



Centre for Ecology & Hydrology NATURAL ENVIRONMENT RESEARCH COUNCIL



31st Task Force Meeting

5th – 8th March 2018

Dessau-Roßlau, Germany







Programme & Abstracts



Organizers:

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

> Dr. Harry Harmens Prof. Gina Mills

Local organizers:

Prof. Ludger Grünhage (Justus-Liebig-University Giessen) Dr. Jürgen Bender (Thünen Institute of Biodiversity) Gudrun Schütze (German Environment Agency)

> Local financial support is provided by the German Environment Agency



PROGRAMME

Venue: Umweltbundesamt, Wörlitzer Platz 1, 06844 Dessau-Roßlau

Monday 5th March, 2018

17:00 – Registration in the Umweltbundesamt

18:30 – Welcome reception and putting up posters

Tuesday 6th March, 2018

- Plenary and moss survey sessions in the auditorium
- Ozone sessions in room 0.172
- Poster session in the exhibition room

08:00 Late registration and putting up posters

| Session 1: | 9:00 - 10:45 | Plenary | Chair: Ludger Grünhage |
|------------|---|--|---|
| 09:00 | Maria Krautzberg | ger, President of the C | German Environment Agency - Welcome. |
| 09:10 | Wolfgang Seidel, Agency – Tasks a | Head of Presidentiand activities. | al Division - The German Environment |
| 09:30 | <i>Harry Harmens e</i> 2017 and future v | <i>et al.</i> – Summary of th vorkplan (2018-2020 | ne achievements of the ICP Vegetation in). |
| 09.50 | Marina Frontasy | eva – Preliminary res | sults of the 2015/16 moss survey. |
| 10:10 | <i>Gina Mills</i> – To Vegetation contri | owards a cleaner air bute? | r environment in 2040: What can ICP |
| 10.20 | Conoral diamaria | | |

10:30 General discussion

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

| Session 2: | 11:30 - 13:00 | Plenary | Chair: Gina Mills | |
|------------|--|---|--|---|
| 11:30 | Katrina Sharps et a developing countri | al. – Quantifying o es. | effects of ozone on crops in developed an | d |
| 11:50 | <i>Kim Oanh et al.</i> collecting and risk | – ICP Vegetatio | on-Asia: A new policy-focused evidencork for ozone. | e |
| 12:10 | Anne-Katrin Presc | <i>her et al</i> . – Updat | e of ICP Forests activities. | |
| 12:30 | <i>Ilia Ilyin</i> – Evaluat EMEP grid using h | ion of spatial distr neavy metal conce | ibution of modelled pollution levels in neventrations in mosses. | W |
| 12:50 | General discussion | L | | |

13:00 - 14.00 Lunch

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

Session 3a: **Ozone - Impacts on food production Chair: Håkan Pleijel**

- 14:00Gina Mills et al. - Tropospheric Ozone Assessment Report: Present day tropospheric ozone distribution and trends relevant to vegetation.
- 14:20 Lisa Emberson et al. - Developing ozone effect modules for crop growth models.
- 14:40 Amos Tai et al. – Evaluation and uncertainty quantification of the impacts of surface ozone on global primary productivity using a coupled atmospheric chemistry-biosphere modeling framework.
- 15:00 Jérôme Schneuwly et al. – Data and model evaluation to estimate O₃-induced crop yield losses in Switzerland.
- 15:20 General discussion

Session 3b: Moss survey - 2015/16 survey **Chair: Harry Harmens**

- 14:00 Alexander Uzhinsky - Data management systems (DMS) of UNECE ICP Vegetation moss survey programme: current status and future perspectives.
- 14:20 Discussion on preliminary results moss survey 2015/16 - heavy metals and nitrogen, led by Marina Frontasyeva:
 - Quality assurance of the data;
 - Spatial distribution: draft maps, resolution of maps; identification of hotspots;
 - Temporal trends: comparison with EMEP deposition trends, identification of anomalies;
 - Mosses as biomonitors in more arid regions. _

15:30 - 16.00 Coffee/tea and poster viewing

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

| Session 4a: | Ozone – Crop-sensitivity | Chair: Kent Burkey |
|-------------|---|---|
| 16:00 | Felicity Hayes et al. – Impact of crops. | ozone on physiology and yield of African |
| 16:20 | Pleijel et al. – Fertilizer efficiency i | n wheat is reduced by ozone pollution. |
| 16:40 | Kent Burkey et al. – Interactive eff soybean biomass production and see | ects of elevated temperature and ozone on ed yield. |
| 17:00 | <i>Victoria Bermejo et al.</i> – Breedin cultivars in Spain causes lower tolera atmosphere. | ng wheat towards more ozone sensitive ance to water stress under an ozone-polluted |
| 17.20 | General discussion | |

17:20 General discussion

| Session 4b: | Moss survey – Results 2015/16 | Chair: Zaida Kosonen |
|-------------|---|---|
| 16:00 | <i>Hilde Uggerud et al.</i> – Temporal trends and in mosses in Norway. | spatial distribution of trace metals |
| 16:20 | Sebastien Leblond et al. – Interspecies moss | comparison in France. |
| 16:40 | <i>Gevorg Tepanosyan et al.</i> – Studying atmosp in Armenia by the moss biomonitoring techn | pheric deposition of trace elements ique. |
| 17:00 | Chrysoula Betsou et al. – Heavy metal co Greece. | oncentrations in moss samples in |
| 17:20 | General discussion | |

17:45 – 18:30 Guided tour UBA building. For further info see:

https://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/4007.pdf https://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/4265.pdf https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/07_flyer_eng _gruenanlagen_einzelseiten.pdf

Wednesday 7th March, 2017

| Session 5: | 08:45 – 10:30 (Two parallel sessions: Ozone and Moss survey) | | | |
|-------------|---|---|--|--|
| Session 5a: | Ozone - Risk assessment | Chair: Ignacio González-Fernández | | |
| 08:45 | Alessandra De Marco et al assessment. | - A multi-model framework for ozone risk | | |
| 09:05 | Sabine Braun – Validation of the drought module of DO ₃ SE for Swiss forest sites. | | | |
| 09:25 | <i>Yasutomo Hoshika et al.</i> – Ozone risk assessment for forest trees as affected by soil water deficit and nutritional availability. | | | |
| 09:45 | General discussion related to the updated Chapter 3 of the Modelling and Mapping Manual | | | |
| | Progress with validationPotential new material foAny other new developm | EMEP soil moisture index modelling; r Scientific Background Document B; ents, including EU NEC Directive. | | |
| Session 5b: | Mosses - Trends | Chair: Sébastien Leblond | | |
| 08:45 | <i>Stefan Nickel et al.</i> – Spatial generalization of canopy drip effects on element concentrations in moss by example of Germany. | | | |
| 09:05 | Zaida Kosonen et al. – The use of mixed archive moss samples for completing heavy metal data in Switzerland from1990-2010. | | | |
| 09:25 | Yulia Aleksiayenak et al. – Res Belarus. | sults of the ten-year study of the territory of | | |

09:45 Pranvera Lazo et al. - Temporal and spatial distribution on multi-element atmospheric deposition in Albania (2010-2015 moss survey).

- 10:05 Continued discussion moss survey results 2015/16.
- 10:30 11:00 Coffee/tea and poster viewing

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

Session 6a: **Ozone - Impacts on grasslands Chair: Jürgen Bender** 11:00 Ignacio González-Fernández et al. - Ozone effects on nitrogen cycling in Mediterranean annual pastures. Seraina Bassin et al. - Combined effects of nitrogen deposition and climate 11:20 change on species composition of subalpine grassland. 11:40 Ane Vollsnes et al. – The double punch: Ozone and climate stresses to sub-arctic vegetation.

12:00General discussion:

- ICP Vegetation workplan;
- Future development of ICP Vegetation Asia.

Session 6b: **Moss survey**

- 11:00 Aneta Krakovská et al. – Assessment of heavy metal deposition and air pollution in the southern part of Silesian coal basin using moss biomonitoring.
- 11:20 Maria Zielińska et al. - Biomonitoring of the forest areas of southern and northeastern Poland.
- 11:40 Annekatrin Dreyer et al. - Persistent organic pollutants (POP) in Germany: Results from the 2015/2016 moss and tree sampling.
- 12:00 Muhammad Adrees et al. - Impact of brick kiln emission pollution on surrounding vegetation in Faisalabad-Pakistan.
- 12:20 Discussion on reporting of heavy metal, nitrogen and POPs concentrations in mosses, led by Marina Frontasyeva:
 - Maps, tables and text on spatial and temporal trends;
 - Country reports;
 - Time schedule for finalising report by July 2018;
 - Printing of report;

Ozone - Impacts on trees

Any new developments, such as role in EU NEC Directive.

13:00 - 14.00 Lunch

Session 7a:

- Session 7: 14:00 – 15:45 (Two parallel sessions: Ozone and Moss survey)
- 14:00Hanieh Eghdami et al. - Time series of ozone flux in German forests comparison of DO₃SE and FO₃REST.

Chair: Rocio Alonso

Chair: Claudia Stihi

- 14:15 *Pierre Sicard et al.* MOTTLES: a new-generation long-term monitoring stations across Europe for forest protection against surface ozone.
- 14:30 *Elisabetta Salvatori et al.* Effects of the antiozonant ethylenediurea (EDU) on *Fraxinus ornus* L.: The role of drought.
- 14:45 *Lulu Dai et al.* A comparative analysis of apoplastic and symplastic antioxidative responses to elevated ozone in the leaves of poplar, tobacco and soybean.

15:00 **Discussion**: - Finalise future work programme, including for ICP Vegetation Asia;

- Feedback from ozone group to plenary (Felicity Hayes);
- Decisions and recommendations related to ozone.

Session 7b: Moss survey

Chair: Marina Frontasyeva

- 14:00 *Caroline Meyer et al.* Comparison of pollen uptake by three forested mosses species in France.
- 14:20 *Vladislav Svozilik et al.* Verification of the mathematical air pollution dispersion models using neutron activation analysis.

14:40 **Discussion** on:

- Preparations 2020 moss survey: monitoring manual, data collection and management; future developments;
- Feedback from moss group to plenary (Marina Frontasyeva);
- Decisions and recommendations related to moss survey.

15:45 – 16:15 Coffee/tea and poster viewing

16:15 Walk to the Bauhaus

16:45 Visit of the UNESCO world cultural heritage site Bauhaus

19:30 Conference Dinner at the restaurant "Brauhaus Zum Alten Dessauer", Lange Gasse 16, 06844 Dessau-Roßlau.

Thursday 8th March, 2018

Session 9: 08:45 – 10:30 Plenary

Chair: Harry Harmens

- Reporting back from ozone (Felicity Hayes) and moss sessions (Marina Frontasyeva): decisions and actions;
- Medium-term work plan ICP Vegetation 2018 2020;
- Decisions and recommendations of the 31st Task Force Meeting;
- 32nd ICP Vegetation Task Force Meeting;
- Other business.

LIST OF POSTERS

OZONE

Title

| Ahmada M.N., Ziaa A. | Monitoring of ambient air pollution and ist effects to agricultural crops in Pakistan: a threat to the future food security of South Asia? |
|--|---|
| Baumgarten M., Grünhage L. | Ozone Risk for Trees – phytotoxic ozone dose and future effects on tree growth in Germany |
| Danh N.T., Oanh N.T.K. | Assessment of surface ozone effects on rice production in Southern Vietnam for possible alternative cropping systems |
| Drapikowska M., Borowiak K., Pagórek C., Lisiak M., Byczkowska K., Drapikowski P. | Image based estimation of anatomical ozone injury responses of Nicotiana tabacum L. |
| Gerosa G., Finco A., Marzuoli R., Chiesa M. | 15 years of measurements of ozone deposition fluxes over forests, crops and bare soils in Italy |
| Leung F., Sitch S., Tai A., Wiltshire A., Gornall J., William K. | Quantifying the impact of present-day and future tropospheric ozone on crop productivity at global and regional scale using JULES-crop |
| Sicard P., Anav A., De Marco A., Paoletti E. | Projected global tropospheric ozone impacts on vegetation under different emission and climate scenariosS |
| Tai, A.P.K., Sadiq, M., Zhou, S., Wong, A.Y.H. | Effects of plant physiological responses to rising ozone and CO2 levels on global air quality via various feedback mechanisms |
| Xu Y., Feng Z., Tarvainen L., Uddling J. | Mesophyll conductance limitation of photosynthesis in poplar under elevated ozone |
| | |

MOSS SURVEY

| Author(s) | Title |
|---|---|
| Allaiheu Sh, Bektechi I, Oarri E, Kane S, Lazo P, Stafilov T | Distribution of trace elements influence from sea coastal line by using moss |
| Aliajueu Shi, Dekleshi L, Wahi F, Kane S, Lazu F, Stahov I. | biomonitoring |
| Aničić Urošević M., Vuković G., Vasić P., Jakšić T., Nikolić D., Škrivanj S., Popović A. | Environmental implication indices by elemental characterisation of the co-located topsoil and moss samples |
| Aslani M.A.A., Haciyakupoglu S. Belivermis M., Kilic O., Ileri .RK., Erenturk S. | Atmospheric deposition of radionuclides by moss biomonitoring technique in Thrace region of Turkey |
| Borowiak K., Lisiak M., Budka A., Kanclerz J., Janicka E., Adamska A., Żyromski A., Biniak-Pieróg M., Podawca K., Mleczek M., Niedzielski P. | Rare earth elements in Taraxacum officinale collected in three different cities |
| Budka A., Mleczek P., Borowiak K., Niedzielski P. | Relationship between concentration of rare earth elements in soil and their distribution in plants growing near a busy road |
| Bukharina I.L., Zhuravleva A.N., Volkov N.A., Vasileva N.A., Bakuleva Y.A., Plotnikova K.V., Frontasyeva M.V. | Moss monitoring of trace elements in the Republic of Udmurtia, Russia |
| Chaligava O., Shetekauri S., Shetekauri T., Kvlividze A., Kalabegishvili T., Frontasyeva M.V., Chepurchenko O.E., Tselmovich V.A. | Atmospheric deposition study of major and trace elements by the moss biomonitoring technique in Georgia: 2014–2016 |
| Ene A., Stihi C., Frontasyeva M., Radulescu C., Iacoban I. | Spatial distribution of heavy metals and nitrogen deposition in Romania based on moss analysis in 2015 |
| Fettig, I., Horvat, M., de Krom, I., Douglas, D., Rajamaki, T. | MERCOX – Metrology for oxidised mercury |
| Fränzle S., Retschke D., Erler M., Blind F. | Chitin-covered sorbent slides for acquiring data on air- or waterborne pollution, subterrain biochemical activities and secondary contributions to climate change |
| Godyń P., Zielińska M., Ziembik Z., Dołhańczuk-Śródka A. | Concentrations of natural radioactive gamma isotopes in Pleurozium schreberi moss |
| Gorelova S.V., Frontasyeva M.V., Vergel K.N. Babicheva D.E., Ignatova T.Yu, | Moss monitoring of atmospheric deposition in Central Russia: Tula region (2015-2016) |
| Haciyakupoglu S., Erenturk S. | Atmospheric deposition of major and trace elements by moss biomonitoring technique in Northwest of Turkey |
| Haciyakupoglu S., Genceli E., Erenturk S. | Atmospheric nitrogen deposition in moss samples in Northwest of Turkey |
| Koroleva Y., Zhurilo D., Ananyan A., Sokhar L., Zegalina L. | Active monitoring of air pollution in the historic area of the city Kaliningrad using Sphagnum mosses |
| Lisiak M., Borowiak K., Budka A., Kanclerz J., Janicka E., Adamska A., Żyromski A., Biniak-Pieróg M., Podawca K., Mleczek M., Niedzielski P. | Relations between land use structure and rare earth elements concentrations in plants |
| Maňkovská, B., Oszlányi, J., Izakovičová, Z., Frontasyeva, M. | Trends of heavy metal accumulation in mosses in Slovakia (1990-2015) |
| Nurgaliyeva D.Zh., Nurkassimova M.U, Makhambet A., Omarova N.M., Glushenko V.N, Solodukhin V.P., Frontasyeva M.V., Chepurchenko O. | Atmospheric deposition of trace elements in Kazakhstan |
| Nurgalieva D.Zh., Nurkassimova M.U., Omarova N.M., Dalelova A.M., Frontasyeva M.V., Morzhuhina S.V. | Atmospheric depositions of heavy metals and radionuclides in Lrtysh areas of Kazakhstan |
| Qarri F., Lazo P., Allajbeu Sh., Bekteshi L., Stafilov T. | Trends of atmospheric deposition of trace elements in Albania studied by the moss biomonitoring technique. |
| Radulescu C., Bintintan A., Gligor M., Ion R.M., Dulama I.D., Stihi C., Teodorescu S., Stirbescu R.M. | Pollution effects on painted pottery of Romanian cultural heritage |
| Salahova S.Z., Topchiyeva Sh.A., Mehrabova M.A., Humbatov F.Y. | State of atmospheric air in different territories of Azerbaijan |
| Saxena D.K., Karuna M.S. | Atmospheric lead deposition during 2011-2014: estimation based on moss analysis |
| Schröder W., Nickel S. | Geostatistically mapping spatial structures of measurement values and percentile statistics of heavy metals and nitrogen accumulation in mossess sampled 1990-2015 |
| Steinnes E., Uggerud H.T. | Metal pollution around Norwegian industries studied by analysis of natural growing moss samples |
| Stihi C., Ene A., Frontasyeva M., Radulescu C., Culicov O., Zinicovscaia I. | Temporal trends of heavy metal concentrations in mosses collected from Romania in 2010 and 2015 |
| Thöni L., Strok M., Mazej D., Schnyder E., Kosonen Z., Jeran Z., Skudnik, M. | Lead concentration and stable lead isotopes in moss in Slovenia and Switzerland |
| Vergel K.N., FrontasyevaM.V., Zinicovscaia I.I., Vikhrova I.M., Strelkova L.P | Biomonitoring of heavy metals and trace elements in North Russia: Tikhvin case study 2017 |
| Vuković G., Aničić Urošević M., Herceg Romanić S., Mendaš Starčević G., Ilić M., Milićević T., Frontasyeva, M.V. | Organochlorine pesticides and polychlorinated biphenyls in the moss Hypnum cupressiforme and topsoil sampled in Serbia |
| Zia A., Ahmad M.N. | Atmospheric nitrogen induced heavy metal leaching |

Author(s)

PLENARY

PRELIMINARY RESULTS OF THE MOSS SURVEY IN 2015/2016

Frontasyeva M.V.¹, Harmens H.², Steinnes E.³

¹Joint Institute for Nuclear Research (JINR), str. Joliot-Curie, 6, Dubna, 141980, Moscow Region, Russian Federation, E-mail: <u>marina@nf.jinr.ru</u> ²ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, Gwynedd LL57 2UW, United Kingdom, E-mail: <u>hh@ceh.ac.uk</u> ³Department of Chemistry, NTNU, NO-7055 Trondheim, Norway E-mail: <u>eiliv.steinnes@ntnu.no</u>

A preliminary report on the moss survey 2015/2016 will be given. In agreement with the longterm strategy of the LRTAP Convention to enhance participation and improve air quality in Eastern Europe, the Caucasus, Central Asia and South Eastern Europe, efforts to extend the moss survey to former republics of the USSR were successfully undertaken in countries such as Armenia, Azerbaijan, Georgia, Kazakhstan, Moldova, and Tadjikistan. In the current moss survey the following territories of the Russian Federation were sampled: Yaroslavl', Tula, Ryazan, Ivanovo, Leningrad (Tikhvin district), Bryansk, and Kaliningrad Regions, Voronezh Reserve, Yamal Penisular, Republic of Udmurtia, and Far East (Kamchatka). In addition to the requested 12 metals (Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, V, Zn), many countries have reported data on Li, Be, B, Na, Rb, Sr, Y, Nb, Rh, Ag, Tl, Cs, Ba, La, Ce, Pr. Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb, Ir, Pt, Te, Bi, Th, U, Mg, S, Ca, Sc, Ti, Mn, Co, