity to ozone: a Holm oak (*Q. ilex*) forest at Castelporziano Estate, Rome; a Ponderosa pine (*P. ponderosa*) forest at Blodgett Forest, California; and a boreal forest, dominated by Scots pine (*P. sylvestris*), at Hyytiälä, Finland. All three sites contribute continuous measurements of plant physiological parameters such as canopy-top latent heat flux and Net Ecosystem Exchange (NEE) to the FLUXNET network, and have observations of ozone concentrations for a number of years. We include species-specific ozone dose-response functions for each physiological model and determine the impact of cumulative ozone damage on physiological processes for a range of assumed ozone threshold values and under different soil water conditions.



## PROJECT ELEMENTAL: OZONE FLUXES IN MEDITERRANEAN VEGETATION

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Tropospheric ozone ( $O_3$ ) is a pollutant and a greenhouse gas affecting human health, ecosystems services and food security. In plants, ozone exposure impairs  $CO_2$  assimilation reducing C sequestration, causes leaf injury, reductions in plant growth and yield, alters food nutrient properties, biomass partitioning and plant water cycle, and eventually may affect biodiversity by changing species composition in natural plant communities.

The so-called flux approach, which considers the  $O_3$  absorbed by plants stomata, is the methodology used to estimate impact on vegetation (e.g crop yields, forest productivity). In Europe, risk assessment is carried out through a modelling approach. EMEP model estimates the relative risk to vegetation using  $DO_3SE$  (Deposition of  $O_3$  for Stomatal Exchange), a dry deposition model designed to estimate total and stomatal  $O_3$  flux for selected land-cover types and plant species. Mediterranean drought prone ecosystems are the most challenging in Europe for adequate  $O_3$  flux modelling, due to important dependence of stomatal conductance to water stress.  $O_3$  fluxes in-situ measurements are still very scarce, and  $O_3$  deposition models have rarely been validated for Mediterranean conditions.

Eddy covariance (EC) flux towers are ideal platforms to perform simultaneously direct measurements of  $CO_2$ ,  $H_2O$  and  $O_3$  flux, thereby allowing to quantify  $O_3$  deposition, to analyze the processes governing  $O_3$  deposition onto vegetation, and to validate  $O_3$  flux models. The overall objective of the project is to use EC flux towers in combination with other experimental methods to quantify and analyze  $O_3$  deposition and assess standard model estimates of  $O_3$  deposition for 4 types of Mediterranean ecosystems of high relevance: Aleppo Pine Forest, Olive Plantation, Citrus Orchard, Holm Oak dehesa (tree + grass system). Continuous EC measurements of  $O_3$  fluxes will be performed during a full phenological year for all studied ecosystems. In addition, subcanopy EC measurements  $O_3$  fluxes will be used to quantify separately the  $O_3$  uptake by tree canopy and by understory/grass layers. The partitioning between stomatal and non-stomatal component of ozone deposition will also be addressed, as well as its temporal variation and its dependence onto abiotic factors and management of understory vegetation. Leaf scale measurements of  $CO_2$  and  $H_2O$  fluxes will be carried out under various environmental conditions and plant phenological stages to parametrize the  $DO_3SE$  model for both Citrus Orchard and Pine forest. The  $DO_3SE$  model will be validated against direct EC  $O_3$  flux measurements, which is of great relevance for the studied Mediterranean ecosystems. The results of the project are expected to contribute to better understand the main factors driving  $O_3$  deposition under Mediterranean conditions, and to have an important impact improving  $O_3$  flux modelling for Mediterranean ecosystems.

## DNA INTEGRITY AND ECOPHYSIOLOGICAL RESPONSES OF SPANISH POPULATIONS OF *ULMUS GLABRA* TO INCREASING OZONE LEVELS

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Wych elm (*Ulmus glabra* Hudson) is a deciduous tree with a wide distribution in the Eurosiberian region, from the Ural Mountains to the Mediterranean region. The most meridional populations, in the Mediterranean area, are fragmented in mountain areas adapted to unique geographical conditions representative of remaining Eurosiberian climate conditions in an area surrounded by Mediterranean climate. These small relict populations of Eurosiberian species in Mediterranean mountain areas can act as sentinel of global change, which includes not only climate change, but also other impacts of human activities such as those of air pollution. Moreover, the scattered distribution, small population size and impact of human activities, can increase the fragmentation of populations along with genetic erosion, increasing the susceptibility to stochastic, genetic, and demographic events.

Wych elm is present in the Guadarrama mountain range in central Spain in small populations with diminishing number of individuals. In this area, high O<sub>3</sub> concentrations have been reported. Besides climate and anthropogenic interventions, O<sub>3</sub> could be an additional stress factor that might be affecting plant physiology, reducing plant vigour and health. Also the oxidative stress caused by O<sub>3</sub> could increase the DNA damage in plants cells. An experiment was developed to test the sensitivity of *Ulmus glabra* to ozone. Wych elm 4-year old seedlings originated from a natural population growing in the Guadarrama mountain range, were exposed in Open Top Chambers to 4 O<sub>3</sub> treatments: charcoal filtered air (FA), non-filtered air (NFA) reproducing ambient levels, non-filtered air supplemented with 20 nl l<sup>-1</sup> O<sub>3</sub> (NFA+) and non- filtered air supplemented with 40 nl l<sup>-1</sup> O<sub>3</sub> (NFA++). The plants were exposed to the different O<sub>3</sub> treatments during the spring of 4 consecutive years. In spring 2018, during the 4<sup>th</sup> year of O<sub>3</sub> exposure, O<sub>3</sub> effects on the DNA integrity were evaluated and the correlation with eco-physiological responses was explored. To test the DNA integrity, the Single Cell Gel Electrophoresis (SCGE), also known as Comet Assay, was adapted to work with plant cells following the methodology developed by Kuzminsky et al. (2016). Chlorophyll content measured with SPAD, photosynthesis and stomatal conductance measured with Li-COR 6400, leaf morphological characteristics and branch growth were also evaluated.

The main result, obtained with SCGE, was that after only 1 month of O<sub>3</sub> exposure, control protoplast samples from FA and NFA treatments showed undamaged nucleoids characterized by low tail moment values, confirming that the protoplast isolation procedure did not affect the DNA integrity. However, the values of mean tail moment significantly increased ( $p < 0.01$ ) with increasing levels of O<sub>3</sub> in NFA+ and NFA++ samples, also showing significant increases in tail length and tail intensity. Relationships with ecophysiological responses and implications for risk assessment will be discussed.

**References:** Kuzminsky et al. (2016). Frontiers in Plant Science 7: article 1168.

**ASSESSMENT OF TWO TROPICAL GRASSLAND PLANTS (*PANICUM MAXIMUM*  
AND *CENCHRUS CILIARIS*) TO FUTURISTIC ELEVATED OZONE  
CONCENTRATIONS**

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Tropospheric ozone (O<sub>3</sub>) is a secondary air pollutant and a greenhouse gas harmful to all ecosystems. Being a phytotoxic gas, its increasing surface level concentrations have great concern in many regions of the world. Since last few decades, O<sub>3</sub> concentrations have been increasing due to enormous generation of its precursor gases. The peak concentration of tropospheric O<sub>3</sub> has gone down in North America and Europe but increasing in Asia (Cooper et al., 2014). It's harmful effects have been widely studied on cultivated plants, but grassland species of tropical region are not assessed. Therefore, the present study was conducted on two tropical grassland species i.e. *Panicum maximum* Jacq. (Guinea grass) and *Cenchrus ciliaris* (buffel grass) growing luxuriantly in Indo-Gangetic plain of Indian sub-continent under futuristic O<sub>3</sub> levels using open top chamber. Both grasses have high forage quality and commonly occur in many region of Indian grassland (*Dichanthium- Cenchrus-Lasiurus* grassland). Plants were assessed based on their growth, biomass accumulation and selected biochemical parameters at 50 and 100 day after transplantation. The O<sub>3</sub> treatments were ambient (mean concentration of 32.7 ppb) and elevated (mean concentration of 63.1 ppb) ozone given for 9 h daily (8.00 to 5.00) for nearly 4 months during June to September, 2016. Early leaf visible injuries were observed in *P. maximum* and in *C. ciliaris* showed late visible injuries. Significant reduction were observed in total chlorophyll, carotenoids, total phenolics, protein, no. of green leaves, no. of tillers, shoot and root length, leaf area ratio and total biomass in both species under elevated O<sub>3</sub> treatment. Significant increases in malondialdehyde (MDA), ascorbic acid (AsA), thiol and proline were found in *P. maximum* while decrease in AsA and thiol content in *C. ciliaris*. Typical decrease in AsA and increase in thiol and proline content showed significant role in detoxifying O<sub>3</sub> effects in *C. ciliaris*. Based on PCA results, It can be conclude that AsA scavenged O<sub>3</sub> effectively in *C. ciliaris* causing lower reduction total biomass, while no direct association of AsA and total biomass in *P. maximum* was observed. Therefore the present study concludes that *P. maximum* was affected more negatively compared to *C. ciliaris* under futuristic O<sub>3</sub> concentration.

