





# 35<sup>th</sup> Task Force Meeting

### 21 – 23 February 2022

Hosted by UK (online)

# **Programme & Abstracts**



Working Group on Effects of the Convention on Long-range Transboundary Air Pollution

### **Organisers:**

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

Felicity Hayes, Katrina Sharps, Mike Perring, Amanda Holder

#### PROGRAMME

Venue: UK (Online) Times listed in Central European Time (CET) zone

#### Monday 21<sup>st</sup> February, 2022

#### Session: Plenary Chair: Felicity Hayes

14:00 *Felicity Hayes* – Opening and welcome

- 14:05 Krzysztof Olendrzynski & Isaura Rabago Latest developments of the Convention
- 14:20 Sophie Standring, Alison Davies & John Salter The Forum for International Cooperation on Air Pollution (FICAP)
- 14:40 Felicity Hayes Overview of ICP Vegetation
- 15:00 Marina Frontasyeva Moss Survey 2020-2021-2022. Sampling in Covid years of 2020 and 2021

15:20 General discussion

15:30 Comfort break

- 15:45 *Ilia Ilyin* Analysis of heavy metal pollution trends in the EMEP region basing on results of atmospheric modelling and moss surveys
- 16:05 Anne-Katrin Prescher Recent ICP Forests activities
- 16:25 *Thomas Scheuschner* Update from CCE including review of ammonia Critical Levels
- 16:35 Alexander Uzhinskiy Moss Survey Data Management System
- 16:45 Miscellaneous announcements, including: Introduction to the new IM PCC (James Kurén Weldon), NOx Critical Levels Review (Mike Perring), microplastics (Julian Aherne), and general discussion (Felicity Hayes)

17:00 Session end

#### Tuesday 22<sup>nd</sup> February, 2022

#### Session: Moss 1 Chair: Winfried Schröder

- 09:30 Konstantine Vergel Moss biomonitoring of atmospheric pollution in the Moscow region
- 09:50 *Pranvera Lazo* A pan-see biomonitoring network for the assessment of potentially toxic elements in urban air.
- 10:10 *Guntis Tabors* Assessment of atmospheric pollution deposition in Latvia from 1990 to 2020 using the moss as absorbent
- 10:20 Stefano Loppi Use of biomonitoring data in environmental forensics
- 10:40 *Mehriban Jafarova* Assessing the atmospheric deposition of microplastics: A lichen biomonitoring study in the city of Milan, Italy

#### 11:00 General discussion

#### 11:15 Comfort break

#### Session: Moss 2 Chair: Antoaneta Ene

- 11:30 *Irena Pavlíková* Monitoring of heavy metals and nitrogen concentrations in mosses in the vicinity of an integrated iron and steel plant: Case study in Czechia
- 11:50 *Michelle Nerentorp* Metal and nitrogen concentrations in moss in Sweden Results from the National Moss Survey 2020
- 12:00 *Winfried Schröder* Canopy drip effect on concentrations of heavy metals in mosses sampled across north-west Germany as part of the European Moss Survey 2021
- 12:10 Dinesh Kumar Saxena Trend of atmospheric metals by moss Hypnum cupressiforme Hedw. in Jammu (India)
- 12:30 Sheyar Abdo Mapping the spatial distribution of (Na, Cl, Ca, Mg) over Kaliningrad Oblast (Russia) by using ArcGIS PRO 2.4

#### 12:50 General discussion

#### 13:00 Session end

13:30 (for as long as needed) Break out rooms for poster viewing and general and informal discussions, including standard mosses and the specimen archive.

Note: Use the separate meeting joining link for breakout rooms.

#### Session: Ozone 1 Chair: Nivedita Chaudhary

- 13:30 *Evgenios Agathokleous* Ozone impacts on plant communities, plant-insect interactions, and plant-soil feedbacks
- 13:50 *Giacomo Gerosa* Ozone risk assessment for a deciduous mature forest from seven years of flux measurements
- 14:10 *Ignacio González-Fernández* Parametrization of soil moisture index in the DO3SE model for ozone risk assessment
- 14:20 Andrea Vannini Foliar applications of sweet chestnut (*Castanea sativa* Mill.) wood distillate shields a common horticultural plant (*Lactuca sativa* L.) from ozone induced damage
- 14:40 Posters, updates, annexes etc:

*Yasutomo Hoshika* – Forest monitoring for forest protection against ozone on the stomatal flux basis: The mottles approach (*Poster*)

Fanny Boublin – Potential role of proline in plant responses to ozone? (Poster)

*Zhaozhong Feng* – Ozone pollution threatens the production of major staple crops in east Asia

Katrina Sharps – Global modelling of ozone impacts on crops

Lisa Emberson – Latest developments with DO<sub>3</sub>SE model and application

Scientific Background Document – B updates

- 15:20 General discussion
- 15:30 Comfort break

#### Session: Ozone 2 Chair: Katrina Sharps

- 15:45 Clare Brewster µCT 3D imaging reveals effects of ozone on wheat grains
- 15:55 *Melissa Chang Espino* Nitrogen and carbon isotopic signalling in Mediterranean wheat under ozone fumigation and additional nitrogen
- 16:15 *Håkan Pleijel* Effects of ozone, drought and heat stress on wheat yield and grain quality
- 16:35 *Pritha Pande* Can ozone-flux response relationships for wheat be derived using photosynthetic based stomatal conductance models?
- 16:55 *Pierluigi Guaita* Use of data from local monitoring network to assess the ozone risk for crops at regional level: The Lombardy region case study

#### 17:15 General discussion including the Workplan

#### 17:30 Session end

#### Wednesday 23<sup>rd</sup> February, 2022

Session:	Moss 3	Chair:	Mike Perring
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- 09:30 *Inga Zinicovscaia* Accumulation of potentially toxic elements in mosses collected in the Republic of Moldova
- 09:40 Jeroen Geurts Moss survey in The Netherlands 2020-2021
- 09:50 Jana Borovská Biomonitoring of atmospheric deposition of heavy metals in Slovakia in 2020-2021
- 10:00 *Ágnes Bálint* Measurement of air deposition of heavy metals in the area of southwest Hungary using moss bioindication
- 10:10 Anastasia Zhuravleva Moss monitoring in the study of the accumulation of trace elements in the Udmurt Republic, Russia
- 10:20 *Musaj Paçarizi* Estimation of elements' concentration in air in Kosovo through mosses as biomonitors
- 10:30 General discussion
- 11:00 Comfort break

#### Session: Moss 4 Chair: Camiel Aggenbach

- 11:15 *Stefan Fränzle* Moss- and chitin-based monitoring: further pieces of information from adsorption thermodynamics
- 11:35 *Fabrizio Monaci* Atmospheric mercury monitoring by moss transplants: Current perspectives and limitations
- 11:55 *Alexander Uzhinskiy* Central Russia heavy metal contamination model based on satellite imagery and machine learning./development of Data Management System and Modelling
- 12:15 Kayla Wilkins Moss biomonitoring in Canada: A community science initiative
- 12:25 General discussion
- 13:00 Session end

#### Session: Ozone (3) and nitrogen

#### Chair: Rocío Alonso

- 13:30 *Per Erik Karlsson* Total deposition and canopy exchange of inorganic nitrogen to Norway spruce forests in Sweden
- 13:50 *Sabine Braun* Nitrogen effects on the vitality of *Fagus sylvatica* and *Picea abies* forests in Switzerland
- 14:10 *Raquel Ruíz-Checa* Use of labelled nitrogen to estimate foliar nitrogen uptake in Mediterranean holm oak forests
- 14:30 Valda Araminiene Situation with ground-level ozone and nitrogen in Lithuania during 2020-2021
- 14:50 *Sirkku Manninen* The relationship between NH<sub>3</sub> in urban air and the diversity of epiphytic macro lichens

#### 15:10 General discussion

15:20 Comfort break

#### Session: Ozone 4 Chair: Jürgen Bender

- 15:30 *Viki Bermejo* Pre and post-pollination tropospheric ozone effects in *Silene ciliate* a Mediterranean alpine species
- 15:50 Ane Vollsnes Ozone-induced early senescence studied in Trifolium repens genotypes from subarctic grasslands
- 16:10 Susana Elvira Risk of ozone injury in leafy crops under Mediterranean conditions
- 16:30 *Sabine Braun* Epidemiological estimate of growth reduction by ozone in *Fagus sylvatica* and *Picea abies*: Sensitivity analysis and comparison with experimental results
- 16:40 *Gudrun Schuetze* German experience and views on reporting exceedance of fluxbased critical levels in the context of EU regulations

#### 17:00 General discussion

17:30 Session end

### **LIST OF POSTERS**

### OZONE

Author(s)	Title	
Boublin et al.	POTENTIAL ROLE OF PROLINE IN PLANT RESPONSES TO	
	OZONE?	
Paoletti et al.	FOREST MONITORING FOR FOREST PROTECTION AGAINST	
	OZONE ON THE STOMATAL FLUX BASIS: THE MOTTLES	
	APPROACH	

### MOSS SURVEY

Author(s)	Title	Break- out Room	
Allajbeu et al.	ATMOSPHERIC DEPSITION STUDY OF		
	ANTHROPOGENIC METALS (Cr, Co, Fe, and Ni) BY MOSS		
	BIOMONITORING		
Bačeva	USING MOSS BIOMONITORS AS AN INDICATOR OF		
Andonovska et	RARE EARTH ELEMENTS DEPOSITS OVER SMALL		
al.	MINING AREA OF As, Sb and Tl		
Barandovski et	DISTRIBUTION OF THE AMBIENT RADIATION DOSE	MBIENT RADIATION DOSE	
al.	LEVEL BY USING PASSIVE MOSS BIOMONITORING IN		
	MACEDONIA		
Cakaj et al.	CENTAUREA CYANUS A NEW POSSIBLE	2	
	BIOINDICATOR FOR HEAVY METALS POLLUTION	2	
Hristozova et	PRELIMINARY DATA FROM THE 2020-2022 MOSS	2	
al.	SURVEY CONDUCTED IN BULGARIA		
Kosior et al.	THE MOSS BIOMONITORING METHOD AND NEUTRON	2	
	ACTIVATION ANALYSIS IN ASSESSING POLLUTION		
	BY TRACE ELEMENTS IN SELECTED POLISH		
	NATIONAL PARKS		
Nezha et al.	PRELIMINARY STUDY OF MICROPLASTICS		
	ATMOSPHERIC DEPOSITION STUDIED BY MOSS	3	
	BIOMONITORING		
Pacín et al.	MONITORING AND MAPPING PAH LEVELS IN PM10		
	AND BULK DEPOSITION USING MOSSPHERES: A PILOT	3	
	STUDY IN AN URBAN ENVIRONMENT		
Sopaj et al.	FIRST STUDY ON NITROGEN PRESENCE IN MOSSES	2	
1 5	SAMPLES IN KOSOVO BY KJELDAHL METHOD	3	
Stihi et al.	REVIEW OF 2010-2020 MOSS SURVEYS FOR HEAVY	4	
	METAL ATMOSPHERIC DEPOSITION IN ROMANIA		
Świsłowski et	MOSSES AS A BIOMONITOR OF AIR POLITION WITH		
al.	HEAVY METALS FROM POINT SOURCE OF POLLUTION		
Tepanosyan et	FACTORS CONDITIONING THE CONTENT OF		
al.	CHEMICAL ELEMENTS IN MOSSES AND SOILS OF		
	ARMENIA		

# PLENARY

### THE FORUM FOR INTERNATIONAL COOPERATION ON AIR POLLUTION (FICAP)

Sophie Standring, Alison Davies & John Salter

Air Quality and Industrial Emissions, Department for Environment, Food and Rural Affairs. UK

The UK and Sweden are co-chairing the new **Forum for International Cooperation on Air Pollution (FICAP)**. This Task Force has been established following the decision taken by the Executive Body for CLRTAP at its forty-first session held in December 2021.

As set out in the <u>mandate</u>, FICAP will promote international collaboration towards preventing and reducing air pollution to improve air quality globally. It will be a forum for international exchange of information and mutual learning on both the scientific/technical and policy levels. It is intended to be a repository for technical information and a convener of countries and organizations, with the goal of increasing international cooperation on addressing air pollution.

The Task Force will be comprised of experts from the Parties and other interested countries and international organizations acting in their personal capacity. Meetings will be open to representatives of intergovernmental or accredited non-governmental organizations, researchers, industry associations and other relevant organizations. Close collaboration with other Task Forces and Centres under Convention will be essential to the success of the new Task Force. The intention is for FICAP to be an efficient platform for mutual learning and information exchange of benefit to countries within as well as outside of the UNECE.

The first meeting of the Task Force is planned to take place in the United Kingdom on the week of  $10^{\text{th}} - 14^{\text{th}}$  October 2022 and the first broader meeting of the Forum will be held in Sweden in spring 2023 in Sweden.

We welcome your interest and involvement in the activities of FICAP and the contact details of the co-chair are below:

Sweden, Anna Engleryd Anna.engleryd@swedishepa.se

UK, John Salter John.Salter@defra.gov.uk

#### MOSS SURVEY 2020-2021-2022 SAMPLING IN COVID YEARS OF 2020 AND 2021

Frontasyeva M.<sup>1</sup>, Chaligava O.<sup>1,2</sup>

<sup>1</sup>Joint Institute for Nuclear Research, str. Jiliot-Curie, 6, 141980 Dubna, Moscow Region, Russian Federation, E-mail: marina@nf.jinr.ru

<sup>2</sup>Georgian Technical University, 77, str. Merab Kostava, 77, 0175 Tbilici, Georgia E-mail: omar.chaligava@ens.tsu.edu.ge

Since 1990, mosses have been used as biomonitors on a regular basis to study trends in the atmospheric deposition of trace elements in Europe [1, 2]. It was announced in 2020 that the planned moss survey for 2020/2021 was extended for 2022 because of the COVID-19 pandemic. Despite the hard pandemic conditions in the summer and autumn of 2020 and 2021, moss collection was undertaken in most of the European countries and in some Asian ones as well. An overview of this sampling campaign is presented and illustrated with a total sampling GIS map, as well as with individual sampling maps for the countries as they were created by the participants of the UNECE ICP Vegetation (moss surveys).

#### References

- Frontasyeva M. V., Steinnes E. and Harmens H. 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, pp.246.
- Frontasyeva M., Harmens H., Uzhinskiy A., Chaligava O. and participants of the moss survey. Mosses as biomonitors of air pollution: 2015/2016 survey on heavy metals, nitrogen and POPs in Europe and beyond. Report of the ICP Vegetation Moss Survey Coordination Centre, Joint Institute for Nuclear Research, Dubna, Russian Federation, pp. 136. ISBN 978-5-9530-0508-1. http://www1.jinr.ru/Books/Books\_rus.html

# **OZONE SESSIONS**

#### OZONE IMPACTS ON PLANT COMMUNITIES, PLANT-INSECT INTERACTIONS, AND PLANT-SOIL FEEDBACKS

#### Agathokleous E. et al.\*

#### School of Applied Meteorology, Nanjing University of Information Science and Technology (NUIST), Nanjing 210044, China evgenios@nuist.edu.cn

Worldwide research programs demonstrate that elevated ozone concentrations induce adverse effects on plants. This talk will summarize how elevated ozone affects directly plants and indirectly plant communities, plant-insect interactions and plant-soil microbe-soil abiotic condition interactions (so called plant-soil feedbacks). Elevated ozone alters plant community composition and diversity by affecting key plant physiological traits determining susceptibility to ozone. Elevated ozone -induced changes in the chemistry of leaves and leaf-emitted volatile organic compounds result in changes in plant-insect interactions, and, thus, insect community composition. Furthermore, elevated ozone affects plant-soil feedbacks by disrupting plant litter deposition, root exudates, soil enzymes activities, and the processes of decomposition and nutrient cycling. Consequently, the community composition of soil microbes is altered, and alpha diversity is reduced. These effects depend upon the environment and across space and time. Predictions of future ozone risks to biodiversity will be presented.

\*Co-authors (and their institutions) are those in Agathokleous et al. (2020)

#### Reference

Agathokleous, E., et al. (2020). Ozone affects plant, insect, and soil microbial communities: A threat to terrestrial ecosystems and biodiversity. Science Advances 6(33): eabc1176.

#### EPIDEMIOLOGICAL ESTIMATE OF GROWTH REDUCTION BY OZONE IN FAGUS SYLVATICA AND PICEA ABIES: SENSITIVITY ANALYSIS AND COMPARISON WITH EXPERIMENTAL RESULTS

#### Braun, S., Rihm, B., Schindler, C.

#### Institute for Applied Plant Biology AG, Witterswil, Switzerland, sabine.braun@iap.ch

The critical level of ozone flux for forest trees is based entirely on fumigation experiments with saplings, mostly in open top chambers. An extrapolation to mature forest asks therefore for a validation which may be performed by epidemiological data analysis. This requires a multivariable regression analysis with a number of covariates to account for potential confounding factors. The sensitivity of the ozone response of volume increment of mature European beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) has been analysed to the addition or removal of covariates. The comparison of the epidemiological dose-response relationship with experimental data shows a very good agreement in beech and a more sensitive relationship in the epidemiological analysis of Norway spruce compared to the experiments. In Norway spruce there was also a strong interaction between the effects of ozone and temperature: at high July temperatures the ozone effect was stronger. This interaction may explain the disagreement between the epidemiological study and the experiments of which the majority were performed in Sweden.

#### NITROGEN EFFECTS ON THE VITALITY OF FAGUS SYLVATICA AND PICEA ABIES FORESTS IN SWITZERLAND

#### Braun, S., Rihm, B., Tresch, S., Schindler, C.

#### Institute for Applied Plant Biology AG, Witterswil, Switzerland, sabine.braun@iap.ch

In large parts of the forest area in Switzerland, the critical load of nitrogen (N) is still exceeded although the deposition has decreased during the last decades. Long-term observations are needed to estimate these effects of N deposition, especially for naturally managed forests. We present long-term investigations from the Intercantonal Forest Observation Program in Switzerland covering 37 years of measuring tree growth, element contents in leaves and needles, crown condition as well as mortality and damages by wind. With the use of multiple binomial regressions we analysed the relation between environmental factors and mortality, uprooting and stem breakage in European beech (85 sites) and Norway spruce (67 sites).

Our results show that beech mortality was increased at low foliar phosphorus (P) and foliar potassium (K) concentrations. As both nutrients are negatively related with N deposition this can be regarded as an indirect effect of excess N deposition. Uprooting of beech was directly positively related to N deposition and drought, with an amplifying interaction between these two predictors. Stem breakage in beech was increased in old stands and with higher temperature of the vegetation period. Both uprooting and stem breakage are thus promoted by climate change.

Norway spruce mortality is mainly caused by bark beetle attacks, which increases after drought and storm damage. Our data show that at sites with high N deposition the drought effect on mortality was strongly increased, suggesting that N is increasing the sensitivity to bark beetle attacks. Stem breakage of spruce was also positively correlated with N deposition. Uprooting was higher at low foliar K concentration. There was also a positive relation with drought.

Uprooting of both beech and Norway spruce was increased at higher temperature during the vegetation period and during winter.

Although the results differ between Norway spruce and beech, both species show a clear effect of N deposition and climate change on the reduction in survival, either by mortality or by wind damage.

#### µCT 3D IMAGING REVEALS EFFECTS OF OZONE ON WHEAT GRAINS

Brewster C.<sup>1,2</sup>, Corke F.<sup>3</sup>, Nibau C.<sup>3</sup>, Fenner N.<sup>2</sup>, Hayes F.<sup>1</sup>

<sup>1</sup>UK Centre for Ecology & Hydrology, Environment Centre Wales, Bangor, UK; <sup>2</sup>Bangor University, School of Natural Sciences, Bangor, UK; <sup>3</sup>Aberystwyth University, The National Plant Phenomics Centre, IBERS, Aberystwyth, UK;

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Elevated levels of ground-level ozone, the dominant air pollutant affecting crop growth, are estimated to reduce global wheat yields, on average, by 7 - 10 %, with grain quality also affected. Determining how and where the yield loss occurs, both on the spike and with changes in grain shape, provide insights into the abiotic stress response. X-ray microcomputed tomography (µCT) imaging enables 3D visualisation of spikes with their grains *in situ*, along with the extraction of grain morphology data with positional information. A line of spring Primary Synthetic Hexaploid (SHW) wheat, along with Triticum aestivum c.v. 'Paragon', and nine lines of synthetic hybrids derived from these parent lines were grown for 3 months in solardomes (Bangor, North Wales) under low (30 ppb), medium (55 ppb), high (80 ppb) and very high (110 ppb) levels of ozone. Chlorophyll measurements of the flag, 2<sup>nd</sup> and lower leaves were made before, at, and after flowering. At harvest, spike biomass was used as an indicator of tolerance/sensitivity and four lines were selected for µCT imaging. The three heaviest spikes from each replicate were scanned and 3D grain traits (volume, surface area, circularity, length, width and depth), as well as grain number and position along the spike, were extracted from the 3D images. A manual count of grain numbers per spikelet was also made. Total grain weight and 1000 grain weight were obtained following threshing, along with protein and starch levels using Near Infrared Spectrometry. 'Paragon' and BC1 maintained their total and 1000 grain weights under medium and high ozone levels by preserving higher grain numbers per spikelet, particularly across the middle of the spike. They also maintained grain size and protein/starch levels. Both BC5 and BC7 had reductions in total grain weight and 1000 grain weight between the medium, high and very high ozone levels, linked to reduced grain volume and grain number per spikelet. Grain volume reductions were driven more by reduced width and depth than by reduced length. Before flowering, there was no effect of ozone on chlorophyll levels in the flag leaves of all four lines, but there were reductions in both 2<sup>nd</sup> leaves and lower leaves in the high and very high ozone levels at flowering and post-flowering, with the least effect shown in Paragon and the greatest in BC7. The causes of ozone-induced yield reductions, and potential commonalities with other abiotic stresses, are discussed.

#### EFFECTS OF OZONE, DROUGHT AND HEAT STRESS ON WHEAT YIELD AND GRAIN QUALITY

Broberg M.C.<sup>(1)</sup>, Hayes F.<sup>(2)</sup>, Harmens H.<sup>(2)</sup>, Uddling J.<sup>(1)</sup>, Mills G.<sup>(2)</sup>, Pleijel H.<sup>(1)</sup>

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<sup>(2)</sup> UK Centre for Ecology & Hydrology, Bangor, UK

Tropospheric ozone (O3) is a phytotoxic plant stressor, known to reduce wheat crop yields even at current concentrations. Emission scenarios predict O3 to increase in many cropgrowing regions, together with higher frequencies of heatwaves and droughts. In this study, wheat crops were grown in solar domes under two levels of O3 in combination with ambient or elevated temperature and two watering regimes. With this experimental setup, we assessed the interactive effects between O3, temperature and watering on wheat yield and grain quality, and measured leaf gas exchange to explore the underlying mechanisms.

Overall, O3, drought and warming all decreased grain yield and average grain mass and increased N concentrations. However, there were also significant interactions between O3 and water supply for light saturated photosynthesis, grain mass and concentrations of several nutrients in the grains (K, Ca, Mg, Mo), with the effects of O3 reduced by drought. In contrast, grain concentrations of K and Ca increased to a larger extent when O3 stress was combined with elevated temperature. Grain concentrations of N, Ca and Zn were closely linked to grain yield regardless of O3, heat and drought stress. P, K, Mg, Mn, Mo were weakly related to grain yield but concentrations were clearly altered by environmental stress. These response patterns were likely linked to the reduction in grain filling period, with starch accumulation reduced to a larger extent than that of N and other nutrients. The modifying effect of water availability is crucial to include in assessments of O3 impacts on global food production, considering effects on wheat yield variables and grain nutrient concentrations.

#### RISK OF OZONE INJURY IN LEAFY CROPS UNDER MEDITERRANEAN CONDITIONS

<u>Elvira S.</u>, González-Fernández I.<sup>1</sup>, Calatayud V<sup>2</sup>., Sanz J.<sup>1</sup>, Alonso R.<sup>1</sup>, Bermejo V.<sup>1</sup>, <sup>1</sup>CIEMAT, Madrid, Spain; <sup>2</sup>CEAM, Valencia, Spain

There is ample evidence that current ozone  $(O_3)$  levels in Europe, especially in the Mediterranean area, induce negative effects on different horticultural crops (Fumagali, 2001). Ozone causes a wide range of damage to agricultural crops, including visible damage, reduced photosynthesis, altered carbon allocation and reduced yield quantity and quality (Ashmore, 2005; Emberson et al., 2018).

Yield data from fumigation experiments have been used to derive exposure and dose-response relationships for some horticultural crops and critical levels of  $O_3$  (CLe) have been established for a set of representative species. The experimental dataset for tomato was considered of sufficient quality for establishing a CLe and was chosen as a representative species of Mediterranean horticultural crops to perform risk assessments of  $O_3$  effects (González-Fernández et al., 2014). However, it has been recognized that the species selected for the derivation of  $O_3$  CLe may not be the most sensitive, which means that the effects of  $O_3$  on production horticultural may be occurring at  $O_3$  levels below the current CLe.

The consumption of leafy crops has a long tradition worldwide both for their organoleptic properties and for their multiple benefits for human nutrition. The characteristic green leaves of this species represent an important source of both minerals and vitamins. Leafy crops also represent one of the most important horticultural crops for many countries in Southern Europe.

Leafy crops have been recognized as highly susceptible to ozone. Visible damage to the leaves leads to yield reduction, sometimes to the total loss of the crop. In addition, alterations in the nutritional value of the leaves have been detected with a reduction in the content of some macronutrients. These crops often have a rapid growth rate associated with high gas exchange rates that favor the uptake of pollutants. For these reasons, leaf crops are probably more sensitive to  $O_3$  than tomato, the representative crop used for risk assessments of  $O_3$  effects on horticultural production in Mediterranean areas.

Studies carried out in the Mediterranean area in recent years present an opportunity to assess the risk of ozone damage in leafy crops. The database provided by the CIEMAT group analyzes the sensitivity to ozone in commercial varieties of chard, spinach, lettuce and endives. These results will be discussed in combination with other studies on  $O_3$  effects on leaf crops in to try to improve the experimental basis for establishing a common  $O_3$  CLe for these crops.

This study is funded by Ministry of Ecological Transition of Spain, ACTUA-MITERD project.

References : Ashmore, 2005, Plant Cell Environ 28(8), 949-964; Emberson et al., 2018, Eur.J.Agron. 100, 19-34;Fumagalli et al., 2001, Atmos.Env. 35, 2583-2587; González-Fernández et al., 2014, Env.Pol. 185, 178-187.

#### OZONE POLLUTION THREATENS THE PRODUCTION OF MAJOR STAPLE CROPS IN EAST ASIA

Zhaozhong Feng<sup>1</sup>, Yansen Xu<sup>1</sup>, Kazuhiko Kobayashi<sup>2</sup>

<sup>1</sup>Nanjing University of Information Science & Technology, Nanjing 210044, China; <sup>2</sup>Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, Japan E-mail:zhaozhong.feng@nuist.edu.cn

East Asia is a hotspot of surface ozone  $(O_3)$  pollution, which hinders crop growth and reduces yields. Here, we assess the relative yield loss in rice, wheat and maize due to  $O_3$  by combining  $O_3$  elevation experiments across Asia and air monitoring at about 3,000 locations in China, Japan and Korea. Based on the field experiments conducted in Asia, the ozone dose-yield response relationships were built for wheat, rice and maize, respectively (Figure 1). China



shows the highest relative yield loss at 33%, 23% and 9% for wheat, rice and maize, respectively. The relative yield loss is much greater in hybrid than inbred rice, being close to that for wheat. Total O<sub>3</sub>-induced annual loss of crop production is estimated US\$ at 63 billion. The large impact of  $O_3$  on crop production urges us to take mitigation action for O<sub>3</sub> emission control adaptive and agronomic measures against the rising surface O<sub>3</sub> levels across East Asia.

**Figure 1** |  $O_3$ -enrichment experiments for rice, wheat and maize conducted in Asia. **a**–**c**, Relationships between AOT40 for 90 d until maturity and RY of rice (**a**), wheat (**b**) and maize (**c**) in Asia. Each point represents the yield relative to that at zero AOT40 for each dataset. The solid lines represent the relationship between AOT40 and RY, whereas the dashed lines represent the 95% CI of the relationship (not the individual observations). In **a**, the filled circles represent hybrid cultivars, whereas unfilled circles represent inbred cultivars.

#### OZONE RISK ASSESSMENT FOR A DECIDUOUS MATURE FOREST FROM SEVEN YEARS OF FLUX MEASUREMENTS

Gerosa Giacomo, Marzuoli Riccardo, Finco Angelo.

Department of Mathematics and Physics, Catholic University, via Garzetta 48, Brescia (Italy), giacomo.gerosa@unicatt.it

Multiannual measurements of ozone  $(O_3)$  fluxes were performed from 2012 to 2020 in a mature oak-hornbeam forest of the Po valley, Italy. Fluxes were measured with the eddy covariance technique on a 41 m tower, 15 m above the forest canopy. A flux partition between stomatal and non-stomatal component was performed based on concomitant water and carbon dioxide measurements.

The analysis of the flux variability and its determinants revealed that the interannual variability of the total  $O_3$  flux was mainly driven by the stomatal activity in summer. Therefore, those factors that influence stomatal conductance were responsible for the flux variability, with soil water content being the main physiological driver. Despite the interannual variability, the stomatal fraction of the total flux was fairly constant around 42% on a 24-hour basis, with an average summer value of 52% and a maximum around 60% during the daylight hours.

The non-stomatal deposition was mainly driven by air humidity, by surface wetness and by chemical sinks such as reaction of  $O_3$  with nitric oxide (NO) emitted by soil in the summer season, or advected in the trunk space in winter. Wind speed, turbulence intensity and surface temperature instead, did not show any increasing effect influence on the magnitude of the non-stomatal fraction, and this would exclude impaction or thermal decomposition on surfaces from being important drivers of the total  $O_3$  fluxes. Deposition on leaf cuticles was the main  $O_3$  removal pathway in the evening and during the first hours of the night.

As far as concerns the  $O_3$  risk analysis for vegetation, the POD<sub>1</sub> (Phytotoxic  $O_3$  Dose above 1 nmolO<sub>3</sub> m<sup>-2</sup> s<sup>-1</sup>) for the whole ecosystem ranged from a minimum of 17.7 mmolO<sub>3</sub> m<sup>-2</sup> (2015) to a maximum of 37.1 mmolO<sub>3</sub> m<sup>-2</sup> (2018), with an annual average of 26.4 mmolO<sub>3</sub> m<sup>-2</sup>. Considering on average a Leaf Area Index of 2.5 m<sup>2</sup>/m<sup>2</sup> between April and October, the annual average value was equivalent to a POD<sub>1</sub> of 10.5 mmol m<sup>-2</sup>. This value is lower than the critical level for total biomass established by the UNECE for the protection of Mediterranean deciduous oak forests, but slightly higher than the critical level for significant negative effects on roots biomass growth. Based on the available dose-response relationships for deciduous oaks, an annual growth reduction of the total biomass ranging between 1.83% and 4.30% was estimated.

Although the effect of  $O_3$  may seem small, these estimations confirm that the current  $O_3$  flux levels represent a persistent stress for this forest ecosystem, with effects at growth level that may be a threat for the ecosystem stability and contribute to the oaks decline already taking place in the site.

#### PARAMETRIZATION OF SOIL MOISTURE INDEX IN THE DO<sub>3</sub>SE MODEL FOR RISK ASSESSMENT

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The assessment of the risk of ozone  $(O_3)$  effects on natural vegetation and crops needs to take into account the effect of climate change variables in plant physiology in order to model the response of plants to  $O_3$  under future climatic conditions. For this, dose-based risk assessment methodologies, such as the calculation of species-specific phytotoxic  $O_3$  doses (POD) with the DO<sub>3</sub>SE model, are better suited than concentration-based approaches. However this methodology still needs adjustments in order to be able to model POD under future pollution and climate scenarios.

Soil moisture is currently one of the main drivers of POD and its importance is foreseen to increase in the coming decades. The EMEP MSC-W Chemical Transport Model have made use of the Soil Moisture Index (SMI) from the European Centre for Medium Range Weather Forecast to model the effect of varying soil moisture availability on POD using a standard parametrization for all the species. However, preliminary sensitivity analysis at the plot scale have shown that the function describing SMI control ( $f_{SMI}$ ) on stomatal conductance ( $g_{sto}$ ) has an important effect on modelled POD and that this relationship may be species-specific.

Species-specific  $f_{SMI}$  function for Mediterranean species are being developed based on predawn leaf water potentials or soil moisture observations and measured  $g_{sto}$  values reported in the scientific literature. The SMI was estimated using site-specific data on soil hydraulic properties or the Mualem- an Genuchten Model (van Genuchten, 1980; Mualem, 1976) parameterized using hydraulic pedotransfer functions for Europe (Szabó et al., 2021) or soil hydraulic database of Europe (Toth et al., 2017). The new species-specific  $f_{SMI}$  are being tested under different soil depths, soil textures and type of forest. Preliminary results will be presented and recommendations for POD modelling and future activities will be discussed.

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References: van Genuchten, Soil Sci. Soc. Am. J., 44, 892–898; Mualem, 1976, Water Resour. Res., 12, 513–522; Szabó et al., 2021, Geosci. Model Dev., 14, 151–175; Tòth et al., 2017, Hydrological Processes 31:2662–2666.

#### USE OF DATA FROM LOCAL MONITORING NETWORK TO ASSESS THE OZONE RISK FOR CROPS AT REGIONAL LEVEL: THE LOMBARDY REGION CASE STUDY

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Ozone  $(O_3)$  toxicity for plants has been widely described in the last decades and the negative effects of  $O_3$  were found to be related to the  $O_3$  stomatal flux rather than the concentration of this gas in the air. However, stomatal flux calculation requires the use of dry deposition models that consider both plant physiology and turbulent exchange between atmosphere and vegetation.

Hourly data of temperature, relative humidity, wind speed, global radiation, rainfall, and  $O_3$  concentration -provided by the air quality monitoring networks of Lombardy and of the nearby regions and states (Switzerland)- for the reference year 2017 were collected to assess the  $O_3$  cumulative stomatal flux for crops in Lombardy region (Italy), and to estimate the related yield losses. Winter wheat was chosen as reference crop, as suggested by the UN/ECE mapping manual.

The altitude dependence of many variables was removed by linear detrending, then a semiautomatic Krieging procedure was used to spatialize the meteo-chemical data. The spatialized data were entered in a deposition model consisting of three submodules: the first submodule calculates the stomatal conductance ( $g_{stom}$ ) by a Jarvisian approach; the second one calculates the soil water content through a simple water balance approach ("bucket" model); the third one calculates the turbulent exchange of heat, H<sub>2</sub>O and O<sub>3</sub> between vegetation and atmosphere through a big-leaf double source/double sink approach. Crop's geometry (plants height, LAI and root biomass) and phenology were calculate by means of thermal sums-based dynamical functions.

The model is analogous to the well-established DO<sub>3</sub>SE model, even though it still does not distinguish between sunlit and shaded canopy.

The implemented tool allowed to develop  $O_3$  cumulative flux maps (based on the POD6 metrics) and  $O_3$  exposition maps (based on the AOT40) for a 280x312 km<sup>2</sup> domain centred on the Lombardy region with a resolution of 1x1 km<sup>2</sup>. At the same time, the tool allowed to visualize the evolution of the flux drivers at some user-chosen grid nodes.

The analysis showed that  $O_3$  stomatal flux exceeded of almost three times (3.93 mmolO<sub>3</sub> m-2) the UN/ECE critical level for crop protection (1 mmolO<sub>3</sub> m-2) and that  $O_3$  might have caused about 16% of grain loss in 2017, corresponding to an economical loss of about 12 MIL euro.

The functions describing the  $O_3$  effects on stomatal conductance ( $f_{O3}$ ) as well as the effects of soil water on  $g_{stom}$ , revealed to be crucial in many grid nodes. Regarding the latter, the hypothetical removal of any soil water limitation led to an increase of the POD6 of about 35%. By presenting this tool and the resulting maps, some relevant aspects related to the mapping procedure will be shown, *e.g.* the importance of altitudinal detrending for orographic complex territories and the optimization of the krieging procedure to reduce the calculation time.

#### TOTAL DEPOSITION AND CANOPY EXCHANGE OF INORGANIC NITROGEN TO NORWAY SPRUCE FORESTS IN SWEDEN

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The dry and wet deposition of nitrate,  $NO_3^-$ , and ammonium,  $NH_4^+$ , were estimated for Norway spruce forests with a full spatial coverage across Sweden for the 20-year period 2001-2022. The particulate dry deposition was estimated based on measurements using Teflon string samplers as surrogate surfaces, in combination with the net throughfall deposition for sodium (throughfall subtracted with wet deposition). The wet deposition was estimated from bulk deposition measurements, corrected for dry deposition to the collectors. The results were based on a novel method to apply estimates of the dry deposition based on measurements at a limited number of sites, to a larger number of sites with only bulk deposition measurements, in turn based on the existence of a strong geographical gradient in the dry deposition of inorg-N from southwest to northeast Sweden. There was a strong gradient for inorg-N deposition across Sweden from north to southwest, ranging from 2 to 20 kg N ha<sup>-1</sup> yr<sup>-1</sup>. Clear time trends were demonstrated for decreased deposition of inorg-N to Norway spruce forests over the 20-year period in all parts of Sweden, in line with the decrease in the reported emissions of inorg-N from Europe. Based on comparisons between total and throughfall deposition, the direct canopy uptake of atmospheric N deposition to Norway spruce forests in Sweden was estimated to be in the range of 0-7 kg N ha<sup>-1</sup> yr<sup>-1</sup>.

**References:** 

- Karlsson, P.E., Pihl Karlsson, G., Hellsten, S., Akselsson, C., Ferm, M., Hultberg H. 2019. Total deposition of inorganic nitrogen to Norway spruce forests – applying a surrogate surface method across a deposition gradient in Sweden. *Atmospheric Environment* 217, 116964. doi.org/10.1016/j.atmosenv.2019.116964
- Karlsson, P.E., Akselsson, C. Hellsten, S., Pihl Karlsson, G. 2022. Twenty years of nitrogen deposition to Norway spruce forests in Sweden. *Science of the Total Environment* 809, 152192.

#### THE RELATIONSHIP BETWEEN NH3 IN URBAN AIR AND THE DIVERSITY OF EPIPHYTIC MACRO LICHENS

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Emissions of reactive N compounds from traffic are implicated in changing the diversity of epiphytic lichens with a shift to nitrophytes (Davies et al. 2017). The increasing use of three-way catalysts in cars (Borsari & de Assuncâo 2017) and Selective Catalytic Reduction systems in diesel vehicles (Stelwagen & Ligterink 2015) reduces the emissions of NO<sub>x</sub> but increases NH<sub>3</sub> emissions (Reche et al. 2012). NH<sub>3</sub> is harmful especially to acidophytic lichens (Wolseley et al. 2009). We studied the relationship between ambient NH<sub>3</sub> concentration and the diversity of epiphytic lichens in Helsinki, southern Finland, to verify the results of a previous study by Manninen (2018) which suggested that NH<sub>3</sub> emissions from vehicles in the area may be high enough to affect lichens.

Epiphytic macrolichens were scored on *Acer platanoides*, *Ulmus glabra*, *Quercus robur*, and *Pinus sylvestris* trunks at 20 sites in Helsinki ( $60^{\circ}10^{\circ}N$ ,  $24^{\circ}56^{\circ}E$ ) in Jul-Oct 2019. The scoring was carried out based on the European Standard EN 16413:2014. Bark samples were collected for pH measurements. Monthly NH<sub>3</sub> concentrations were measured for two years (Oct 2019 - Sep 2021) with passive samplers (ALPHA<sup>®</sup>, Tang et al. 2001). Lichens species with eutrophication scores of 1-4 were classed as acidophytes and those with 5-9 as nitrophytes (Wirth 2010). A Lichen Diversity Value was calculated separately for each tree species per site (LDV<sub>site</sub>) as were the corresponding values for acidophytes (LDVA<sub>site</sub>) and nitrophytes (LDVN<sub>site</sub>).

The monthly NH<sub>3</sub> concentrations ranged from 0.0 to 3.3  $\mu$ g/m<sup>3</sup>. The average bark pH values were: *Pinus* 3.30, *Quercus* 4.84, *Acer* 5.35, *Ulmus* 5.65. The nitrophyte *Physcia tenella* had the highest abundance across the sites, followed by the nitrophytes *Xanthomedoza fulva* and *Parmelia sulcata*, and the acidophyte *Hypogymnia phyosodes*. LDVA<sub>site</sub> was negatively correlated with both NH<sub>3</sub> concentration and bark pH, while LDVN<sub>site</sub> increased with increasing bark pH across the tree species. At the tree species level, the diversity of macro lichens on *Quercus* seemed to be the best indicator of NH<sub>3</sub>.

Borsari & de Assuncâo 2017, Transport and Environment, 51, 53-61; Davies et al. 2007, Environ. Pollut. 146, 299-310; Manninen 2018, Sci. Total Environ. 613-614, 751-762; Reche et al. 2012, Atmos. Environ. 57, 153-164; Stelwagen & Ligterink 2015, TNO report R11005, 45 pp.; Tang et al. 2001, The Scientific World, 1, 513-529; Wirth 2010, Herzogia 23, 229-248; Wolseley et al. 2009, In: Sutton et al. (eds), *Atmospheric Ammonia*. Springer Science + Business media B.V., pp. 101-108.

#### CAN OZONE-FLUX RESPONSE RELATIONSHIPS FOR WHEAT BE DERIVED USING PHOTOSYNTHETIC BASED STOMATAL CONDUCTANCE MODELS?

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Ozone causes a range of impacts to wheat, an ozone-sensitive crop (Feng, Kobayashi, and Ainsworth, 2008). Ozone known to alter stomatal conductance, reduce net photosynthesis, and induce early senescence (Gelang et.al., 2000; Mashaheet et.al., 2020). A study has estimated ozone-led wheat yield losses of around 85 million tonnes globally (Mills et.al.,2018). It is a problem given the importance of wheat as a staple crop to approximately 35% of the world population (Grote *et al.*, 2021), and 747 million tonnes of wheat are consumed worldwide in a year (FAO., 2020). Thus, accurate estimation of yield losses due to ozone is vital. Studies have used the empirical multiplicative stomatal conductance model (gsto) to estimate phytotoxic ozone flux (POD), a flux-base index (Pleijel et.al., 2007). This is used to derive flux (ozone)-response (relative yield) relationships. They are used to establish critical levels for wheat crop within Europe (Mapping Manual, 2017). An alternate to this model is the mechanistic photosynthesis- stomatal conductance (Anet-gsto) model, which becomes entirely environment-driven when coupled with the photosynthetic model. Hence, perhaps provide a more 'real' estimate of the POD than multiplicative model. However, to provide a valid alternative to empirical models, mechanistic models should predict comparable flux-response curves and estimates of gsto. Therefore, this study focus on i) to compare the ability of Anet-gsto and multiplicative to derive flux-response relationship, ii) to compare the Anet-gsto model ability to simulate gsto, and, iii) to assess the ability of Anetgsto models to simulate ozone damage to photosynthesis and leaf senescence.

Feng Z, Kobayashi K, Ainsworth EA .,2008. Impact of elevated ozone concentration on growth, physiology, and yield of wheat (Triticum aestivum L.): a meta-analysis. *Glob Change Biol* 14: 2696–2708.

Johanna Gelang, H. Pleijel, E. Sild, H. Danielsson, S. Younis, G. Sellden.Rate and duration of grain filling in relation to flag leaf senescence and grain yield in spring wheat (Triticum aestivum) exposed to different concentrations of ozone.,2000. Physiol. Plant., 110, pp. 366-375

A Mashaheet M, K Burkey O, C Saitanis J, A Abdelrhim S, R Rafiullah, D Marshall S.,2020. Differential ozone responses identified among key rust-susceptible wheat genotypes. Agronomy, 10, Article 1853

G. Mills, K. Sharps, D. Simpson, H. Pleijel, M. Broberg, J. Uddling, F. Jaramillo, W.J. Davies, F. Dentener, M. Van den Berg, M. Agrawal, S.B. Agrawal, E.A. Ainsworth, P. Büker, L. Emberson, Z. Feng, H. Harmens, F. Hayes, K. Kobayashi, E. Paoletti, R.Van Dingenen.,2018. Ozone pollution will compromise efforts to increase global wheat production.Global Change Biol., 24, pp. 3560-3574

H. Pleijel, H. Danielsson, L. Emberson, M.R. Ashmore, G. Mills.,2007. Ozone risk assessment for agricultural crops in Europe: further development of stomatal flux and flux–response relationships for European wheat and potato.Atmos. Environ., 41, pp. 3022-3040

U. Grote, A. Fasse, T.T. Nguyen, O. Erenstein.,2021.Food security and the dynamics of wheat and maize value chains in Africa and Asia.,2021.Front. Sustain. Food Syst., 4, p. 617009

LRTARP ConventionManual on Methodologies and Criteria for Modelling and Mapping Critical Loads & Levels and Air Pollution Effects, Risks and Trends., 2017.(Chapter 3): Mapping critical levels for vegetation

#### PRE AND POST-POLLINATION TROPOSPHERIC OZONE EFFECTS IN Silene ciliata A MEDITERRANEAN ALPINE SPECIES

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Due to the proximity to cities and the Mediterranean climatic conditions, alpine ecosystems of Madrid area are under a great pressure from air pollutants. This is the case of tropospheric ozone ( $O_3$ ), which precursors are formed in cities and industrial zones but transported in the atmosphere by dominant winds, travelling long distances and finally causing large amounts of  $O_3$  in areas far away from the source of emissions. Mountainous area surrounding the northwest of Madrid area falls under this situation. At "*Sierra de Guadarrama*" the actual  $O_3$  concentration chronically exceed the levels for plant conservation. The main objective of this study was to evaluate the possible effects of this pollutant on the reproduction of insect-pollinated alpine plants, many of them very valuable because their status of endemic or protected flora.

To assess the possible  $O_3$ -effects on the pre and post-pollination on the alpine species of Madrid, we performed an OTC (Open Top Chamber) experiment. Ozone treatments ranged from preindustrial  $O_3$  levels to the maximum actual levels recorded in Madrid mountains. An additional treatment without OTC was used to control for OTC microclimatic effects (mainly characterize by a temperature increase) on the studied variables. The selected species for this study was *Silene ciliata* (Figure 1A), an alpine species which was exposed to the different  $O_3$  treatments for 84 days. As pre-pollination variables, flower phenology and nectar production were measured. Pollen tube growth inside the stile (Figure 1B), fruit formation and number of seeds were taken as post-pollination variables.

As pre-pollination  $O_3$ -effect, we detected a delay of the flower phenology. After pollination, the  $O_3$  affect negatively the number of pollen tubes, fruits and seeds. The modification of the flowering time may mismatch the flower phenology with the pollinator activity, and also affect the reproductive fitness in an alpine drought context. To this, we have to add the negative effects after the pollination, decreasing the reproduction fitness in this species.



Figure1. A) Silene ciliata flower. B) Pollen tubes growing inside the style.

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#### USE OF LABELLED NITROGEN TO ESTIMATE FOLIAR NITROGEN UPTAKE IN MEDITERRANEAN HOLM OAK FORESTS

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Atmospheric nitrogen (N) deposition exceeds the empirical critical loads established for the conservation of some ecosystems in Spain. Previous risk studies have identified Mediterranean sclerophyllous forests of Holm oak (*Quercus ilex*) as one of the ecosystems threaten by atmospheric N deposition (1). To comprehend the effects of this pollutant, it is important to understand and complete the N cycle in this ecosystem, including the input of wet and dry N deposition, the retention and transformation that occurs within the canopy, plant absorption and remobilization, and losses as soil gases emissions or leaching.

An important part of this cycle is the rate of nitrogen uptake by the canopy. To estimate foliar N retention and possible seasonal changes in the retention rates in Holm oak forest, a shortterm fertilisation experiment with labelled ammonium (15N-NH<sub>4</sub>) and nitrate (15N-NO<sub>3</sub>) has been carried out. Solutions were prepared to simulate conditions of low and high N deposition, based on deposition data reported from previous studies (2). Ten branches in six trees were marked and prewashed before fertilisation. Once dry, 2 branches per tree were thoroughly sprayed with 5 different treatments: control, low and high NH<sub>4</sub>, low and high NO<sub>3</sub>. Two consecutive fertilisations were performed. Branches were collected 1 hour after the last fertilisation and brought to the lab for processing. Branches were rinsed with deionized water to remove nutrients retained on plant surfaces and current and one-year leaves were separated before grinding for isotope analyses. In addition to fertilisation, ecophysiological measurements were taken to assess whether there is a relationship between uptake rates and plant activity and meteorological conditions. All measurements were performed 4 times throughout the year on a seasonal basis. Preliminary results will be presented showing that Holm oak leaves are able to absorb both oxidised and reduced N compounds, with higher rates of NH<sub>4</sub> absorption.

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- (1) García-Gómez H, Garrido JL, Vivanco MG, et al. 2014. Sci Total Environ 485-486:450-460.
- (2) García-Gómez, H., Izquieta-Rojano, S., Aguillaume, L., et al. 2018. Environmental Pollution, 243, 427-436.

#### GERMAN EXPERIENCE AND VIEWS ON REPORTING EXCEEDANCE OF FLUX-BASED CRITICAL LEVELS IN THE CONTEXT OF EU REGULATIONS

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Article 9 and 10 of the EU National Emission Ceilings Directive (2016/2284/EU, NECD) oblige Member States to perform monitoring of impacts of air pollution on ecosystems and to report the results to the European Environment Agency (EEA). As a part of this reporting Germany provided information on exceedance of flux-based Critical Levels for ozone for 21 stations of the National Air Monitoring Network. While much more stations of this network can provide hourly data on ozone concentrations, such stations were selected, which could provide measured meteorological data needed for the calculation of the species specific Phytotoxic Ozone Dose (POD<sub>Y</sub>SPEC) and its exceedance.

The international recommended model for POD<sub>Y</sub>SPEC calculation is DO<sub>3</sub>SE, but it requires various input data, which were not measured at the monitoring stations. Therefore, a simplified model was used, developed by L. Grünhage and programmed in Excel. It is based on the methodology as in chapter 3 of the Modelling and Mapping Manual and its variants enable calculation for beech and spruce (model variant Random Forest, rFO<sub>3</sub>REST), wheat (rCRO<sub>3</sub>PS) and grassland (rGRASSLANDO<sub>3</sub>). To run these models only hourly data on ozone concentration and temperature are needed. The other meteorological parameters are modelled or defined by a default value. Approximative results gained by use of these models have good agreement with results of more complex models such as DO<sub>3</sub>SE, but an uncertainty interval due to the simplification has to be declared.

The selection of indicators and monitoring networks or models for the reporting to the NECD is up to the countries. In the "First analysis of ecosystem Monitoring as required under Art 9 of the NECD" provided by the EEA (Reference 3417/B2017/EEA) it showed up that only few countries provided data on flux-based Critical Level exceedance. We think that the application of this indicator in the reporting could be extended, if either modelled meteorological data could be used or if simplified models would be applied.

The start of legislative work for the revision of the EU's Ambient Air Quality Directive is scheduled for 2022. The monitoring work under this Directive focuses on fixed stations. From the German perspective indicators for assessing local risks of ozone for vegetation should be based on calculations of  $POD_YSPEC$ . However, non-exceedance of the Critical Levels might be too ambitious, so that target values should be defined as interim goals. A methodology has been derived by L. Grünhage and published in VDI Guideline 2310 Part 6 to calculate target loads based on the ozone pollution level of the 1980ths, but also other options for target load derivation are thinkable.

#### FOLIAR APPLICATIONS OF SWEET CHESTNUT (CASTANEA SATIVA MILL.) WOOD DISTILLATE SHIELDS A COMMON HORTICULTURAL PLANT (LACTUCA SATIVA L.) FROM OZONE-INDUCED DAMAGE

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Since the mid-20<sup>th</sup> century, global background ozone (O<sub>3</sub>) concentrations have rapidly increased, with the present concentrations being estimated as responsible for a 3-15% reduction in crops yield, thus generating a remarkable economic loss. Currently, the use of antioxidants – i.e. vitamins, phytohormones, flavonoids, and polyamines – represents a very promising strategy to protect crop plants from O<sub>3</sub> phytotoxicity. However, further investigation is still needed towards the identification of the best and indeed sustainable strategy for the protection of horticultural plants from the phytotoxic action of the O<sub>3</sub>.

Wood distillate (WD), commonly known as pyroligneous acid and wood vinegar, is a bio-based liquid product obtained from the distillation of the gases produced during the pyrolysis of woody biomass for the production of green energy. Such product, still unknown in many agricultural sectors (especially those not involved in organic farming), is now having great success in agriculture as a phytostimulant for crop plants since its use can enhance both plant productivity and endogenous defenses against pathogens. Results from a study conducted on the horticultural plant *Lactuca sativa* (L.) reveal that foliar applications of 0.2% WD deriving from sweet chestnut (*Castanea sativa* Mill.) can enhance the content of chlorophyll and biomass of this model species (Vannini et al. 2021), probably thanks to its higher content of antioxidant compounds, such as polyphenols (Fačkovcová et al. 2020). The effectiveness of WD in contrasting the phytotoxic action of O<sub>3</sub> on plant metabolism is still unexplored.

This study examines whether foliar applications of WD have a protective effect on photosynthesis and nutritional values of lettuce exposed to an ecologically relevant  $O_3$  concentration. Seedlings of lettuce were fumigated daily with 60 ppb of  $O_3$  (slightly higher than the 50 ppb measured on average in Europe during Summer) for 30 days, for five hours per day; once per week, 50% of the fumigated plants were treated with foliar applications of 0.2% WD. The results of the present study clearly showed the ability of WD to protect lettuce plants from ozone-induced damage. Specifically, treated plants exhibited lower damage to the photosynthetic machinery (assessed through a number of chlorophyll fluorescence parameters), a higher content of chlorophylls, a higher concentration of nutritional molecules (i.e. caffeic acid and quercetin), and higher biomass.

#### References

Fačkovcová, Z., Vannini, A., Monaci, F., Grattacaso, M., Paoli, L., & Loppi, S. (2020). Effects of wood distillate (pyroligneous acid) on sensitive bioindicators (lichen and moss). Ecotoxicology and Environmental Safety, 204, 111117.

Vannini, A., Moratelli, F., Monaci, F., & Loppi, S. (2021). Effects of wood distillate and soy lecithin on the photosynthetic performance and growth of lettuce (Lactuca sativa L.). SN Applied Sciences, 3(1), 1-6.

#### OZONE-INDUCED EARLY SENESCENCE STUDIED IN *TRIFOLIUM REPENS* GENOTYPES FROM SUBARCTIC GRASSLANDS

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Previous experiments have shown that several European clovers may develop more visible injuries due to ozone when the night is not dark. At high latitudes, the summer nights are bright, giving the background for the question whether plants adapted to midnight sun also have this response of being more easily injured by ozone when the night is not dark.

The plants included in the present experiment are expected to be adapted to light exposure during night, since there is midnight sun from the time they melt out of the snow cover in spring until the end of July, in the sites where they were collected. This constitutes about 50 % of the growing season for grassland species in these areas.

Cuttings of two genotypes of white clover (*Trifolium repens*) collected in two sites in subarctic Norway were cultivated under controlled environment conditions. Using a factorial design, the plants were exposed to two different night-time light conditions and two different ozone exposure levels. We studied the development of visible injuries, foliar chlorophyll concentrations and N concentration as signs of premature senescence due to ozone.

# **OZONE POSTERS**

#### POTENTIAL ROLE OF PROLINE IN PLANT RESPONSES TO OZONE?

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Plants are subjected to numerous environmental constraints such as low or high temperatures, drought or tropospheric pollutants like ozone (O<sub>3</sub>). Ground-level ozone is considered a pollutant of concern in many regions of the world, due to its toxicity for humans and also for its phytotoxicity.

We addressed the question of the putative involvement of proline in plant ozone response. Indeed, proline is known to accumulate in plants during numerous environmental stresses (drought, salinity, UV radiation, etc.). This accumulation of proline has been described as having an antioxidant effect conferring stress tolerance, in particular by trapping hydroxyl radicals which can cause damage in plants.

Four *Arabidopsis thaliana* ecotypes: Ts-1, Col-0, Ler and Cvi-0 (classified from more to less tolerant to ozone according to Brosché et al., 2010) and two mutants derived from Col-0, which present different proline concentrations: *p5cs* (low proline content by inhibition of synthesis) and *prodh1xprodh2* (high proline content by reduction of catabolism), were subjected to 240 ppb of ozone for 10 days (Ts-1, Col-0, Ler, Cvi-0) or 16 days (Col-0, *p5cs, prodh1xprodh2*). Several allometric parameters were measured (total chlorophylls content, biomasses, leaf area) as well as proline contents and carbonylation level of proteins. The results show no effect of ozone, nor accumulation of proline for the Col-0 ecotype and for the mutants *p5cs* and *prodh1xprodh2*.

On the other hand, for the Ler and Cvi-0 ecotypes, we observe leaf necrosis, early senescence as well as a decrease in the total chlorophylls content and an accumulation of proline. Contrary to our expectations, proline accumulation could not be correlated with variations in protein oxidation (carbonylation). On the other hand, flavonols content, measured here, using non-destructive methods, reflected exactly the genotypes ranking according to ozone sensitivity.

#### FOREST MONITORING FOR FOREST PROTECTION AGAINST OZONE ON THE STOMATAL FLUX BASIS: 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<sub>3</sub> effects on forests depend on gas uptake through stomata (stomatal fluxes). The European MOTTLES project contributes to the NEC (National Emission Ceiling) Italy and ICP Forests network for O3 monitoring in 17 sites in France, Italy and Romania. These monitoring stations allowed: (1) estimating the accumulated exposure AOT40 and stomatal O<sub>3</sub> fluxes (PODY) with an hourly threshold of uptake (Y) to represent the detoxification capacity of trees (POD1, with Y = 1nmol  $O_3 \text{ m}^{-2} \text{ s}^{-1}$  per leaf area); and (2) collecting data of forest-response indicators, i.e. crown defoliation and visible foliar O<sub>3</sub>-like injury over the time period 2017–2019. The soil water content was the most important parameter affecting crown defoliation and was a key factor affecting the severity of visible foliar O<sub>3</sub>-like injury on the dominant tree species in a plot. The soil water content is thus an essential parameter in the PODY estimation, particularly for waterlimited environments. An assessment based on stomatal flux-based standard and on real plant symptoms is more appropriated than the exposure-based method for protecting vegetation. From flux-effect relationships, we derived flux-based critical levels (CLef) for forest protection against visible foliar O<sub>3</sub>-like injury. We recommend CLef of 5 and 12 mmol  $m^{-2}$  POD1 for conifers and broadleaved species, respectively. Before using PODY as legislative standard in Europe, we recommend using the CLec for  $\geq 25\%$  of crown defoliation in a plot: 17,000 and 19,000 ppb h AOT40 for conifers and broadleaved species, respectively.

## **MOSS SURVEY SESSIONS**

#### MAPPING THE SPATIAL DISTRIBUTION OF (Na, Cl, Ca, Mg) OVER KALININGRAD OBLAST (RUSSIA) BY USING ARCGIS PRO 2.4

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The present work aims to demonstrate the possibilities of advanced interpolation and Geospatial techniques in the elaboration of accurate maps of the spatial distribution of some of Marine minerals (Na, Cl, Ca, Mg) in Kaliningrad oblast (Russia), as well as to explore the factors that play an essential role in modeling this spatial distribution.

To draw maps of the spatial distribution of chemical elements Empirical Bayesian kriging regression prediction was used. Empirical Bayesian kriging regression prediction (EBKRP) is a relatively new geostatistical interpolation approach. this approach considers different additional explanatory indicators (in raster format) that are known to influence the estimation of the dependent variable (chemical elements)—acting as prior information (Krivoruchko, 2012).

In this study, several environmental and anthropological variables (terrain derivatives, NDVI index, distance from the coastline, wind and rainfall data, distance from settlements) were used

as explanatory variables due to their influence on the spatial distribution of the selected chemical elements.

The monitoring network consists of 33 points, the number of which is determined according to methodological requirements - 2.5 samples per 1000 km<sup>2</sup> (Moss survey protocol, Manuals, 2020). The algal plant species Hylocomium splendens, Hypnum cupressiforme, and Pleurozium schreberi were collected throughout the study area to determine the concentration of chemical elements in the moss cover, one of the methods of the ICP-Vegetation program was used - the bioindication method or "Moss technique".

EBK Regression Prediction **results** showed clear spatial heterogeneity concentration of (Na, Ca, Mg, Cl) throughout the study area<sup>1</sup>.

Due to the important contributions of sea spray and seawater for Na in coastal regions, in addition to the natural other sources of Na, it was found that the Na content in the algae samples decreased with increasing distances of the sampling sites from the coastal areas where Na concentrations are high in the west and decrease towards the east.

The content of Cl in moss samples showed higher variation than Na and took a different distribution, where Cl concentrations were high in the south and east (inland areas) and low in the north and west (coastal areas). The spatial distribution of concentrations of Mg and Ca shows a high increment in the inland areas and a decrease toward coastal areas. This indicates a relationship between Ca, Mg, and Cl in the present samples, and enrichment of Mg, Ca, and Cl in inland areas is derived mostly from different geogenic and anthropological factors of the areas and less from the sea spray sources.



Figure 1. Spatial distribution of (Na, Cl, Ca, Mg) in Kaliningrad oblast.

To download high-resolution maps from this link: https://drive.google.com/drive/folders/ldR\_rXzy0BgCiW-xCzYzAF5empaY8EXSZ?usp=sharing

#### A PAN-SEE BIOMONITORING NETWORK FOR THE ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS IN URBAN AIR

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Moss transplants of two species, Hypnum cupressiforme and Sphagnum girgensohnii, were used for investigation of airborne potentially toxic element pollution in urban areas of ten Southeast European (SEE) countries. The mosses in bags were exposed at five sites in each of the selected urban areas, next to/in the vicinity of air quality (AQ) monitoring stations and with respect of different land use classes (typical urban, residential, urban background) and one rural site. The moss bags were exposed for two months during the winter season (2019/2020). The concentrations of 35 potentially toxic elements – PTEs (Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hg, In, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sc, Se, Si, Sr, Th, Tl, U, V, Y, and Zn) were determined in the samples using inductively coupled plasma mass spectrometry (ICP-MS). This study is the first attempt to apply a uniform biomonitor form/species to active biomonitoring of PTEs on a regional scale.

The elements Ag, Ba, Be, Bi, Ga, Sb, U, and Zn in both moss species, showed high variation among exposed sites (CV % > 75%), by indicating the data are affected by several factors, and/or the data of elements with low concentration are affected from high uncertainty of the analysis. High relative accumulation factors were found for Cr, Cu, Fe, Ni, Sb, and V in moss bags indicating these elements are the most abundant in most sampling sites. The median values of contamination factors in both moss species ranged mostly from 1.2 to 2.17, indicating the exposure sites show no contamination to slight contamination status (C1 to C2 scales).



**Fig. 1** Linear regression of average concentrations (logarithmic data) of elements in *H. cupressiforme* vs. *S. Girgensohniibiomonitor* 

**Fig. 2** CF spatial distribution plot of As, Cr, Cu, Ni, Sb, Se, V and Zn along moss bags exposure sites

The differences between accumulation capacities of both moss species were tested by RAF values. High RAFs were found for Cr, Cu, Fe, Ni, Sb, and V in moss bags indicating these elements are the most abundant in most sampling sites. The median values of CFs ranged mostly from 1.2 to 2.17, indicating no contamination to slight contamination status (C1 to C2 scales).

The roadside soils are heavy affected by historical total metal concentrations, so, the soil dust emission could be considered a strong factor affecting the level of total metal content in moss bag samples. It is clearly showed by high correlations between the crustal elements Fe, Ti, Cr and Co. Besides, the tyres are the main sources of Zn and Cd, while brake linings are shown to be the main source for Cu and Sb in a heavy traffic environment.
# MEASUREMENT OF AIR DEPOSITION OF HEAVY METALS IN THE AREA OF SOUTH-WEST HUNGARY USING MOSS BIOINDICATION

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The aim of our study is to present a moss bioindication method, based on measurements in the southwestern part of Hungary.

To carry out the study, three sampling points were taken in the southwestern part of Hungary, 40-50 km apart. Given the possibilities, moss samples were collected in accordance with the sampling protocol.

The samples were dried at 40°C for 48 hours as specified in the procedure. The dried plants were weighed.

This was followed by grinding and then digesting in the Anton Paar multiwave 3000 Microwave Reaction System. After digestion, a solution of the remaining dry residue was prepared with distilled water and the heavy metal content was measured by Thermo Scientific ICE 3000.

In a first step, the differences between the results measured at the sampling points were investigated, with the focus on changes in the sampling point environment to determine the possible causes of higher values.

In the second step, we compared our own results with those of the measurement already carried out in 1997 and analysed changes in the country as a possible cause of the differences.

Finally, the results of the 2005 Europe-wide survey were selected from the countries directly linked to the Western part of the country and compared with our own results.

At the beginning of our study, we made three assumptions about the different sampling points and the results of the comparison.

The first was that we would measure the lowest value for all five elements at sampling point 1. However, this assumption was disproved, as the measured concentrations at sampling point 1 were the highest for two elements and the lowest for three.

Our second assumption against the results was that sampling point 2 would be the most polluted. However, the measured results showed the highest value in two cases and the lowest in one case.

The third assumption, that there would be a decrease compared to the 1997 measurements, was also not fulfilled in all cases. A slight increase was also observed for copper and nickel compared to the previous measurement.

The measured results show that the background air pollution of heavy metals in the southwestern region of Hungary has not changed significantly compared to the 1997 measurement. Only two elements showed a significant increase, copper and nickel, which were linked to the expanding metal and electrical industries.

In the course of our study, we have gained a wealth of information on the quantity, quality and complexity of airborne pollutants. Our assumptions were based on a simple train of thought, which proved to be inadequate once the actual values were determined.

We propose to carry out further investigations in the area and in the rest of the country, taking into account the pollutant emissions and measurements of neighbouring countries. A particular focus is on nickel, which has shown an increase compared to previous measurements and higher values compared to the results of neighbouring countries. It would also be useful to carry out soil sampling in the sampling points. This would provide a more complex result with a better understanding of the pollution factors.

#### BIOMONITORING OF ATMOSPHERIC DEPOSITION OF HEAVY METALS IN SLOVAKIA IN 2020-2021

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The use of bryophytes as pollutant accumulators for monitoring changes in atmospheric deposition of heavy metals in Slovakia started in 1990. In cooperation with ICP Forest Slovakia was established a permanent monitoring sites arranged in regular 16x16 km grid. In the current Survey 2020-2022, with a new team, the network of monitoring plots was extended with another 100 sites. They include both sites with a high risk of heavy metal exposure and background localities. Samples from 2020-2021 are from 158 monitoring sites. Predominant sampled pleurocarpous mosses are *Pleurozium schreberi, Hylocomium splendens, Hypnum cupressiforme* and *Dicranum* sp.div.

Collected mosses will be analysed by INAA techniques in the JINR in Dubna (RU) and they are analysed by ETAAS and EA techniques in the laboratory of the National Forestry Centre in Zvolen (SK). In the Comenius University in Bratislava (SK), radioactivity of moss samples from selected localities are measured in order to map the annual inhalation dosage of <sup>137</sup>Cs and <sup>210</sup>Pb isotopes by the Slovak population.



So far, we have the first results from laboratories in Slovakia covering the sampling from 58 localities.

**Figure 1**: Map of Slovakia with sampling sites 2020 from 2020 (red) and 2021(blue)

С	Ν	S	Al	Fe	Mn	Zn	В	Cu	Cd	Hg
%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
47,28	1,68	0,15	592,179	589,110	284,109	30,670	8,892	8,014	0,415	0,036
47,00	1,57	0,15	469,055	514,655	237,237	28,933	7,513	7,478	0,319	0,031
42,00	0,97	0,10	150,833	178,326	32,879	17,420	3,321	4,955	0,035	0,010
51,30	2,52	0,20	3013,869	2950,116	841,794	53,092	39,835	13,660	2,216	0,131
50,00	1,91	0,19	1200,697	936,920	660,275	40,760	13,232	10,606	0,724	0,061
	%           47,28           47,00           42,00           51,30	%         %           47,28         1,68           47,00         1,57           42,00         0,97           51,30         2,52	%         %         %           47,28         1,68         0,15           47,00         1,57         0,15           42,00         0,97         0,10           51,30         2,52         0,20	%         %         %         mg/kg           47,28         1,68         0,15         592,179           47,00         1,57         0,15         469,055           42,00         0,97         0,10         150,833           51,30         2,52         0,20         3013,869	%         %         mg/kg         mg/kg           47,28         1,68         0,15         592,179         589,110           47,00         1,57         0,15         469,055         514,655           42,00         0,97         0,10         150,833         178,326           51,30         2,52         0,20         3013,869         2950,116	%         %         mg/kg         mg/kg         mg/kg           47,28         1,68         0,15         592,179         589,110         284,109           47,00         1,57         0,15         469,055         514,655         237,237           42,00         0,97         0,10         150,833         178,326         32,879           51,30         2,52         0,20         3013,869         2950,116         841,794	%         %         mg/kg         mg/kg </th <th>%         %         mg/kg         mg/kg<!--</th--><th>%         %         mg/kg         mg/kg<!--</th--><th>%         %         mg/kg         mg/kg<!--</th--></th></th></th>	%         %         mg/kg         mg/kg </th <th>%         %         mg/kg         mg/kg<!--</th--><th>%         %         mg/kg         mg/kg<!--</th--></th></th>	%         %         mg/kg         mg/kg </th <th>%         %         mg/kg         mg/kg<!--</th--></th>	%         %         mg/kg         mg/kg </th

Figure 2: Metal (mg/kg) and nitrogen (%) concentrations in moss samples from 2020 sites

	Hermanovce	Studienka	Veľke Zlievce	Ďurkovec
137Cs	$3.3\pm0.3$	15.1 ± 0.6	4.2 ±0.3	$2.5\pm0.2$
40K	343 ± 9	$144 \pm 5$	$114 \pm 4$	$231\pm7$
232Th	$0.8 \pm 0.3$	$1.7\pm0.2$	$1.4 \pm 0.3$	$1.9\pm0.4$
226Ra	4.6±0.3	< 2	3.6± 0.4	$3 \pm 0.5$
210Pb	$177\pm5$	$223\pm7$	$319\pm11$	$585 \pm 18$

Figure 3: Results of measurement of the natural radionuclides in moss samples (Bq/kg)

# METAL AND NITROGEN CONCENTRATIONS IN MOSS IN SWEDEN – RESULTS FROM THE NATIONAL MOSS SURVEY 2020

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On behalf of the Swedish Environmental Protection Agency and the framework of the national environmental monitoring, we have conducted measurements of levels of metals and nitrogen in moss collected all over Sweden in 2020. Metal measurements in moss have been carried out in Sweden every five years since 1975. Nitrogen analyses were carried out for the first time in 2020. 500 collected moss samples have been analysed for the levels of 15 metals and nitrogen, and results show that most metals measure low levels in Sweden, especially compared to levels in Southeast Europe.

A general south-north gradient was observed for most of the analysed metals and nitrogen, with the highest levels in the south and southwest of Sweden and lowest in the north, especially in the mountain regions. However, locally elevated metal levels due to air emissions from local emission point sources, sometimes break this general pattern. A strong statistical correlation was found between levels of nitrogen in moss and the estimated total deposition of nitrogen to coniferous forest based on deposition measurements. Also, the nitrogen deposition calculated based on the nitrogen content in moss matched relatively well with the total deposition of nitrogen, estimated based on deposition measurements at different locations in Sweden.

For Pb and Cu, the statistical analysis showed that the median levels in moss for the whole of Sweden were lower in 2020 compared to 2015. On the contrary, for As, Cr, Ni, Hg, Fe, V, Zn, Al and Co the median levels were somewhat higher in 2020 compared to 2015. The reason for the small level increase is unknown. For Cd, Mn and Mo there was no significant change during the same period. Over the past 45 years (1975 – 2020) the metal levels in moss in Sweden have decreased the most for Pb, Cr, Ni, Cd and As. Over the last 30 years (1990 – 2020), the decrease was not as large as for the period from 1975, and in the last 20 years (2000 - 2020) only the levels of Pb and Cd in moss have decreased statistically significantly in Sweden.

The reduction in moss metal levels has been in good consistency with the emission reductions that are presented for Sweden and for the EU27+UK from 1990 for As, Pb, Cu, Ni and Cr. On the other hand, the levels of Cd, Zn and Hg in moss have decreased less in percentage terms compared to the emission reductions.

#### References

Danielsson, H., Nerentorp, M. & Pihl Karlsson, G. 2021. Metaller och kväve i mossa, 2020. Nationell undersökning i bakgrundsmiljö. IVL Rapport C614 (*In Swedish with English summary*).

# MOSS- and CHITIN-BASED MONITORING: FURTHER PIECES OF INFORMATION ON ADSORPTION THERMODYNAMICS

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Recently this author presented arguments that studying amounts of environmental contaminants by adsorption to chitin (both grafted and on living arthropods, lichens) does come with some advantages with respect to moss monitoring, particularly including the opportunity to determine non-equilibrium processes at a water/sediment interface. These include photochemical processes above the interface, using Eu adsorbed to chitin at ambient concentrations and different geochemical and biogeochemical transformations involving several elements adsorbing to chitin which take place in the sediment. Chitin surfaces placed in the pathway thus provide information which cannot be obtained by any other known method. Additionally, while mosses and lichens become more and more rare, chitin from shrimp peeling will give an opportunity to protect the former organisms especially in scenarios of repeated or periodic large-scale environmental monitoring. Possible setups which can replace local water bodies and their boundaries to bottom and shore for monitoring are presented in the lecture. They are being developed and soon to be tested in my lab. Thus, this way of monitoring can be extended from bogs or small water pools to dry areas (where mosses do not persist either). Studies on ants and cravfish revealed to which extent results using living arthropods match those obtained by grafted chitin, and provide information on how metals make their way into some arthropod organism – by adsorption to the chitin cover or via mouth. Bi, REEs, V, Cu, and Pb produce strongest enrichment on chitin from water.

Items of studies include most elements of the PSE ( $M^{2+}$  and higher charged,  $Ag^+$  and their complexes) and also some organics such as PAHs. Once chitin was dissolved in a Li<sup>+</sup>-doped organic medium, behavior of adsorbates also can be studied by electrochemical methods. We do assume from previous experiments that certain ions (Mn, LREEs) adsorbed to chitin will also catalyze certain transformations of both inorganic and organic substrates on chitin. In lakes or ponds environmental dynamics of these elements and substrates thus will be influenced by zooplankton undergoing diurnal vertical migration and depositing chitin after death.

#### **MOSS SURVEY IN THE NETHERLANDS 2020-2021**

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Atmospheric deposition of nitrogen is exceeding the critical loads of vulnerable ecosystems in many N2000 areas in the Netherlands. Therefore, in 2018 a governmental program (PAS) was initiated that aims at a long-term decline of N-deposition and a short-term application of extensive mitigating measures in N2000 areas in order to preserve the current habitat area and quality at high N-deposition levels. The elaboration of this program is based on fine-scale modeling of N-deposition with atmospheric transport-deposition models and knowledge on the ecological effects of mitigating measures. Currently the only monitoring activity in N2000 areas related to atmospheric N-input is a fine-scale monitoring network for measurements of NHx air concentrations. The Netherlands participated in the moss survey of ICP only in 2005 for measurement of N-content. Therefore, the prospect on a sound evaluation of the effect of PAS measures on the actual N-deposition in N2000 areas is weak. For this reason, KWR initiated a project for measurements of N-content in mosses with the financial aid of drinking water companies that manage vast N-sensitive nature areas and provinces responsible for implementing the PAS program. Besides N-content, heavy metals and macro-elements in mosses were also measured in the moss survey of KWR. Currently fine scale monitoring of heavy metal deposition is lacking and the Netherlands only participated in the ICP moss survey for heavy metals in 1990 and 1995.

In total we sampled 40 locations in the Netherlands according to the ICP protocol: 34 scattered along the coast in dune areas, 4 in an inland heathland area, and 2 in a forest. We also sampled some reference sites in UK, Denmark, Norway and Germany with lower N-deposition, for comparison. On 23 of these locations, we sampled both in 2020 and 2021 to investigate the (temporary) effect of the COVID-19 lockdowns on N-deposition.

N-content in mosses was 6% lower in 2021 than in 2020, and in moss tips 7,5% lower. In individual cases close to a highway or main road the decrease was even 21-23% between the years. This could have been caused by a reduction of traffic during the COVID-19 lockdowns. N-isotope ratios ( $\delta$ 15N) in mosses show negative values, meaning that reduced N (NH<sub>y</sub>) prevails in the N-deposition. However,  $\delta$ 15N values were less negative in 2021, probably due to differences in precipitation and drought between the years, which also leads to a different uptake in mosses.

There was no clear relationship between the measured N-content in mosses and the modelled N-deposition by the Dutch OPS-model. This could be due to N-saturation in mosses as a result of the high N-deposition values in the Netherlands (11-28 kg N/ha/y), the limited N-deposition gradient over the sampling locations, a bias in the modelled N-deposition of the coastal dune areas, or the influence of precipitation/evaporation on the vitality and N-uptake of the mosses. More sample locations in a larger deposition gradient are needed for a better validation of N-deposition patterns in the Netherlands, preferably also in habitats with less drought stress. Moreover, other moss species may have to be used at high N-deposition levels.

#### USE OF BIOMONITORING DATA IN ENVIRONMENTAL FORENSICS

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Lichen or moss bioaccumulation studies may be very useful in the framework of environmental forensics, since they provide evidence of the biological effects of pollutants and allow the production of detailed zonal maps which may serve as base for epidemiological studies.

It is mandatory to distinguish biomonitoring data from ambient concentrations data, which can be obtained through physico-chemical measurements, and from emission data, which can be obtained through computer models. Lichen and moss bioaccumulation data thus provide biologically relevant, time- and space-integrated information on the atmospheric deposition of important pollutants such as potentially toxic elements (PTEs).

For a forensics use of bioaccumulation data, it is of paramount importance that great care is taken in the selection of the proper sampling design, in the clear and formal expression of the uncertainty affecting the results, and in the overall error inherent the final zonal maps. Moreover, being bioaccumulation data affected by a wide array of environmental parameters, not limited to atmospheric pollutants, it is extremely important that other confusing effects e.g. soil contamination of samples, are clearly isolated.

It is very important to add in any study a sensitivity analysis, which plays a crucial role in assessing the robustness of the findings or conclusions. This may take the form of e.g. varying the cut-off levels in defining air pollution zones, or changing the methods of data analysis, or determining the influence that minor protocol deviations may have on the conclusions.

# ASSESSING THE ATMOSPHERIC DEPOSITION OF MICROPLASTICS: A LICHEN BIOMONITORING STUDY IN THE CITY OF MILAN, ITALY

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Although there is a huge literature showing that microplastic pollution is greatly affecting marine and coastal environments, studies of the atmospheric deposition of microplastics are still scanty.

There is evidence that lichens and mosses, which are well known for their ability to accumulate atmospheric pollutants such as potentially toxic elements, can be profitably used for assessing the atmospheric deposition of microplastics (Roblin, B. & Aherne, J 2020; Loppi et al., 2021). In this study, lichen transplants exposed for three months in the city of Milan, Italy, and in a control area have been digested by the wet peroxide oxidation method and examined under a stereomicroscope for plastic microfibers based on the hot needle test and other standard criteria used in similar studies.

The results showed a great difference in the number of microfibers accumulated in remote and urban areas of Milan and clearly showed that lichens can effectively be used to monitor the deposition of anthropogenic plastic microfibers.

References:

Loppi, S., Roblin, B., Paoli, L. and Aherne, J., 2021. Accumulation of airborne microplastics in lichens from a landfill dumping site (Italy). *Scientific reports*, 11(1), pp.1-5.

Roblin, B. & Aherne, J. Moss as a biomonitor for the atmospheric deposition of anthropogenic microfbres. Sci. Total Environ. 715, 136973 (2020).

#### ATMOSPHERIC MERCURY MONITORING BY MOSS TRANSPLANTS: CURRENT PERSPECTIVES AND LIMITATIONS

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The moss transplant technique is widely employed all over Europe to provide spatial and temporal information on source and deposition patterns of atmospheric persistent contaminants. This technique consists in nylon net bags holding transplanted moss (moss bags) which are deployed over a given geographic area for a defined exposure time. The moss bag approach typically applies in polluted areas lacking suitable native moss species and it is especially effective in urban areas, where it may support conventional monitoring programmes based on instrumental techniques. Although biomonitoring by moss transplants has a long history dating back to the early 1970s (Goodman and Roberts, 1971), it is not without drawbacks and uncertainties. A crucial weak point is the lack of standardized experimental protocol (e.g.: species to be used, bag features and geometry, exposure conditions) that inevitably impact the comparability of results produced by different studies. Moreover, target analytes of moss transplants studies commonly include pollutants with very different chemicalphysical properties (e.g., solid or vapour), which affect chemical uptake and retention of a given chemical by the moss, and consequently the effectiveness of transplants for biomonitoring. In this regard, mercury (Hg) is an exemplary case within the group of potentially toxic elements. Differently from other airborne metals, which are predominantly adsorbed to the atmospheric particulate, Hg occurs mainly as gaseous elemental mercury (GEM; often > 95%). As a probable result of this specificity, it has not been possible yet to identify clear relationships between Hg concentration in air or in bulk deposition and those in exposed cryptogamic organisms (Bargagli, 2016). Moreover, much of the available data on the performance of moss transplants for airborne metal biomonitoring does not generally apply to Hg. However, the recent availability of a novel GEM passive monitoring sampler (McLagan, 2019) is disclosing unprecedented possibilities for gaseous Hg monitoring and supporting comparisons with transplanted moss data. Here we present preliminary data from our ongoing research exploring these new possibilities and we provide useful framework to understand current perspectives and limitations of the use of moss bags for atmospheric Hg biomonitoring.

Bargagli, R., 2016. Moss and lichen biomonitoring of atmospheric mercury: A review. Sci. Total Environ. 572, 216–231.

Goodman, G.T., Roberts, T.M., 1971. Plants and soils as indicators of metals in the air. Nature 231, 287.

McLagan, D.S., Monaci, F., Huang, H., Lei, Y. D., Mitchell, C. P. J., Wania, F. 2019. Characterization and quantification of atmospheric mercury sources using passive air samplers. *Journal of Geophysical Research: Atmospheres*, 124(4), 2351–2362.

#### ESTIMATION OF ELEMENTS' CONCENTRATION IN AIR IN KOSOVO THROUGH MOSSES AS BIOMONITORS

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The pollution with potentially toxic elements in the environment in Kosovo is reported, particularly for the district of Mitrovica [1]. High presence of these elements was found in different location also as a result of atmospheric deposition [2]. In this study, elements atmospheric deposition in Kosovo was studied by mosses method. Mosses are a very useful tool for atmospheric deposition of elements monitoring, owing to their physiological and morphological characteristics. The collection of moss samples was performed during the dry season of summer, August to September in 2019. Moss samples were collected from 45 locations, they were cleaned from leaves, twigs and other materials, they were grinded, digested in a microwave system and analyzed by spectroscopy Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). A total of 25 elements concentration in collected moss samples was determined: Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sr, Ti, Tl, V and Zn. Extremely high concentrations of Pb and Zn were found in moss samples from the areas of Zveçan and Stanterg where the ore processing facilities are located, as well as the tailings landfill in Mitrovica which is nearby in the south, which reflects eminent air pollution. High concentrations of As and Cd were also measured in the same sampling points. The obtained results were processed by multivariate statistical analysis/factor analysis, which resulted in four factors, one anthropogenic and three geogenic or mixed geogenic-anthropogenic. The contamination factor (CF) and the polluted load index (PLI) were calculated for potentially toxic elements. The factor analysis revealed that the area with the highest atmospheric deposition of potentially toxic elements is the basin of Kosovo, from the north in Leposaviç to the south in Hani i Elezit because of the industrial plants laying in this line.

Keywords: Kosovo; air; pollution; elements; mosses; ICP-AES; ICP-MS; factor analysis.

- [1] G. Kastrati, M. Paçarizi, F. Sopaj, K. Tašev, T. Stafilov, M.K. Mustafa, Investigation of concentration and distribution of elements in three environmental compartments in the region of mitrovica, kosovo: Soil, honey and bee pollen, Int. J. Environ. Res. Public Health. 18 (2021) 1–17. https://doi.org/10.3390/ijerph18052269.
- M. Paçarizi, T. Stafilov, R. Šajn, K. Tašev, F. Sopaj, Estimation of elements' concentration in air in Kosovo through mosses as biomonitors, Atmosphere (Basel). 12 (2021). https://doi.org/10.3390/atmos12040415.

#### CANOPY DRIP EFFECT ON CONCENTRATIONS OF HEAVY METALS IN MOSSES SAMPLED ACCROSS NORTH-WEST GERMANY AS PART OF THE EUROPEAN MOSS SURVEY 2021

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Background and Aim. Germany's contribution to the European Moss Survey 2020/2021, financed by the Federal Environment Agency, comprises the determination of the levels of persistent organic pollutants and microplastics in mosses collected in 2021 at 25 of 400 sites in the Moss Survey 2015 (investigation part 1). In addition, the concentrations of 12 heavy met-als (HM: Al, As, Cd, Cr, Cu, Fe, Hg, Pb, Ni, Sb, V, Zn) and nitrogen (N) were determined in the mosses at the 25 sites mentioned (investigation part 2). In a third part of the investigation, which, like the second, was only carried out financially by the project partners themselves, the effects of the canopy drip on the HM and N contents was measured in mosses collected in north-west Germany. Only from this third partial investigation, first results of statistical data analyses are presented below. The aim of this study was to verify corresponding canopy drip effect studies conducted in 2012 and in 2013 (Meyer et al. 2015; Schröder et al. 2018). Materials and Methods. At eight monitoring sites of the European Moss Survey in Germany 25 moss samples were collected from a respective number of subplots, each representing the lo-cation categories "under tree canopies" and neighbouring "open land", respectively. The sam-pling as well as the chemical analyses and the recording of sample- and site-describing metadata were conducted according to ICP Vegetation (2020). Results. The results again demonstrate an overall higher HM and N accumulation in moss samples of "canopy" sites compared to neighbouring "open land sites" (grassland, heath). The ratios between the "cano-py" and "open land" sites of 1.18 to 1.69 and significant correlations of r > 0.8 in case of five elements agree well with corresponding values from samplings in 2012 and in 2013 (Kluge et al. 2013; Meyer et al. 2015) and the Moss Survey 2015/2016 (Schröder & Nickel 2018). Conclusions. With regard to the question of whether and to what extent moss samples should preferably be taken from "open land" or "canopy" sites, the following can be concluded: The recommendations of ICP Vegetation (2020) with regard to the minimum distance to be main-tained from trees and shrubs should not be interpreted to mean that "open" sites are funda-mentally more suitable for moss sampling in Germany than, for example, clearings in forests. The mostly higher variability of the measured values compared to the "canopy" sites rather suggests that in the open country a much higher number of influencing factors could be signif-icant for the element accumulation in mosses in addition to the background pollution through atmospheric deposition. This is also supported by the fact that the HM contents in the moss samples of the "open" sites can clearly exceed those of the neighbouring "canopy" sites in in-dividual cases. With regard to "open" land, grassland areas seem to be less suitable for moss sampling than bog and heathland sites. In grassland, moss occurrences are often sparser and / or cut short by meadow mowing, so that the removal of three-year-old shoots on grassland, as recommended by ICP Vegetation (2020), must be replaced in places by one-year old shoots. The comparatively higher state dynamics of grassland areas also make the resampling of moss at previously sampled sites more difficult. References. ICP Vegetation 2020. Heavy metals, nitrogen and POPs in European mosses. Monitoring manual survey 2020. Bangor, Wales, UK and Dubna, Russian Federation. Kluge M et al 2013 Environ Sci Eur 25(26):1-13. Meyer M et al 2015 Sci Total Environ 538:600-610. Schröder W & Nickel S 2018 Environ Sci Pollut Res 25(27):27173-27186.

#### BIOMONITORING OF HEAVY METALS AND NITROGEN CONCENTRATIONS IN THE VICINITY OF IRON AND STEEL WORKS: CASE STUDY IN CZECHIA

1

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A small-scale biomonitoring study using terrestrial mosses was carried out in the vicinity of the metallurgical factory near the Czech-Polish border. Moss samples (Brachythecium rutabulum (Hedw.)) were collected within one day in two seasons (June, October) so that the effect of the heating season on the pollution levels in the moss could be examined. Metal contents (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb, As, Sb and Hg) were determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption Spectroscopy (AAS) and N, C, H contents by elemental analysis. The influence of the proximity of the plant, heating season and modelled particulate matter  $<10 \,\mu m$  (PM<sub>10</sub>) on the determined element concentrations was studied via multivariate statistical methods using clrtransformed data. This approach led to the first demonstration that not only the distance from the industrial source, but also the sampling period and the concentration of PM<sub>10</sub> significantly affect the content of elements in the moss. The association of emissions from the source and the determined concentrations of elements in the moss samples was more evident in the collection carried out after a period outside the heating season (October). Hereby, for evaluating an industrial source impact, sampling following the warm season is encouraged in order to avoid skewing the results due to the influence of other sources connected to heating. Analysis of the transformed data revealed the association of Fe, Cr, V, As and Al with coarse particles and their dominant spatial distribution depending on the prevailing wind directions (see Fig. bellow). While the spatial distribution of Mn, Zn and Cd, which are bound to fine particles in emissions, depended more on atmospheric dispersion and long-distance transport, and therefore these metals should be considered as weak indicators of pollution in the close surroundings of an industrial resource. Nevertheless, the applicability of the results of this case study should be assessed by replicating the study in different industrial, geographical and climate settings since the novel aspects of this study prevent a direct comparison now.



Fig.: Interpolated October Fe concentrations in mosses within the case study area

# TREND OF ATMOSPHERIC METALS BY MOSS *HYPNUM CUPRESSIFORME* HEDW IN JAMMU (INDIA)

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Atmospheric pollutants, such as metals, are extremely variable in space and time and it is cumbersome and expensive to deduce detailed information over a vast area using traditional instruments. Consequently, a cost-effective bio-monitoring approach was preferred in the present study to analyse the trend of atmospheric metal load in western Himalayan region during 2014 to 2016. For this purpose, amongst available moss species, common and widely distributed moss Hypnum cupressiforme Hedw was inducted amongst moss species to evaluate the intensity and trend of atmospheric deposition of Zn, Cu, Cd, and Pb in Jammu in the state of Jammu and Kashmir, India for a period of three years, 2014-2016. The biomonitoring experimentation was performed by transplanting uniform size moss bags prepared from Hypnum cupressiforme, after validating its tolerance against metals using a portable photosynthetic efficiency analyser in the field. Moss Hypnum cupressiforme Hedw exposed seasonally, covering summer, monsoon, and winter periods, upon the analysis provided time-integrated patterns of metal bioavailability at the study sites. An attempt was made to compare the seasonal variations during the three years of study and findings exhibited significant seasonal variations in metal. The gradient of the metal load was in the order of Cu>Cd>Zn>Pb. The total average percentage increase in the metals under consideration, Zn, Pb, Cu, and Cd, was 40%, 37%, 79%, and 76%, respectively during three subsequent years. It is worth mentioning here that biomonitoring studies on atmospheric metals have never been explored from this region despite luxuriant growth of bryo-cover.

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Percentage increase in copper in moss

Percentage increase in cadmium

#### ASSESSMENT OF ATMOSPHERIC POLLUTION DEPOSITION IN LATVIA FROM 1990 TO 2020 USING THE MOSS AS ABSORBENT

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Biomonitoring is a technique for using organisms to determine air quality. Moss has been used as a bioindicator to assess the concentration of heavy metals in the atmosphere in many countries because of its ability to adsorb heavy metals and nitrogen. Mosses are suitable bioindicators because they obtain most of the nutrient supply directly from rainwater and dry deposition.

The moss biomonitoring technique in Latvia has been used in 1990, 1995, 2000, 2005, 2015 and 2020. *Pleurozium schreberi* moss was collected from 101 sampling sites during the autumn of the mentioned years. The sampling and chemical analyses were done by strictly following the Monitoring Manual Survey of the ICP Vegetation.

Generally, in this study, when assessing the situation in Latvia, it is observable that the atmospheric pollution with heavy metals is not high and has a decreasing tendency at regional levels. The main results show that concentrations of heavy metals are associated with local emission point sources in Liepāja (Cd, Cu, Ni, Pb, V, Zn), Brocēni (Cr, Cu), Rīga (Cr, Cu, Pb, Zn), Daugavpils (Cr, Cu) and Ventspils (Cd). Increased concentrations of heavy metals (Cd, Cr, Cu, Ni, Pb, V, Zn) in the western part of Latvia are due to the long-range transboundary transport of pollution from Europe and local metallurgical and other factories sources in Liepāja city. The overall concentrations in mosses at all plots in the period from 1990 to 2020 have declined the most for lead (15 times), vanadium (8.5 times), nickel (5.4 times). A lower reduction trend was observed for iron, chromium and cadmium, respectively 3.5, 3.3 and 2.7 times, but the lowest reduction for heavy metals pollution was for zinc concentrations, which have fallen by 1.4 times.

The level of pollution of heavy metals decreased due to the economic situation changes over this period (1990-2020). When the national monitoring started in 1990, many post-soviet industries and thermal power plants were still operating. Nowadays, many industries have already been shut down or their manufacturing intensity has greatly decreased. This is also confirmed by the fact that the concentrations of heavy metals have decreased by 2020, in comparison with the results of 1990.

Keywords: moss biomonitoring, air pollution, heavy metals, Latvia.

# CENTRAL RUSSIA HEAVY METAL CONTAMINATION MODEL BASED ON SATELLITE IMAGERY AND MACHINE LEARNING

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Atmospheric heavy metal contamination is a real threat to human health. In this work, we examined several models trained on in situ data and indices got from satellite images. During 2018-2019, 281 samples of naturally growing mosses were collected in the Vladimir, Yaroslavl, and Moscow regions. The samples were analyzed using Neutron Activation analysis to get a concentration of 18 heavy metal elements. The Google Earth Engine platform was used to calculate indices from satellite images that represent summarized information about sampling sites. Statistical and neural models were trained on in situ data and the indices.

We focused on the classification task with 8 levels of contamination and used balancing techniques to extend the training data. Three approaches were tested: variations of gradient boosting, multilayer perceptron, and Siamese networks. With the limits in training data, we try to show the advantages and prospects of using satellite data together with machine learning for HM contamination prediction. With the help of the method, we can monitor and evaluate the situation when needed, get detailed information about areas of interest, check the situation in the areas where sampling is forbidden, and partly automate the environment control process.

Unfortunately, we cannot determine which approach is better because each approach has differing merits and demerits. Nevertheless, we believe that the Siamese network is more versatile, as there is a lot of direction for evaluation. In our future research, we are going to examine other loss functions and training procedures. We see the direction of future research in the improvement of calculation techniques of satellite indices, the examination of new modeling approaches, and the extension and automation of our pipeline.

The median accuracy of the models for 9 heavy metals (Al, Fe, Sb, Na, Sc, Sm, Tb, Th, U) exceeded 89%. Al, Fe, and Sb contamination of 3,000 and 12,100 sites on a 500 km2 area in the Central Russia region for 2019 and 2020 was modelled. The output of the model was assessed by experts competent in the ecological situation of the Central Russia region as logical.

Modern satellite programs such as Sentinel-5 provide a great deal of data. The Sentinel-5 mission possesses a high-resolution spectrometer system operating in the ultraviolet to the shortwave infrared range, with 7 different spectral bands ranging from 270 to 2,385 nm. We believe that data of such programs, together with an advanced neural architecture, can broaden the horizon of environmental monitoring and contribute to improving the environmental performance in the world.

#### MOSS BIOMONITORING IN CANADA: A COMMUNITY SCIENCE INITIATIVE

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While moss biomonitoring is widely carried out across Europe, the technique has gained little ground in North America. Barriers to developing a moss biomonitoring program in North America are the large sampling area and vast remote regions. These characteristics make it logistically challenging to collect samples at a meaningful resolution and in a timely manner. To address this challenge, we developed a pilot project in Canada for collecting moss samples for biomonitoring through a community science model.

The purpose of our initiative, called "Bryomonitoring Canada", is to attract community volunteers to collect moss samples across Canada during the 2021 and 2022 field seasons, and submit them for analysis of trace metals and nitrogen. We connect to community science volunteers through an online hub, <u>www.bryomonitoring.ca</u>. The website provides background information about moss biomonitoring and our community science project. We instruct volunteers to sample moss through three steps:

1. Reserve your turf: An interactive map allows volunteers to select the grid where they will sample. A shopping cart linked to the map allows volunteers to request a sampling kit, or choose to make their own.

2. Spot your moss: Instructional text, images and videos teach volunteers to identify the two species we have selected for sampling (*Hylocomium splendens* and *Pleurozium schreberi*).

3. Pick and package: Instructional text, images and videos teach volunteers how to collect and store moss samples as per ICP Vegetation guidelines. Instructions are provided for mailing samples to Trent University for analysis.

After our first season of sampling (stating July 2021), we have received moss from 60 out of 900 grids covering Canada. This spring prior to the 2022 field season, our efforts will primarily focus on promotion of the project, particularly to increase participation in under-sampled regions. The results of the project will be submitted to ICP Vegetation under the 2020–2022 moss biomonitoring survey. Further, this pilot project will enable us to assess whether employing community science volunteers is an effective way to conduct moss biomonitoring, particularly in remote regions.

# MOSS MONITORING IN THE STUDY OF THE ACCUMULATION OF TRACE ELEMENTS IN THE UDMURT REPUBLIC, RUSSIA

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The results of atmospheric deposition of trace elements in the moss survey in the autumn of 2020 in the Republic of Udmurtia, Russia, are reported. 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., 2020). A total of 35 elements were determined by neutron-activation analysis and atomic absorption spectrometry. Analysis of the results of determining the accumulation of chemical elements in the biomass of the moss Pleurozium schreberi (Brid.) Mitt. and Hylocomium splendens (Hedw.) Bruch et al. on the territory of the Udmurt Republic showed that the highest content is observed in the southern and central parts of the study area.



The content of chemical elements in the biomass of mosses, in Udmurtia, 2020

#### References

Yu.S. Pankratova, M.V. Frontasyeva, A.A. Berdnikov, and S.S. Pavlov. Air pollution studies in the Republic of Udmurtia, Russian Federation, using moss biomonitoring and INAA. In *Nuclear Physics Methods and Accelerators in Biology and Medicine-2007*", Edts: C. Granja, C. Leroy, I. Stekl, AIP Conference Proceedings, Vol. 958, American Institute of Physics, New York, 2007, p. 236-237; http://www1.jinr.ru/Preprints/2008/096(P18-2008-96).pdf

I.L. Bukharina, A.N. Zhuravleva, N.A. Volkov, Plotnikova K.V., Frontasyeva M.V. Moss monitoring in study of the accumulation of trace elements in the Udmurt Republic, Russia // ICP Vegetation 33th Task Force Meeting: 27th-30th January 2020, Riga, Latvia: Programme & Abstracts / ICP Vegetation Programme Coordination Centre, Centre for Ecology & Hydrology. Riga, 2020. - P. 61.

#### ACCUMULATION OF POTENTIALLY TOXIC ELEMENTS IN MOSSES COLLECTED IN THE REPUBLIC OF MOLDOVA

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For the second time, the moss biomonitoring technique was applied to evaluate the deposition of potentially toxic elements in the Republic of Moldova. The study was performed in the framework of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops. Moss Hypnum cupressiforme Hedw. samples were collected in May 2020 from 41 sampling sites distributed over the entire territory of the country. The mass fractions of 35 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Se, Rb, Sr, Sb, Cs, Ba, Cd, La, Ce, Sm, Eu, Tb, Hf, Ta, Th, Pb, and U) were determined using neutron activation analysis and atomic absorption spectrometry. Comparing with 2015/2016 moss survey data, significant differences in the mass fractions of Cr, As, Se, Br, Sr, Sb, Cd, Pb, and Cu were found. Main air pollution sources (natural processes, transport, industry, agriculture, mining) were identified and characterized using factor and correlation analyses. GIS maps were built to point out the zones with the highest element mass fractions and to relate this to the known sources of contamination. Contamination factor, geo-accumulation index, pollution load index, and potential ecological risk index were calculated to assess the air pollution levels in the country. According to the calculated values, Moldova can be characterized as unpolluted to moderately polluted, with low potential ecological risk related to the degree of atmospheric deposition of potentially toxic elements. The cities of Chisinau and Balti were determined to experience particular environmental stress and are considered moderately polluted

# **MOSS SURVEY POSTERS**

# ATMOSPHERIC DEPSITION STUDY OF ANTHROPOGENIC METALS (Cr, Co, Fe, and Ni) BY MOSS BIOMONITORING

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This paper gives a view of the anthropogenic pollution from trace metals (Cr, Co, Fe, and Ni) that pose risk to human health. Moss biomonitoring (Hyppnumm cupressifforme sps.) and metals atmospheric deposition was used to evaluate air quality in Albania. Metals concentrations were determined by induced couplet plasma-atomic emission spectroscopy (ICP-AES). The elements considered in this study (Cr, Co, Fe, and Ni) are mostly affected by anthropogenic sources. We tried to identify and assess the most polluted areas and the pollution sources. The concentration data of the elements were standardized bringing the data at the same digits numbers. The concentration data were statistically processed to understand spatial and temporal variability, the relationship between the elements, and to assess the most probable pollution sources. Significant variations were detected in the concentration data of the elements under investigation. The main pollution source was pointed from soil dust particles, and the anthropogenic inputs originated from mining, metal high-temperature processing, vehicle emissions, waste incineration, etc.

#### USING MOSS BIOMONITORS AS AN INDICATOR OF RARE EARTH ELEMENTS DEPOSITS OVER SMALL MINING AREA OF As, Sb and TI

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Natural and anthropogenic emissions contribute to the enrichment of atmospheric pollution, lead to atmospheric deposition and contribute to contamination of individual elements of the environment and for mankind. Mining and smelting of ore can release large quantities of toxic elements into the atmosphere, including REEs and dust particles, and create pollution problems. Using biomonitors (moss, lichens) in the measurement of air pollution can help to get a reliable picture of pollution. Currently, regulatory monitoring of air pollution does not involve the measurement of rare earth elements (REEs) content. The increasing number of REEs studies in the past decade has been induced by their wider applications in industry, including electronics and high technology.

This investigation provides an overview of REEs distribution in the moss samples collected in the area of the hydrothermal volcanogenic As-Sb-Tl deposit of Allchar, North Macedonia. The elemental contents were determined by inductively coupled plasma - mass spectrometry (ICP-MS). From the results, it can be conducted that both light and heavy REEs have a very similar distribution in the volcanogenic area of the Allchar site. The median of total REEs content in the moss ( $\Sigma$ REEs moss) in the Allchar area was 2.89 mg/kg, and the mean content ( $\Sigma$ REEs moss) was 4.63 mg/kg. The median contents of particular REE in the moss samples collected across Allchar area were in the range 0.887–0.005 mg/kg, following the following order: Ce > Nd > La > Y > Sc > Pr > Gd > Dy > Sm > Er > Yb > Eu > Ho > Tb > Tm > Lu. Higher contents of these elements were predominant to be found on the areas of Pliocene Quaternary latite breccia and Pliocene Quaternary tuffs in the south-eastern part of the study area.

*Keywords:* rare earth elements, moss, biomonitoring indicator, ICP-MS, As-Sb-Tl Allchar deposit, North Macedonia

#### DISTRIBUTION OF THE AMBIENT RADIATION DOSE LEVEL BY USING PASSIVE MOSS BIOMONITORING IN MACEDONIA

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For the first time the ambient radiation dose level has been measured in situ at the same sampling sites where the moss samples have been collected in order to determine and describe the air pollution in the Republic of North Macedonia. The measurements and moss sampling were performed in the period from August to September 2010 at 72 location across the country. The dose rates have been measured by dose rate detector ATOMTEX AT1117M with BDGK-01 probe with a dose rate range from 0.01 µSv/h to 10 Sv/h. It has been found that the ambient dose levels are in the interval from 53 nSv/h to 340 nSv/h. The content of Ba, K, La, Rb, Sr, Th and U in moss samples were determined by neutron activation analysis (NAA) and atomic emission spectrometry with inductively coupled plasma, ICP-AES). The ambient dose rate was modelled through the contents of some elements in the mosses collected from the same locations where radiation dose was measured, that contribute the most to the ambient dose rate (U, Th, K) as well as the elements that have radioactive isotopes (Ba, La, Rb and Sr). The obtained equation can be used to determine the ambient dose rates using content of the mentioned elements in the moss collected from the whole country. The spatial distribution of the measured and predicted radiation dose rates on the territory of North Macedonia is presented at Fig. 1 from which it can be noticed that both distribution maps are very similar, almost identical to the measured and predicted values. The model is made just on a territory of Macedonia which have a specific geology and the equation cannot be used in general for other areas.



Fig. 1. Spatial distribution of measured (A) and predicted radiation dose rate (B)

# CENTAUREA CYANUS A NEW POSSIBLE BIOINDICATOR FOR HEAVY METALS POLLUTION

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The multiply use of heavy metals in various applications has led to their wide distribution in diverse environments. However, this increasing distribution of heavy metals, including living beings, has many negative consequences. In addition, those metals are not destroyed; on the contrary, they accumulate at an accelerated pace, leading to environmental contamination. Therefore, exposure to heavy metals is potentially harmful. Consequently, it is necessary to know the amount of those metals in living beings and environments and take action against them.

In the environment, there are numerous techniques to detect heavy metals concentration. However, one of the essential parts is knowing the effect and level of heavy metals in living organisms. For this purpose, bioindicators are used. Hence, the presented research aims to evaluate the possibilities of using *Centaurea cyanus* as a bioindicator for heavy metals pollution. In order to obtain results of air pollution, plants were exposed to three experimental sites nearby the air monitoring station in Poznań (Poland).

The distribution of metals in plant tissues was quantified at the organ, cellular and subcellular level concerning the negative impact caused by these elements. For this purpose, complementary methods were used: LA-ICP-MS for the direct in vivo analysis, EDX for the measurement of the metal from the fixed samples, and confocal microscopy for the in vivo imaging of the generation of reactive oxygen species (superoxide anion and hydrogen peroxide). In addition, oxidative stress markers in cells were detected. After samples preparation and chemical analyses, graphic and statistical elaborations of the obtained results were done.

#### THE MOSS BIOMONITORING METHOD AND NEUTRON ACTIVATION ANALYSIS IN ASSESSING POLLUTION BY TRACE ELEMENTS IN SELECTED POLISH NATIONAL PARKS

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The concentrations of trace elements in feather moss Pleurozium schreberi (Brid.) Mitt. were used to indicate the relative levels of air pollution by trace elements in Polish national parks. Pleurozium schreberi was collected from nine national parks. The highest concentrations were recorded in the moss samples from the southern and most industrialised part of the country; the lowest from northern and north-eastern Poland. A comparison of data obtained from Polish national parks in the 1970s and 1990s showed a significant decrease in the concentrations of heavy metals. In the linear covariability estimation, the t quantile approach was used for multi-element comparison. A number of positive covariabilities were observed. This is a result of anthropogenic activity and the geochemical characteristics of the local environment, including crust composition to which soil composition is related. The statistical approach of t quantile to study common relationships between element concentrations can be used in the interpretation of biomonitoring research results in similar studies.

# PRELIMINARY STUDY OF MICROPLASTICS ATMOSPHERIC DEPOSITION STUDIED BY MOSS BIOMONITORING

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Microplastics have been identified in the atmosphere and atmospheric deposition over the continental and ocean areas, suggesting their long-range transport in atmosphere. This is a preliminary study of microplastics atmospheric deposition performed by moss biomonitoring. Moss samples used for trace metals atmospheric deposition were used for microplastics atmospheric deposition. Sampling was done in accordance with ICP Vegetation sampling manual. The identification of microplastics is done based on the microplastic characteristics, such as size, shapes, colors, and FTIR analysis. Fibers and fragments were the dominant shapes and the types of plastics founded in this study.



Fig. 1 Sampling sites Fig. 2 Schematic diagram of microplastics analysis



Fig. 3 Visual identification of microplastics (Electronic microscope: Kozo XJP304; zoom 100X; digital camera: Sony TCC-8.1, Image Software: View version 7.3.1.7



**Fig. 3** FTIR spectra of microplastics (FTIR) spectra were recorded in the range of 400–4000 cm<sup>-1</sup> with a Nicolet 6700 Spectrometer (Thermo Electron Company) using Attenuated Total Reflection (ATR) method.

#### Sample 1:

**LDPE** (low density polyethilene); **PET** (polyethilene tereftalate); **PU** (polyurethane); **EVA** (ethyl vinyl acetate) were identified.

#### Sample 2:

**PP** (polypropylene), **PU** (polyurethane), and **Nylon** (polyamides) were identified.

#### **Conclussions:**

Microfibers and microplastics identified in moss samples of rural area of Kanina, Vlora Region, derived by atmospheric deposition.

Mosses could successfully used as biomonitor of microplastic atmospheric deposition.

This is a preliminary study that needs more works in method validation and standardization. The pollution by microplastic atmospheric deposition needs a continues monitory to assess the pollution level and to prevent the health effects.

# MONITORING AND MAPPING PAH LEVELS IN PM<sub>10</sub> AND BULK DEPOSITION USING MOSSPHERES: A PILOT STUDY IN AN URBAN ENVIRONMENT

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Monitoring polycyclic aromatic hydrocarbons (PAHs) in  $PM_{10}$  and bulk deposition (BD) capturing the spatial variability in the concentrations of these compounds is not economically feasible with conventional methods. In the present study we tested the use of innovative, inexpensive passive air samplers known as "Mosspheres". The samplers, filled with a devitalised Sphagnum palustre L. moss clone, were used to monitor and map the concentrations of 15 priority PAHs, including benzo(a)pyene, in PM<sub>10</sub> and BD. For this purpose, we placed 84 Mosspheres on a regular sampling grid of side 575 m in a medium-sized European city. The samplers were exposed for three months, and the PAH concentrations determined in the moss were used to estimate the concentrations in PM<sub>10</sub> and BD with the equations proposed in a recent study. Low concentrations of PAHs were generally detected, with only a few enriched points never exceeding the legal thresholds, near industrial areas and busy roads. In addition, spatial structure was detected in the concentrations of pyrene, benzo(a)pyrene, benzo(e)pyrene, benzo(ghi)perylene, 5-ring and 6-ring PAHs. Consequently, high-resolution pollution maps were constructed for these compounds. The study findings demonstrate the high sensitivity and suitability of Mosspheres not only for mapping PAHs levels when spatial structure is present, but also for quantitative (i.e. PAHS with 4 or more rings) and qualitative (3-ring PAHs) monitoring. Thus, Mosspheres are ideal complements to conventional monitoring methods, even for PAHs occurring at low concentrations.

References:

Capozzi, F., Giordano, S., Aboal, J.R., Adamo, P., Bargagli, R., Boquete, T., Di Palma, A., Real, C., Reski, R., Spagnuolo, V., Steinbauer, K., Tretiach, M., Varela, Z., Zechmeister, H., Fernández, J.A., 2016. Best options for the exposure of traditional and innovative moss bags: A systematic evaluation in three European countries. Environ. Pollut. 214, 362–373.

Aboal, J.R., Concha-Graña, E., De Nicola, F., Muniategui-Lorenzo, S., López-Mahía, P., Giordano, S., Capozzi, F., Di Palma, A., Reski, R., Zechmeister, H., Martínez-Abaigar, J., Fernández, J.A., 2020. Testing a novel biotechnological passive sampler for monitoring atmospheric PAH pollution. J. Hazard. Mater. 381, 120949.

#### FIRST STUDY ON NITROGEN PRESENCE IN MOSSES SAMPLES IN KOSOVO BY KJELDAHL METHOD

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The nitrogen content in mosses samples for the first time in the whole territory of Kosovo, were studied in 2019. In total 45 mosses samples were collected during August to September, and the procedure of sampling was in accordance with the Monitoring Manual of "International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops, 2020". The concentrations of nitrogen in mosses samples were determined by Kjeldahl method. The descriptive statistics and the distribution map of concentrations were prepared. The minimum content of nitrogen in the collected mosses was 0.81% and the maximum value was 1.47%, while the median value was 1.10%. The obtained results were compared with data in similar studies in neighbouring countries (North Macedonia and Croatia), European countries and Finland as an expected low pollution area. The median of Nitrogen concentration is lower than that in Croatia (1.49%), very close to that of North Macedonia (1.06%) and higher than in samples from Finland (0.70%) in 2010 study [1]. High concentrations of nitrogen ( $\geq$ 1.45%) were found in Drenas, Skenderaj and Ferizaj as the result of agricultural activities, industry, and traffic.

Keywords: Kosovo; air; pollution; nitrogen, mosses; Kjeldahl method.

 Zdravko Špirić, Trajče Stafilov, Ivana Vučković & Marin Glad (2014) Study of nitrogen pollution in Croatia by moss biomonitoring and Kjeldahl method, Journal of Environmental Science and Health, Part A, 49:12, 1402-1408, DOI: 10.1080/10934529.2014.928532

# REVIEW OF 2010-2020 MOSS SURVEYS FOR HEAVY METAL ATMOSPHERIC DEPOSITION IN ROMANIA

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Moss biomonitoring technique was applied for heavy metals atmospheric deposition in Romania in the framework of the *International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops* and through the research projects jointly implemented by the Romanian partners "Valahia" University of Targoviste (UVT), "Dunarea de Jos" University of Galati (UDJG), and Joint Institute for Nuclear Research (JINR) at Dubna, Russian Federation. The concentrations of the elements: Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Sb, Ba, Cs, La, Ce, Sm, Tb, Pb, Th and U in moss samples were determined by atomic absorption spectrometry, mass spectrometry with inductively coupled plasma and instrumental neutron activation analysis.

The comparison between the moss surveys conducted in 2010, 2015 and 2020 shows a decreasing trend of heavy metals concentration. The changes of elements concentration in mosses were mapped. A significant decrease of heavy metal concentrations has been detected in the north and west parts of Romania.

#### MOSSES AS A BIOMONITOR OF AIR POLLUTION WITH HEAVY METALS FROM POINT SOURCE OF POLLUTION

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Mosses are one of the best bioindicators in the assessment of atmospheric aerosol pollution by heavy metals. Studies using mosses allow both short- and long-term air quality monitoring. The increasing contamination of the environment (including air) is causing a search for new, cheap and effective methods of monitoring its condition. Once such method is the use of mosses in active biomonitoring. The aim of the study was to assess the atmospheric aerosol pollution with selected heavy metals (Ni, Cu, Zn, Cd, Hg and Pb) from the smoke of fireworks used during New Year's Eve in the years 2019/2020 and 2020/2021. In studies a biomonitoring moss-bag method with moss *Pleurozium schreberi* (Willd. ex Brid.) Mitt. was used. The research was conducted in the town Prószków (5 km in south direction from Opole, opolskie voivodship, Poland). The moss was exposed 14 days before 31 December (from 17 to 30 of December), on New Year's Eve (31 December and 1 January) and 2 weeks after the New Year (from 2–15 January) (Figure 1).



Figure 1. Photos of mosses: (a) Pleurozium schreberi close-up, (b) moss exposure.

Higher concentrations of analysed elements were determined in samples exposed during New Year's Eve. Increases in concentrations were demonstrated by analysis of the Relative Accumulation Factor (RAF). The results indicate that the use of fireworks during New Year's Eve causes an increase in air pollution with heavy metals. In addition, it was shown that the COVID-19 induced restrictions during New Year's Eve 2020 resulted in a reduction of heavy metal concentration in moss samples and thus in lower atmospheric aerosol pollution with these analytes. The study confirmed moss usefulness in monitoring of atmospheric aerosol pollution from point sources.

#### FACTORS CONDITIONING THE CONTENT OF CHEMICAL ELEMENTS IN MOSSES AND SOILS OF ARMENIA

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The chemical characterization of the different environmental compartments is of great interest and provide a solid base to trace the environmental changes conditioned by the intensive anthropogenic activities. This study identifies the links between the Cr, V, Ti, Sr, Rb, As, Zn, Cu, Co, Fe, Mn, Pb, and Ba contents in mosses and soil, their spatial patterns and potential sources in the Republic of Armenia. The combined use of the compositional data analysis and geospatial mapping allows to reveal the hidden pattern of relationship between the studied elements in different media. Strong link was identified between mosses and soil Cr, Sr, Rb, As, and Pb for acrocarpous (Syntrichia ruralis) moss species contents associated with the soil resuspension whereas for pleurocarpous (Homalothecium philippeanum) moss species Sr, Mn, Zn, As, Rb, Ba, and Cu contents depends on the mechanisms determining the transfer of elements to mosses from dead or living plant materials. In soil, the geological base was the key factor determining elements geochemical associations, whereas for mosses, the identified clusters were distributed in line with the urban-rural gradient and known sources of pollution. Moreover, in both medias the same sampling sites hosting natural mineralization and mining and smelting activities were characterized by the presence of multivariate outliers. In addition, moss samples located in the urban areas was characterized by the high contents of urban specific anthropogenic elements (Pb, Cu, Zn). The results of this study confirmed the applicability of the studied moss species in pollution sources identification and can serve as a basis for identifying the most suitable sites in Armenia for the next moss survey.