**Key words:** Ozone, grass, growth, biomass, AsA, plant response, sensitivity.

# TIME SERIES (1998-2015) OF OZONE FLUX ON FOREST IN RHINELAND PALATINATE (GERMANY)

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POD<sub>Y</sub> is often calculated with the DO<sub>3</sub>SE model, which includes species-specific parameterizations for the environmental response of stomatal conductance. However, the effect of soil water content (SWC) on stomatal flux is often ignored.

In the present study the estimation of POD<sub>1</sub> is studied for the forest tree species (Norway spruce (*Picea abies*) and Beech (*Fagus sylvatica*)), investigated on five sites across Rhineland Palatinate (Germany) from 1998 to 2015 with active Ozone measurements. The investigation includes in regard to soil water influence on Ozone flux the five different, realized soil water approaches (PAW, SWPlin, SWPexp, LWPnss and LWPss) of the DO<sub>3</sub>SE-model.

The results suggest that soil water has a dominant effect on the leaf conductivity and couldn't be neglected by the calculation of ozone flux to assess the potential by O<sub>3</sub> to forest trees.

The effect of the five soil water model approaches in DO<sub>3</sub>SE and suggestions for their application or further development regarding their exactness are discussed.

POD<sub>Y</sub> (Y=1) calculated with all soil water approaches exceed the Critical Level in all years, for all considered tree species on the five level II plots in Rhineland-Palatinate.

**Keywords:** Time series of Ozone flux, Soil Water Models, DO<sub>3</sub>SE model, Exceedance of Critical Level,

# MODELLING OZONE UPTAKE BY URBAN AND PERI-URBAN FOREST: A CASE STUDY IN THE METROPOLITAN CITY OF ROME, ITALY

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Green Infrastructure (GI) in urban areas deliver a wide range of regulating Ecosystem Services (ES) (Manes et al., 2016; Marando et al., 2019). In particular, urban and peri-urban forests significantly contribute to air quality improvement by removing harmful air pollutants such as tropospheric ozone (O<sub>3</sub>) (Manes et al., 2012). In order to quantify such important ES in different contexts, a reliable estimation of gas exchanges between vegetation and atmosphere is needed. In this study, the process-based model “Growth of Trees is Limited by Water” (GOTILWA+), was used to model the O<sub>3</sub> stomatal uptake at canopy level in two *Quercus ilex* stands in the Metropolitan City of Rome, namely an urban forest (Villa Ada, VA) and a peri-urban one (Castelporziano Presidential Estate, CP), during the years 2013 – 2014 (Fusaro et al., 2018). GOTILWA+ was chosen because of its capacity to estimate the influence that climate, tree stand structure, and management practices have on forest growth and gas exchanges. Site-specific seasonal FO<sub>3</sub> trend showed that the urban and peri-urban forests are subjected and adapted to different environmental conditions (Fusaro et al. 2015), resulting in a different seasonal contribution to O<sub>3</sub> removal. In particular, in CP FO<sub>3</sub> was limited by drought during late summer and fall, while in VA fluxes were lower in spring, when canopy conductance (G<sub>c</sub>) was negatively affected by the higher air temperature and VPD of the urban site (Fusaro et al., 2018). Under similar O<sub>3</sub> concentrations between sites, irrigation practices in the urban forest sustained higher G<sub>c</sub> in VA during late summer 2013 and fall 2014, thus determining higher FO<sub>3</sub>. Considering the demand of regulating ES as air quality improvement in our cities, it appears necessary to set up appropriate management practice of urban forests, in order to increase the provisioning of this important regulating ES. Furthermore, our study outlines the need of a reliable estimate of O<sub>3</sub> uptake at the local scale, through site-specific model parameterization, that could enhance the capability to manage and prioritize intervention on key green infrastructure as urban forests.

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# EVIDENCE OF IMPACTS OF OZONE ON ECOSYSTEM SERVICES OF GRASSLANDS

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Ozone pollution can directly or indirectly cause impacts on many ecological processes that underpin ecosystem services. Over recent years we have performed many experimental studies on the impacts of ozone on grassland vegetation in solardomes. Here we collate datasets from these to provide evidence for ozone impacts on ecosystem services provided by grasslands.

The ecosystem services included in this overview are ‘supporting’, ‘provisioning’, ‘regulating’ and ‘cultural’. Presented evidence includes:

- *Impacts of ozone on flower numbers and timing (cultural and regulating services).* Our results show that several iconic species show a strong decline in flower number with increasing ozone concentration and flux, including harebell (*Campanula rotundifolia*). These results have recently been used to establish critical levels for ozone in Europe. Timing of maximum flowering was significantly advanced by ozone in *Lotus corniculatus*.
- *Above- and below-ground biomass (supporting and regulating services).* We have shown that ozone can reduce whole plant photosynthesis, and in addition, following early leaf senescence carbon allocation can be altered to maintain above-ground biomass at the expense of roots.
- *Litter quantity and quality (supporting services).* Ozone has been shown to alter the chemical composition of plant material, including the timing, quantity and quality of litter. This can subsequently affect nutrient cycling and other soil processes.
- *Water cycling (supporting services).* In addition to alterations in stomatal responses to environmental stimuli following ozone exposure we have shown changes in the water-holding capacity of soils, linked to changes in root biomass.

In addition, impacts on provisioning services are considered using effects of ozone on pasture quality and quantity. A case study of how this could affect lamb production in the UK is presented. This showed that modest increases in ozone concentration could have large impacts on lamb production in regions where lamb numbers are high, due to the negative impact on pasture quality.

## **Acknowledgement**

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# QUANTIFYING THE IMPACT OF PRESENT-DAY AND FUTURE TROPOSPHERIC OZONE ON CROP PRODUCTIVITY AT GLOBAL AND REGIONAL SCALE USING JULES-CROP

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Tropospheric ozone (O<sub>3</sub>) is the third most important anthropogenic greenhouse gas. It is harmful to human health and detrimental to plant productivity, causing significant crop production losses. Currently, O<sub>3</sub> concentrations are to increase globally if we are following the business as usual scenario (RCP8.5), which could have a significant impact on food security. The Joint UK Land Environment Simulator modified to include crops (JULES-crop) is used here to quantify the impacts of present-day and future tropospheric O<sub>3</sub> on crop production at the regional scale until 2100 using RCP2.6 and RCP8.5 scenarios. The studied regions include the main crop producing countries. The model will thus contribute to the understanding of the impacts of climate change on food production. With increasing carbon dioxide (CO<sub>2</sub>) in the future, models predict CO<sub>2</sub> fertilisation with induced stomatal closure would reduce O<sub>3</sub> damage and increase the productivity of vegetation. Factorial runs of the combination of RCP2.6 and RCP8.5 CO<sub>2</sub>, climate and ozone scenarios are performed to investigate the sensitivity of the crops to each climate forcing. The factorial run also explores if climate change mitigation or clean air policy are more important regarding increasing crop yield. The relative impact of CO<sub>2</sub>, O<sub>3</sub> and climate change is quantified and compared in all important agricultural regions. The factorial simulations show that CO<sub>2</sub> has the largest impact on regional yield, followed by climate then ozone. The CO<sub>2</sub> fertilisation and CO<sub>2</sub> induced reduced O<sub>3</sub> damage effect is, however, masked by the negative impacts of tropospheric O<sub>3</sub> in regions with high O<sub>3</sub> concentration such as South Asia and China. The modelled yield in 2050 is compared with Food and Agriculture Organisation (FAO) statistic, and it shows that FAO estimation of future scenario is more conservative than JULES-crop simulation, and it is closer to our JULES-crop RCP8.5 scenario with a combination of ozone and CO<sub>2</sub> and climate.

## OZONE DEPOSITION OVER A MIXED SUBURBAN TEMPERATE FOREST

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Half-hourly fluxes ( $F$ ) and deposition velocity ( $v_d$ ) of ozone ( $O_3$ ) were measured over a mixed temperate suburban forest during the period 2005-2015. The long-term average (median)  $O_3$  flux ( $F$ ) from the selected dataset was  $-0.142$  ( $-0.088$ )  $\text{ppb m s}^{-1}$ , corresponding to an average (median)  $O_3$  concentration of  $24.8$  ( $23.4$ )  $\text{ppb}$  and  $v_d$  of  $0.70$  ( $0.46$ )  $\text{cm s}^{-1}$ .

The study of the halfhourly  $v_d$  and  $F$  revealed the importance of the precipitation form, which was also shown in other flux studies. Especially dew-wetted canopies led to higher  $v_d$ . The analysis further evidenced that traffic volume led to increased deposition due to the presence of chemical reactions between  $O_3$  and nitric oxide ( $NO$ ) above the canopy surface. During the working week, daytime values of  $v_d$  and  $F$  were found to be significantly higher than the weekend values, especially during the winter half-year.

In a next step, half hourly deposition data were aggregated into day- and night-time monthly values. Average monthly daytime  $v_d$  ranged between  $0$  and  $2 \text{ cm s}^{-1}$ , whereas monthly daytime varied between  $0$  and  $1 \text{ cm s}^{-1}$ . An analysis of covariance (ANCOVA) was conducted with one nominal variable (traffic volume) and continuous predictor variables (maximum amount of allowed turbulence ( $v_{d\text{max}}$ ), vapor pressure deficit ( $VPD$ ), relative humidity and temperature at the canopy surface ( $RH(z_0')$  and  $T(z_0')$ , resp.), level of water below ground surface ( $gwt$ ), soil temperature ( $T_s$ ), solar radiation ( $Sun$ ), precipitation amount and interactions between them. Monthly average night-time/daytime  $v_d$  was positively correlated with the  $RH(z_0')$  and negatively correlated with  $gwt$ . During the daytime, monthly  $v_d$  was additionally increased during the working-week when traffic volume was high. During working-weeks the monthly  $v_d$  was  $0.3 \text{ cm s}^{-1}$  higher compared to weekend conditions.

The explained variability was, however, low and it was speculated that inclusion of other unaccounted variables as biogenic volatile compounds (BVOC) and net ecosystem  $CO_2$  exchange (NEE) should be included in future analysis. It was conjectured that, especially, in some spring months (e.g. April 2017) monoterpene emission might have controlled the deposition at the site.



## TOWARD THE DEFINITION OF EPIDEMIOLOGICALLY-BASED STOMATAL-FLUX CRITICAL LEVELS FOR FOREST PROTECTION AGAINST OZONE: THE MOTTLES APPROACH

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Current European directives for the protection of vegetation from the phytotoxic ozone ( $O_3$ ) are based on atmospheric exposure (AOT40) that are not always representative of the actual field conditions. Such discrepancy is known to be related to the fact that  $O_3$  effects on forests depend on gas uptake through stomata (stomatal fluxes). MOTTLES is an EC LIFE project establishing a permanent network of forest sites based on active monitoring in areas at highest and medium risk of ozone injury, in order to define new standards based on stomatal fluxes, i.e.  $POD_Y$  (Phytotoxic Ozone Dose above a threshold  $Y$  of uptake). In the present analyses, based on the first year of MOTTLES data, we describe the typical monitoring station, together with measure protocols and index calculation methods. AOT40 and  $POD_Y$ , computed with different approaches, are then compared and correlated with plant-response indicators (radial growth, crown defoliation, leaf visible injury). For 2017, the average AOT40 calculated according with the European Directive was almost twice the EC legislative standard of 5,000 ppb h. The metrics obtained following European protocols (Directive, ICP) resulted well correlated to those calculated on the basis of the real duration of the growing season (MOTTLES method) and are thus representative of the actual exposure/flux. AOT40 showed an opposite trend compared with  $POD_Y$ , hence it cannot be recommended as an optimal metric for forest protection from  $O_3$ . Visible foliar injury appeared as the best plant-response indicator of tree responses to  $O_3$  under field conditions and more easily detected at the forest edge than inside the forest. The present work may help the set up of further long-term forest monitoring sites dedicated to ozone assessment. Such experience is fundamental in Europe where stomatal  $O_3$  fluxes shall now be monitored at different habitats according with the new National Emission Ceiling Directive.

## ICP VEGETATION SMARTPHONE APP FOR RECORDING INCIDENCES OF OZONE INJURY ON VEGETATION.

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Exposure of vegetation to ozone pollution can cause visible injury on the leaf surface of ozone-sensitive species. In 2007, the ICP Vegetation published a report documenting over 500 incidences of visible ozone injury on crops, grassland species and shrubs growing in the field under ambient air conditions in 17 countries of Europe (Hayes et al., 2007). Field-based evidence is needed to verify predictions from experiments and to validate risk maps. It also demonstrates the negative impact of ambient ozone to policy makers. To build upon the evidence gathered in the 2007 report, we developed an ozone smartphone App, with the aim of creating a global database of injury records.

The App, suitable for use on iPhones, Android or Windows phones, allows participants to upload photographs of ozone injury and the coordinates of the location where the injury was detected. There is also an online recording form, for those without a smartphone. Users are asked a series of questions designed to assist with quality assurance, including details on their previous experience of identifying ozone damage and recent weather conditions. For guidance, the App also contains an ‘Ozone Information’ section, which provides details of the key visible injury symptoms and example photographs for a variety of different species. Since its development in 2014, we have received injury records from Europe, the USA and Asia for 20 different species. We are keen for many more people to take part to increase the number of records we receive from around the world. One way to collect evidence and report it via the App is to expose sensitive ozone species (SOS) to ambient air, and upload the injury photos. Information on how to download the App and a method for exposing sensitive ozone species are available on the recently updated ICP Vegetation website:

<http://icpvegetation.ceh.ac.uk>

### **Reference:**

Hayes, F., Mills, G., Harmens, H., Norris, D. (2007) Evidence of widespread ozone damage to vegetation in Europe (1990 – 2006). Programme Coordination Centre of the ICP Vegetation, Centre for Ecology and Hydrology, Bangor, UK. ISBN 978-0-9557672-1-0.

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# ESTIMATING THE IMPACTS OF OZONE POLLUTION AND CLIMATE CHANGE ON TERRESTRIAL ECOSYSTEM PRODUCTIVITY USING AN OFFLINE ECOPHYSIOLOGICAL MODEL

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Under the changing climate and air pollution, ecosystems face more extreme conditions, impacting their state thus services provided. The urgent task of evaluating the resultant impacts is then apparent where devastating ramifications affect food security, biodiversity, air quality, public health etc. Further complications arise when the consequential feedbacks are taken into account. For instance, increasing surface ozone concentrations worldwide have been shown to damage vegetation and significantly reduce food production. The impaired ecosystems then exacerbate the severity of the ozone pollution as vegetation uptake of ozone via dry deposition is reduced in response to this oxidative stress. If we account for the effects of droughts and heat waves, many observed that ozone pollution further intensifies due to the multiple stresses which severely reduce dry deposition. The complexity of these interactions limits the possibility to attribute the significance of individual processes and reflects the need for tools that can differentiate between different interactive pathways without disregarding the intricacies of each process. We present an asynchronously coupled modeling framework that utilizes prescribed meteorology to isolate interactions between the coupled biosphere and atmosphere at each stage of feedback.

## Model description

The biosphere is represented by the Terrestrial Ecosystem Model in R (TEMIR) v1.0 at global or site levels. Under meteorology provided by NASA GMAO or FLUXNET, the key traits of plant ecophysiology is represented by the Farquhar et al. (1980) description of photosynthesis and the stomatal conductance devised by Ball et al. (1987). These two leaf-scale parameters are treated separately according to the sunlit and shaded partitioning as calculated from canopy radiative transfer. Partitioned leaf-level parameters are scaled up to give a canopy representation using the big-leaf approach.

## Conclusion

- Current modeling efforts of terrestrial ecophysiology produce noteworthy results, reasonably capturing spatial and temporal characteristics.
- Ozone damage on vegetation is prominent. It may worsen under climate change but may be alleviated under rising CO<sub>2</sub> due to stomatal closure, leading to further ramifications through feedbacks.
- Complexities of feedbacks lead to uncertainties warranting further research that involves comprehensive mechanistic representation with yet decoupling capabilities.

# **MOSS SURVEY POSTERS**



# ASSESSMENT OF ANOMALIES IN DISTRIBUTION OF RARE EARTH ELEMENTS ACROSS SERBIA USING MOSS BIOMONITORING

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In the recent decades, rare earth elements (REEs) are recognised as xenobiotics due to their growing mining and application in agriculture, medicine, high-tech electronics and communication systems. The increasing use of REEs in different areas of human activity has led to environmental contamination and bioaccumulation persists for a long time. Airborne particulate matter is a carrier of many potentially toxic elements including REEs. Mosses have been studied as biomonitors of positive or negative anomalies in REE distribution over large areas induced by deposition of atmospheric particulate matter.

In this study, 16 REEs (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were determined in the samples of moss *Hypnum cupressiforme* collected across Serbia in 2015/2016. The obtained REE concentrations were normalised to their values in European Shale (EUS), North American Shale Composite (NASC), Post Archean Australian Shale (PAAS) and Upper Continental Crust (UCC) (Figure 1). Deviation of the element concentrations from the natural values was estimated by calculating their enrichment (EFs) in the moss samples, and particular element ratios, as well. According to Al and Sc as reference elements, the median EFs showed slightly enrichment of the REEs in the moss samples (0.6–2.8 and 1.7–3.5, respectively). The statistically significant correlations were obtained between the REE concentrations in the moss (among light REEs:  $R \geq 0.80$ , and among heavy REEs  $R \geq 0.95$ ; both at the  $p < 0.05$ ). These strong correlations imply the similar origin of the elements, probably geogenic.

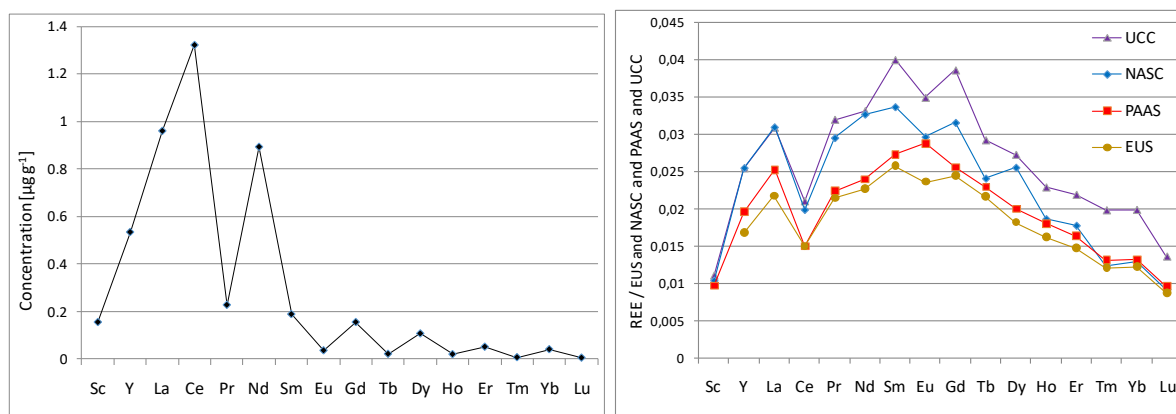


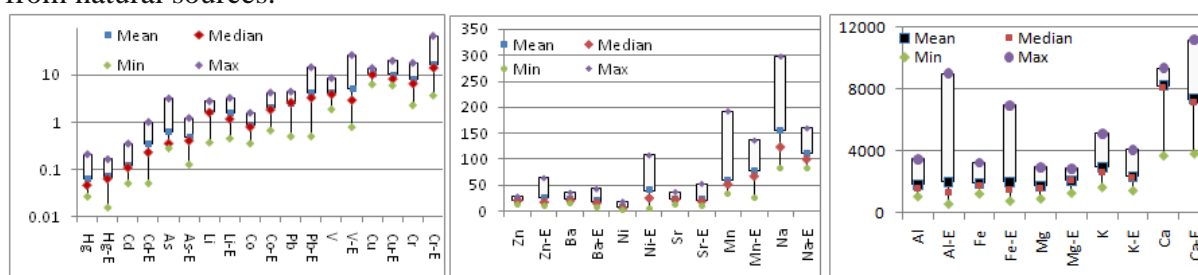
Figure 1. Median REE concentrations ( $\mu\text{g g}^{-1}$ ) in *H. cupressiforme* (left); EUS, NASC, PAAS and UCC normalised patterns of the element concentrations in the moss (right).

# ASSESSMENT OF AIR QUALITY IN ALBANIA BASED ON ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS IN COASTAL AND INLAND AREAS

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Since 2010, Albania had contributed to the data onto the European moss survey (EMS), which is repeated at five-yearly intervals. This study was conducted in the framework of 2015 ICP Vegetation in order to compare the 2010 and 2015 moss survey data, and to provide an assessment of air quality throughout Albania for better identification of contamination sources and improving the potential for assessing environmental and health risks associated with toxic metals. Albania is exposed to high levels of trace metals particularly for elements linked with geogenic factors, mining operations, and mineral mine wastes. The country has been appointed as a “hotspot of heavy metal contamination in Europe” (Lazo et al., 2018; Harmens et al., 2015). In this study are presented the data collected from 2015 moss survey. Moss samples (*Hypnum cupressiforme*) were collected during August and September, 2015 from 55 sites, distributed over the entire country. Sampling was performed in accordance with the LRTAP Convention–ICP Vegetation protocol (Frontasyeva and Harmens, 2015) and sampling strategy of the European Programme on Biomonitoring of Heavy Metal Atmospheric Deposition. The data of two different transects (13 sites at each transect) positioned respectively along the western coastal area and the eastern inland are included in this presentation. Inductively coupled plasma–atomic emission spectrometric (ICP–AES) (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V, and Zn), AAS (As and Cd) and CVAAS (Hg) analytical techniques were applied to study multi-element atmospheric deposition in Albania. The obtained data show significant differences in spatial distribution of the elements in each transect derived from different emission sources. High emission loadings of anthropogenic elements (Cr, Ni, Cu, As and Zn) were detected in the East affected by geogenic factors and mining industry, and of sea salt elements, particularly Na and K, in the Western coastal line. The differences in the deposition fluxes of the pollutants between different monitoring sites may be affected by the differences on their atmospheric concentrations and their scavenging ratios from atmosphere to terrestrial ecosystems. Cluster and factor analysis was applied to distinguish elements mainly of anthropogenic origin from those predominantly originating from natural sources.



**Fig. 1** Box-plot diagram of elements in coastal (Me) and inland (Me-E) areas

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## HEAVY METAL ACCUMULATION IN *TARAXACUM OFFICINALE* L. AT URBAN AREAS

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The study assessed the accumulation of selected trace elements (chromium, cadmium, nickel and lead) in *Taraxacum officinale* in urban areas of three Polish cities (Poznań, Wrocław and Warsaw). The aim of the study was to evaluate the usefulness of *Taraxacum officinale* L. as a bioindicator of trace elements in urban areas. In May 2017 samples of plants (aboveground part and root) and soil from their root zone were taken from selected locations with different characteristics in terms of the structure of use. After the preparation of the tests, chemical analyzes were carried out and graphic and statistical elaborations of the obtained results were made. The coefficients of pollution (*C*), translocation (*TF*) and accumulation (*BAF*) were also calculated.

The results confirmed the usefulness of dandelion for the purpose of bioindication of certain trace elements in the environment. The aboveground parts of dandelion is especially good indicator of cadmium accumulation, while roots revealed higher concentration of nickel. The latter one information might suggest that this species can be treated as a good phytoremediation plant at polluted areas by nickel. The translocation factor revealed higher values for cadmium. Soils of three analysed cities revealed relatively low level of pollution by chromium and nickel, while higher levels of pollution were noted for cadmium in Poznan and Wrocław.



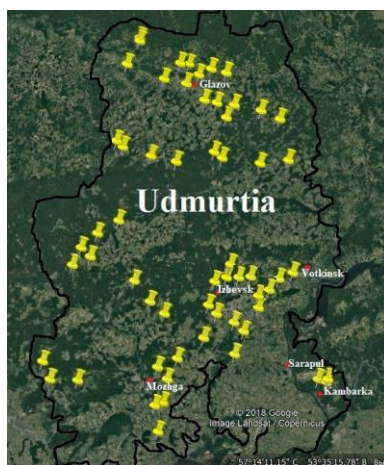
## MOSS MONITORING OF TRACE ELEMENTS IN THE REPUBLIC OF UDMURTIA, RUSSIA

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The results on atmospheric deposition of trace elements in the moss survey in the summer of 2017 in the Republic of Udmurtia, Russia, are reported. Udmurtia is an industrial region allocated in the east of the East-European Plain where it goes to the Western Urals. An important role in its economy belongs to enterprises of the military-industrial complex, machine tools and automotive, building materials and mining. Samples of moss were collected over the territory of the Republic in accordance with the guidelines of the Moss Manual 2015/2016 of the UNECE ICP Vegetation. Coordinates of the sampling sites were very close to those used in the first moss survey in Udmurtia carried out in 2005-2006 (Pankratova et al., 2007, 2008). Conducted research supplements the information on the moss surveys in Udmurtia in 2005, 2006 and 2016, 2017 (Pankratova et al, 2007, Bukharina, etc., 2017, 2018). A total of 39 elements were determined by neutron-activation analysis and atomic absorption spectrometry (Pb, Cd, and Cu). Multivariate statistics (factor analysis) and geochemical mapping were applied for data interpretation.



Moss monitoring network in Udmurtia, Wester Urals, in 2016-2017

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# INVESTIGATION ATMOSPHERIC DEPOSITION OF HEAVY METALS IN NORTH AND WEST REGION OF THE REPUBLIC OF KAZAKHSTAN USING THE METHOD OF MOSS-BIOMONITORING

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This article aims to analyze the data obtained by researching the atmospheric deposition of heavy metals in north and west region of Kazakhstan using the method of moss-biomonitoring. This method was applied for the north and west parts of the Republic of Kazakhstan to assess the environmental situation in these regions. In Kazakhstan, due to the current socio-economical system saturated with varied companies of very different technological orientation.

The twenty eight moss samples were collected in autumn of 2017 growth periods. A total of 43 elements were determined by the epithermal neutron activation analysis. Multivariate statistical analysis of the obtained results was used to assess the pollution sources in the companied area (Aktobe, Atyrau, Aktau regions).

A comparison of concentration Kazakhstan showed the increased values for most of heavy metals (Cr, Al, Ti, V, Ni, Fe, Co, Sr, As, U, Th, etc.) in the studied samples that apparently are due to the state of the industrial sector of Kazakhstan. The main potential sources of air pollution from to industrial sector location of large oil and gas and industrial enterprises. In Aktobe region are the second largest in the world deposit of chrome ores, large plants chromium compounds and alloys. In the neighbouring Atyrau region there is a large boron field and oil and gas fields. As a result of the production activities of Aktau gas processing plant, various chemicals are released into the atmosphere, spreading over a considerable distance and accumulating in environmental facilities.

The average concentrations of elements are given in the table obtained by NAA. Was found a correlation coefficient , which is 0,8296.

*The average concentrations of elements, obtained by method NAA.*

Elements	Cr	Al	Ti	V	Ni	Fe	Co	Sr	As	U	Th
By NAA method, mcg/kg	9,29	9331	644	11,71	3,30	4327	2,99	74,31	1,32	13,27	18,25

A performed preliminary investigation shows that the moss biomonitoring of the atmospheric deposition heavy metals is an efficient technique to study the environmental situation Kazakhstan. The experience of this study can be successfully used in the other region of Kazakhstan. Also, there will be maps of the spatial distribution of elements by area, based on the statistical analysis of the data created with the use of maps of the distribution elements.

INTRACELLULAR RESPONSE TO CADMIUM IN THE MOSS  
*LEPTODICTYUM RIPARIUM*

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Heavy metals pose a problem for many plants that grow in contaminated environments, due to their toxicity effects. One of the most toxic metals is cadmium (Cd), a non-essential element, particularly harmful to most living organisms. Phytochelatin synthase (PCS) is a  $\gamma$ -glutamylcysteine transpeptidase (Grill et al., 1985) that, starting from glutathione (GSH), is able to synthesize phytochelatins (PCn), thiol peptides having a general structure  $\gamma$ -(glutamate-cysteine)<sub>n</sub>-glycine, with n commonly included between 2 and 5. By virtue of their thiol groups, PCn can bind Cd and other heavy metals, sequestering them in the vacuole and thus reducing their toxic effects for the plant cell. The presence of widespread and constitutive PCSs has been found in a number of early plants, including bryophytes (Degola et al., 2014; Petraglia et al., 2014); amongst mosses, only *Sphagnum palustre* showed to possess a PCS with a molecular mass of about 36 kDa, able to synthesize PCn up to the oligomer PC<sub>4</sub> (Petraglia et al., 2014). By contrast, no PCS is expressed by the “model-moss” *Physcomitrella patens*. In the present work, we functionally characterized for the first time the PCS of *Leptodictyum riparium*, a cosmopolitan moss that appears to be capable of accumulating a wide amount of heavy metals compared to other plants. Indeed, HPLC-ESI-MS-MS assays of *L. riparium* exposed to 36 or 360  $\mu$ M Cd allowed to detect the presence of PCn up to PC<sub>4</sub>, other than GSH and  $\gamma$ -glutamylcysteine. Moreover, TEM observation and Comet assay showed ultrastructural alterations and damage to DNA, proportional to the supplied Cd concentrations. Likewise, the increase in Cd concentration led to a progressively risen ROS level, with activation of antioxidant- (catalase, superoxide dismutase) and detoxifying- (glutathione transferase) enzymes. Thus, also in *L. riparium*, PCn and other detoxifying intracellular mechanisms come simultaneously into play to counteract Cd toxicity.

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## NUCLEAR AND ATOMIC TECHNIQUES USED FOR HEAVY METAL POLLUTION INVESTIGATIONS IN AGROECOSYSTEMS

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The paper is reviewing several applications of nuclear and atomic techniques for the assessment of heavy metal pollution in an agroecosystem, by investigation of related environmental samples – soils and cultivated plants.

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

A discussion is made regarding their suitability to be used in soil-crop metal transfer studies, for the investigation of level of contamination with metals and toxicants occurrence in environmental factors, as well as for human health risk assessment. Based on the obtained results, coefficients of transfer of heavy metals from soils to tissues of related plants and vegetables have been determined and a calculation of health risk for population by consuming food items from industrial areas has been performed.

## AIR POLLUTION STUDY IN DIFFERENT REGIONS OF TAJIKISTAN USING THE MOSS BIOMONITORING TECHNIQUES, NAA AND AAS

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Within the framework of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops, for the first time were investigated the distribution of heavy metals and radionuclides in mosses in Tajikistan. From different regions of Tajikistan was collected a 21 samples the most dominant and widespread moss species *Hylocomium splendens* in 21 sampling sites. The research was carried out for the air quality assess in different regions of Tajikistan. In this study were determined 44 elements (Na, Mg, Al, Cl, K, Sc, Ca, Ti, Cr, V, Mn, Ni, Fe, Co, Zn, Pb, Cu, Se, As, Br, Sr, Rb, Zr, Mo, Cd, Sb, I, Ba, Cs, La, Ce, Nd, Eu, Gd, Sm, Tb, Yb, Tm, Hf, Ta, W, Hg, Th, U) using the instrumental neutron activation analysis at the reactor IBR-2 and atomic absorption spectrometry in Dubna (Russia) [1]. To distinguishing of elements and those anthropogenic and vegetation origins was used factor analysis. To identify of the lithogenic and anthropogenic origin of the elements in moss samples was used correlation analysis. The GIS technology software was used to visualize data. Comparison of the concentrations of elements Tajikistan-Kazakhstan showed elevated values for most heavy metals and REE.

From the data obtained it can be concluded that, main anthropogenic sources of heavy metals are heat-electric center, transport and small industrial activities. If one of the main reasons are factories for the productions of aluminum, cement and coal mining, another reason can be called the often occurring in the warm season the dust-storm from Afghanistan. The relatively inexpensive methodology of mosses survey shown a high effectivity in atmospheric deposition studying of heavy metals and other trace elements, also to identify of pollution sources [2]. The received results will be use to better identify of pollutant sources and makes a database for future surveys. This allows to documenting the effectiveness of emission reduction measures. With a view to a detailed study of the state of the atmosphere proceeding from the small number of investigated territories, it can be concluded about the need to increase the sampling area and further work on the entire territory of the Republic of Tajikistan. It is important to continue the moss survey in all of the territories of Tajikistan.

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## PAHS MEASUREMENTS IN MOSS PLEUROZIUM SCHREBERI IN KALININGRAD REGION

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Moss technique was used in the Kaliningrad region to study atmospheric deposition of PAHs for the first time, in 2017 year.

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

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

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

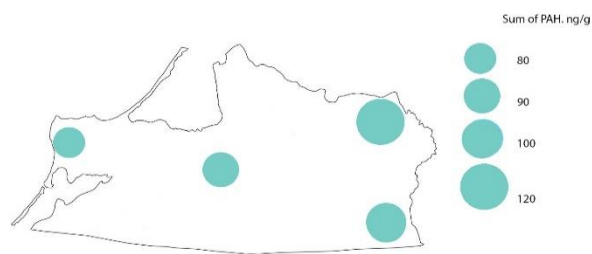


Fig. 1. Plots and sums of PAH in Kaliningrad region

## IDENTIFICATION OF THE POLLUTION SOURCES BY MOSS BIOMONITORING IN THE UPPER SILESIA REGION

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Moss biomonitoring in the Black Triangle II is applied on areas of a small scale unlike the whole country researches. A regular network of sampling points was created for improvement of the monitoring system in the industrial region. In the years 2015/2016, 85 moss-sampling points were used. The samples were analysed by neutron activation analysis in Frank Laboratory of Neutron Physics in Department of Neutron Activation Analysis and Applied Research. As results, 46 elements were determined.

The factor analysis was used for grouping the elements. Cattell's scree test shows an ideal scenario for three and a less ideal but acceptable one for four factors. In the case of three factors, six elements constitute factor 2 (Zn, As, Br, Sb, I, Ba). The most significant samples that are considered in factor 2 are situated around mining cities with plenty of power plants and above the underground brines in Poland.

Factor 3 is composed of four elements (Ca, Se, Mo, Cd). The research works with an assumption that Ca, Se and Mo are of a vegetation origin. The distribution of significant samples in factor 3 contributes to the previous assumption. All these samples are situated in unpolluted localities, even in a nature reserve.

In the case of the results for the four factors, the group of elements contained in factor 2 in the previous case, is extended by Sb and Mn for the same localities. Factor 3 contains Ca, Cr, Fe, Rb, Sr and Mo elements. The most significant sampling point is near ironworks, however, others are located in the mountains. The last group of elements consists of Se, Cd, W. All significant localities are in moderate-size cities with light industry.

# PRELIMINARY STUDY OF SOME ORGANIC POLLUTANTS IN MOSS AND PINE NEEDLES IN TIRANA REGION, ALBANIA

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In Albania there is a lack of data on air pollution from organic compounds. Monitoring atmospheric POPs and VOCs using conventional methods is difficult and expensive, and levels in air samples represent an instantaneous value at a sampling time. Biomonitoring methods can overcome this limitation, because bio-monitors can accumulate organic compounds, serve as long-term integrators and provide reliable information to assess the impact of pollutants on the biota and various ecosystems<sup>1</sup>. Mosses are suitable organisms to monitor spatial patterns and temporal trends of atmospheric concentrations of POPs<sup>2</sup>. Also, conifers have widely been accepted as reliable bioindicators due to their high leaf wax content<sup>3</sup>. The purpose of our study was to investigate the concentrations of some volatile and semi-volatile organic pollutants, such as: BTEX, organochlorine pesticides (OCPs) and indicator PCBs in moss and pine needles samples from Tirana National Park, Albania. Samples were blended and homogenized with sodium sulphate anhydrous, ultrasonically extracted with n-C<sub>6</sub>H<sub>14</sub>/ MeCl<sub>2</sub>, treated with activated Silica gel (H<sub>2</sub>SO<sub>4</sub>- 40%), cleaned-up in an activated Florisil column (40% water) and injected in Varian 450 GC-FID, column RTX-5 (30m x 0.25mm i.d. x 0.50µm).

Groups of HCH-s, aldrine/endrine and heptachlor were found in higher concentrations. Pesticides' profiles were not similar with the ones found in soil and biota samples (Figure 1 and 2). Mosses had the ability to adsorb most of OCPs and PCBs in higher levels, representing a very useful class of bio-monitor, to evaluate the atmospheric pollution from POPs (Figure 3 and 4). BTEX concentrations in moss were higher than in pine samples. In both species, however, the range is getting closer to the detection limit of the analytical method. Benzene was the most abundant component of BTEX mixture concentrations.

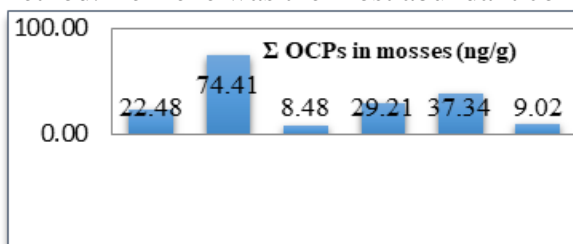


Fig. 1. Sum of OCPs in moss samples

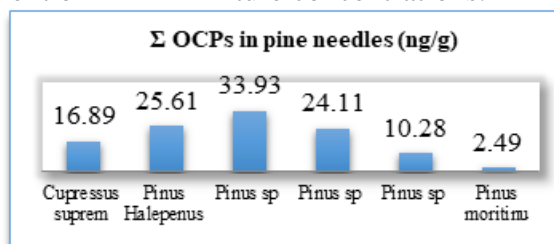


Fig.2. Sum of OCPs in pine needle samples

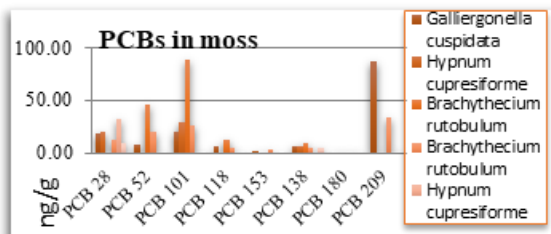


Figure 3. PCBs in moss samples

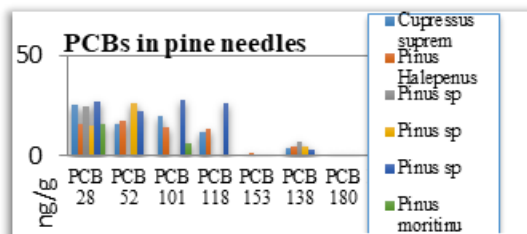


Figure 4. PCBs in pine needle samples

<sup>1</sup> Qimei Wu, XinWang, Qixing Zhou; Biomonitoring persistent organic pollutants in the atmosphere with mosses: Performance and application. *Environment International* Volume 66, May 2014, Pages 28-37

<sup>2</sup> Harmens, H., Foan, L., Simon, V., Mills, G. (2011). Mosses as biomonitors of atmospheric POPs pollution: A review. Report for Defra contract AQ08610, available at <http://icpvegetation.ceh.ac.uk/> and <http://uk-air.defra.gov.uk/library/>.

<sup>3</sup> S. Herceg Romanić, B. KRAUTHACKER. Are pine needles bioindicators of air pollution? Comparison of organochlorine compound levels in pine needles and ambient air. *Arh Hig Rada Toksikol* 2007;58:195-199



## BIOMONITORING OF AIR POLLUTION IN AZERBAIJAN

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The purpose of this work was a qualitative and quantitative assessment of atmospheric air pollution by heavy metals in order to study regional and local pollution of both air, soil and the waters of the studied area by environmental pollutants during biomonitoring of biosphere pollution.

We studied samples of moss, soil (near Mingechaur) and water (the Kura River flowing in the area) to identify the bioindicator properties of moss and for bioindication of air, soil and water.

The activity of radionuclides and concentrations of heavy metals were determined on an Gamma Spectrometer and Agilent Technologies 7500 Series ICP-MS (7500cx) instrument using inductively coupled plasma mass spectrometry (ICP-MS, USA).

The content of heavy metals in samples of moss, soil and water, which amounted to samples of moss in mg / kg: Cr (28.4390), Mn (509.2683), Fe (16487.8049), Cu (14.9927), Zn (26.0244), Cd (0.0438), Ba (163.8049) and Pb (5.0829); for soil samples, Cr (14.1573), Mn (476.1797), Fe (12687.6404), Cu (11.1168), Zn (19.7977), Cd (0.0379), Ba (85.3258) and Pb (4.1685), and in water samples the content of heavy metals ranged from: - Cr (0.0179), Mn (1.487), Fe (0.461), Cu (0.645), Zn (<0.0001), Cd (0.00265), Ba (18.17) and Pb (<0.0001), respectively.

The activity of radionuclides:

	Bq/kg	Bq/kg	Bq/L
	<b>moss</b>	<b>soil</b>	<b>water</b>
<sup>7</sup> Be	<79.08	<34.00	<2.99
<sup>40</sup> K	648,1	570,5	<7.64
<sup>60</sup> Co	<11.34	<4.68	<0.39
<sup>134</sup> Cs	<12.15	<5.41	<0.39
<sup>137</sup> Cs	<14.01	<4.92	<0.41
<sup>208</sup> Tl	<12.01	<5.56	<0.42
<sup>210</sup> Bi	<12.93	<5.64	<0.50
<sup>212</sup> Bi	ND	ND	ND
<sup>212</sup> Pb	ND	9,37	ND
<sup>214</sup> Bi	<28.74	19,44	<0.88
<sup>214</sup> Pb	<62.62	31,88	<0.85
<sup>226</sup> Ra	ND	ND	ND
<sup>228</sup> Ac	ND	ND	ND
<sup>234</sup> Pa	ND	ND	ND
<sup>234m</sup> Pa	ND	298,5	ND

## RELATION BETWEEN LAND USE, INDUSTRIAL ACTIVITY AND METAL ACCUMULATION IN PLANTS

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The aim of this study was to determine the distribution pattern of selected metals in agricultural soils and cultivated plants in the vicinity of an important iron and steel industrial region in Romania, in relation with the land usage. Research undertaken over the last few years has shown that the different ways of using land have a great influence on soil quality and on its productivity and human health. In the agricultural areas adjacent to the industrial platforms, in addition to the elements accumulated by the use, often non-rational, of fertilizers in the soil there are also stored elements from the industrial activity. Considering the soil-plant transfer relationship, it was found that, depending on the species, the crop plants assimilate variable amounts of heavy metals under different conditions of temperature, humidity and soil physical and chemical characteristics, with the risk of contamination of agricultural products. 12 soil samples were collected from three territories in the vicinity of the Iron and Steel Plant in Galati County, Romania, on standard depths of 0-5 cm and 5-30 cm, as well as 6 samples of plants, separated on physiological sections. Leaves and seeds of wheat and sunflower, the most favorable plant species in the mapped region, were investigated. Concentrations of Pb, Co, Cr, Zn, Cd, Ni, Cu and Al in both soil and plant samples were determined by High Resolution Continuum Source Atomic Absorption Spectroscopy (HR CS AAS) at INPOLDE research center, Dunarea de Jos University of Galati. In order to identify the mineralogical composition of the soils, a complementary analysis of the spectra obtained by using Attenuated total reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) technique was performed. At the same time, there were obtained results on the soil moisture at the time of sampling, the soil pH and the organic matter content.

## ESTIMATION OF ATMOSPHERIC FALLOUT RADIONUCLIDES ACTIVITY USING MOSES: ARMENIA

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Mosses are promising medium for the monitoring of airborne radionuclide depositions due to their widespread occurrence, perennial features, accumulation of radioactive substances in high concentrations, as well as ease of sampling and possibility of measurements without chemical preparation treatments of samples. Usage of bio indication methods is a developing technique for the assessment of radionuclide contamination in different regions. The present study was undertaken to assess the activity concentrations of atmospheric fallout radionuclides ( $^7\text{Be}$ ,  $^{40}\text{K}$  and  $^{137}\text{Cs}$ ) using the most abundant species of mosses in Armenia.

35 moss samples were taken through Armenia within the frames of ICP Vegetation project in September-November 2016. The ranges of sampling altitude were 468-2213 m above sea level. Sampling points were located at non-urban areas, 300 m away from highways, villages and industries and 100 m away from short roads. All sampling sites were carefully selected to avoid possible contact of mosses with surface and running waters on slopes. Samples were situated away from influences of trees, shrubs, large-leafed herbs or other plants. The most common moss species (*Brachythecium rutabulum*, *Homalothecium philippeanum*, *Ptilium crista-castrensis*, *Syntrichia ruralis*) of the region were sampled.

Mosses were cleaned manually and dried at room temperature to a constant weight. The dried samples were packed and sealed into plastic boxes. All the sealed samples were analysed for radionuclide using high purity germanium (HPGe) coaxial detector coupled to multichannel analyser, counting time 30000 sec. Gamma background was measured weekly using empty plastic boxes. After correcting for background, the activity concentrations of  $^7\text{Be}$  (477.60 keV),  $^{137}\text{Cs}$  (661.5keV) and  $^{40}\text{K}$  (1460.0 keV) were determined in Genie 2000 software.

Activity concentrations of studies radionuclides didn't exhibit any correlation with the altitude. No statistically significant differences were recorded for accumulation of radionuclides by different species.  $^{40}\text{K}$  was the most abundant radionuclide in mosses,  $^{40}\text{K}$  was detected in all studied samples. The activity concentration varies from 8.30 to 34.70 and averaged to 15.5 Bq/g.  $^7\text{Be}$  was detected in 27% of studied mosses (8 samples) with the highest 1.64 Bq/g activity concentration at altitude of 1784 m a.s.l.  $^{137}\text{Cs}$  was detected in 16 samples (43.2 %). The highest level of  $^{137}\text{Cs}$  was 0.21 Bq/g (1075 m).

This pilot study will continue in order to reveal pattern of airborne radionuclides accumulation in different geochemical conditions and correlation of activity concentrations of radionuclides in different environmental compartments: snow cover, dry atmospheric depositions and soil.

## BIOMONITORING OF ATMOSPHERE AIR IN IMPORTANT ECOTOURISM REGIONS OF AZERBAIJAN

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Pollution with heavy metals creates greater pressure on the ecosystem every day and thus becomes a major source of danger for all living things. One of the most accurate methods of studying heavy metals pollution is the use of bioindicator species. In this regard, moss can be considered as the best bioindicators. They collect and store heavy metals and radionuclides in the atmosphere.

The aim of this study is to study heavy metals and radionuclides in the atmosphere of Goygol using moss like bioindicator.

Under the agreement between the Department of Ecological Engineering of the Azerbaijan University of Technology and Joint Institute for Nuclear Research, a scientific research is underway on the study of Goygol's atmospheric air under the UN Environment Program.

The researches were carried out with the most advanced systems at the Azerbaijan University of Technology and Joint Institute for Nuclear Research.

19 samples from the Shahriyar, Karamli, Dozular, Tulallar, Zurnabad and lake Goygol National Parks of Gökgöl region were collected and sent to Joint Institute for Nuclear Research for analysis. 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). It is planned to conduct this study in different regions of Azerbaijan.

# BIOMONITORING OF TOXIC METAL AIR POLLUTION USING MOSSES IN ALBANIA

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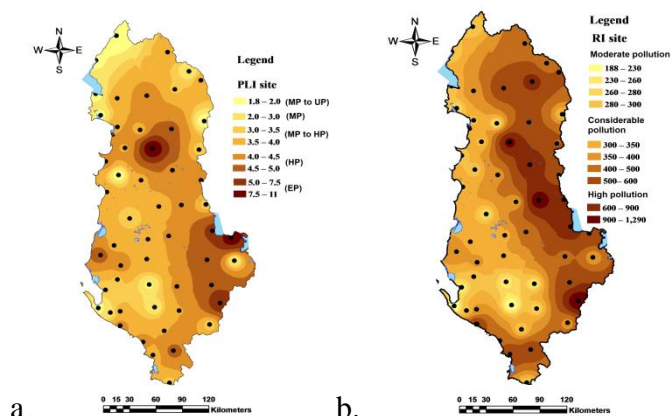
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Environmental pollution is a global issue that is strongly linked with the level of toxic chemicals in the environment. The concentration data onto heavy metals (HM), Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn in carpet-forming moss samples (*Hypnum cupressiforme* Hedw.) are considered in this study, because those are known as toxic elements that pose threats to human health and natural ecosystems. The concentration of HM in moss was determined by ICP-AES, ETAAS (As and Cd) and CVAAS (Hg) analysis. Moss samples were sampled during the August and September 2015 from 55 sampling sites that more or less homogeneously covered the entire territory of Albania. The elements show high variability ( $CV > 75\%$ ), that may reflect the spatial distribution patterns of heavy metal concentrations on the moss that is site specific and may show the local variation in TM deposition and the location of the areas with high contamination levels of each element. Spatial distribution and the trend of the distribution of the elements since 2010 was discussed in this study. Significant differences were found in concentration level of As, Cr, Cu, Hg, Ni, Pb and Zn by comparing the data of current moss and 2010 moss samples. We suggest that the differences between two moss surveys may be strongly affected by the differences on bioavailability of the elements during deposition process under wet and dry deposition that were different during 2010 and 2015 moss monitoring surveys.

GIS technology was used to identify the areas with high content of HM and high pollution level that are based on the values of the degree of contamination and the ecological risk of heavy metal atmospheric deposition of each sampling point. The contamination scale evaluated by the contamination factors of each element were ranged from the suspected to severe contamination scale. The CF scales were mostly remained in the same level for both monitoring surveys. Data onto the pollution load index show a moderate pollution level in the whole territory. Beside it, the potential ecological risk, that takes in consideration the toxicity of the elements, was investigated for the most toxic elements. It was found that As, Cd, Cr, Hg, Ni and Pb show high ecological risk in the most part of the territory of Albania.



**Fig. 1.** GIS maps of PLI and RI

Factor analysis was applied to investigate the probable sources of the elements and the factors which affect to the concentration level of the elements in current moss samples. It was suggested that Al and Fe were mostly originated from natural pollution sources, such as wind blowing soil dust. It is an important finding in defining the pattern of wind blow dust pollution in Albania. The elements As, Cd, Hg, Pb, Cu, Zn, Ni and Cr were mostly originated from anthropogenic contamination sources. Their anthropogenic sources are likely more clear than their natural background. Hg was mostly originated from long-range pollution and transboundary pollution.

**Keywords:** atmospheric deposition; heavy metals; moss biomonitoring; contamination indexes; factor analysis.

MICROCLIMATIC MONITORING AND ENVIRONMENTAL IMPACT  
ASSESSMENT ON HERITAGE MATERIALS OF TROPAEUM TRAIANI MONUMENT,  
ADAMCLISI

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D.D.<sup>2</sup>, Bucurica I.A.<sup>2</sup>, Olteanu L.<sup>2</sup>, Stirbescu N.M.<sup>2</sup>, Teodorescu S.<sup>2</sup>, Stanescu S.G.<sup>2</sup>,  
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The present paper is focuses on the microclimatic analysis and weather-climatic phenomena matrix assessment, which can be generated for heritage objectives at different spatial and temporal resolutions, correlated with complex physicochemical investigations of the materials. The microclimatic analysis of the Tropaeum Traiani monument was performed to assess the suitability of a closed environment, located outdoors according to the conservation requirements of heritage materials. The Tropaeum Traiani is a monument in Roman Civitas Tropaensium (site of modern Adamclisi, Romania), built in 109 in then Moesia Inferior, to commemorate Roman Emperor Trajan's victory over the Dacians, in the winter of 101-102, in the Battle of Adamclisi. Outside, on the monument walls were 54 metopes depicting Roman legions fighting against enemies; most of these metopes are preserved in the nearby museum. By the 20th century, the monument was reduced to a mound of stone and mortar, with a large number of the original bas-reliefs scattered around.

The present edifice is a reconstruction, dating from 1977, after one of the hypothetical models of the old monument ruins. First stage of this research was to identify climatic and microclimatic risk factors in the warm, cold and transition seasons, the causes and the potential consequences on the original archaeological substrates of Tropaeum Traiani Monument. Environmental conditions (indoor and outdoor) can significantly influence the degradation processes of the monument materials components, and the effects of these processes was observed and classified on different levels as well. Air temperature and relative humidity are key variables of research in the field of environmental protection. Both parameters are hard to monitor, especially on a national scale, due to spatial heterogeneity. The temperature is expected to increase in the course of this century, and the extreme values (53.7 °C) have been recorded in 2017. The variations in the minimum and maximum temperatures recorded were usually those that influenced the degradation process of the original materials.

It is well-known that organic and inorganic materials are extremely sensitive to thermo-hygrometric cycles, especially to the shorter ones (i.e. daily cycles, repeatedly dilated/contracted), because they generate steep gradients starting from the outer surface of the object, giving rise to inner tensions which result in dimensional variations and may lead to irreversible changes in chemical composition of the original materials. Excessive humidity observed inside the monument (100% in two days of monitoring campaign of the August 2018), accelerated the harmful effect of atmospheric pollutants and other toxic substances which irreversibly accentuating the degradation process. At the opposite end, during the cold

season when humidity was lower inside the monument, efflorescence was observed on the original materials, explained by high salt content (60 km from Black Sea).

In addition with temperature and humidity (indoor and outdoor), wind speed, wind gust, wind direction, dew point, and atmospheric pressure (outdoor) were monitored. In conclusion, even if an outdoor confined environment may not be suitable for conservation of the original heritage materials, depending on the climatic region, several solutions can be proposed in order to reduce the impact of the external climatic risk. Consequently, the thermo-hygrometric variation inside the monument shortens the durability of the preserved materials.

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## MOSS BIOMONITORING IN ROMANIA AS INTEGRATED IN EUROPEAN SURVEYS: CONTINUITY, EXTENDING AND PERSPECTIVES

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Moss biomonitoring technique was applied in Romania as integrates in European surveys. In the period 1995–2001 the first systematic study in Romania of atmospheric pollution from heavy metals and other toxic elements based on moss analysis was undertaken as a Romanian–Russian–Norwegian collaboration. The results on moss samples collected in different regions of Romania in 1990, 1995 and 2000 were unified and reported by Harmens et al., 2008. Results for the nationwide moss survey undertaken in 2010/2011 by four Romanian Universities from Targoviste, Galati, Iasi and Baia Mare were compiled in Harmens et al., 2013; Harmens et al., 2015; Stihl et al., 2017. The study continued with the campaign in 2015/2016, in order to complete the pollution database with nitrogen, besides the assessment of trends of heavy metal and toxic element pollution.

Although the concentrations of heavy metals in mosses collected in Romania are high compared to other (Eastern-) European countries, the temporal trends based on the reported and obtained values for mean concentration of selected metals reveal a decrease in 2015 for the majority of the elements, with the exception of As, as well as Fe, V and Cr.

The obtained results reveal that was and is a considerable problem in the northern and north-western parts of Romania named by us historical pollution. Romanian moss monitoring should be used in the future as a supplement of national air monitoring programs due to the fact that it could provide additional data on heavy metals air pollution at a higher number of sites and also to monitor any future trends in heavy metal deposition in Romania.

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## MISSING VALUES IN BIOMONITORING DATA: EXAMPLE FROM BIOMONITORING SURVEY IN BELARUS

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In the field of biomonitoring, missing data occur commonly because of the sensitivity of measuring or analytical technique, inaccurate measurements, measurement errors, or various other reasons. Nevertheless, significantly distorted results may occur when performing statistical analysis on the dataset containing missing values. Moreover, multivariate statistical methods should not be performed on the such a data. Thus, proper dealing with missing values is crucial.

This study aims to find out what is the maximum percentage of missingness for yielding correct results. Data from one-year of biomonitoring survey in Belarus subjected to multivariate analysis. Since the dataset originally did not contain any missing values, pseudo-random number generator was used to remove three percentage levels (specifically 5%, 10% and 15%). Missing values were then imputed using k-nearest neighbour (knn) algorithm which uses distance measure to find the k-most similar observation to a composition containing missing values and, subsequently, to replace the missing values by using the available information of the neighbours. Afterwards, data were subjected to multivariate analysis. Principle Component Analysis (PCA) was used to assess and visualise the relationships between observations and elemental concentrations, while Hierarchical Clustering on Principal components (HCPC) was then used to group observations into clusters of supposed similar pollution source profiles. First, analyses were performed on the original dataset (without missing values), then on the datasets with 5%, 10% and 15% of missingness, respectively, and finally on the datasets with knn-imputed missing values for each percentage level.

The results imply that multivariate analyses produce more accurate results when carried out on datasets with knn-imputed values then on the datasets with missing values. Moreover, only the dataset with 5% of missingness led to replicating the original, after knn-imputation was applied. Our experiment definitely proved the sensitivity to yield skewed results when dealing with data improperly, especially data involving missing values.

# VERIFICATION OF THE AIR POLLUTION MATHEMATICAL MODELLING RESULTS USING SPECIAL MONITORING AND ANALYTICAL METHODS

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## Background

Upper Silesian industrial agglomeration and its surroundings are highly affected by exceeded air pollution concentrations. Air pollution entails a lot of negative health, economic and social impacts. The situation requires systematic air quality monitoring and assessment. Mathematical modelling is an alternative approach to air quality assessment. Mathematical modelling is a suitable method for assessing the influence of specific pollution sources in a particular place. Uncertainties arise during modelling. These uncertainties must be considered when interpreting the modelling results. It is necessary to perform a verification of the models for the evaluation of the uncertainties influence.

## Mathematical modelling

The main goal of the present research is to perform a verification of the Analytical Dispersion Modelling Supercomputer System (ADMOS) model, which was developed by the Department of Environmental Protection in Industry at VŠB-TUO. ADMOS is a modular system composed of GIS (Geographic Information Systems), modelling methodology, supercomputers and routines which control these technologies. The modelling methodology of ADMOS is SYMOS'97, which is designed for air pollution modelling in large areas.

## Verification

A verification of modelling results is performed by comparison with air pollution monitoring results and special air pollution monitoring methods, such as moss biomonitoring, air pollution monitoring by unmanned airship and height located air pollution monitoring.

The moss samples were collected in a territory covering 36000 km<sup>2</sup> in accordance with the AIR TRITIA project area [1]. There were 244 moss samples collected in 2017. The samples were analysed by the Neutron Activation Analysis (NAA) within the Sector of Neutron Activation Analysis and Applied Research (SNAAPI) in the FLNP JINR. SNAAPI carries out a multi-elemental analysis. Consequently the data is processed in GIS using the spatial analysis. The preliminary results indicate a wider and more compact high concentrations area than mathematical modelling results.

The second approach for verification are measurements of vertical atmospheric profiles by a special unmanned airship. The aim of these measurements is to examine the vertical distribution of pollutants and compare the measured quantitative information and shape metrics of smoke plume with the SYMOS'97 modelling results. The airship measurement data are complemented by height located air pollution monitoring on a former coal mine tower operated within the framework of the AIR BORDER project [2].

[1]AIR TRITIA: Uniform approach to the air pollution management system for functional urban areas in tritia region / air tritia. Available from: <http://www.interreg-central.eu/Content.Node/AIR-TRITIA.html> [Accessed 08 January 2019].

[2]AIR BORDER: *Společná česko-polská měření přeshraničního přenosu znečišťujících látek v ovzduší*. Available from: <http://airborder.vsb.cz/cs/> [Accessed 10 January 2019].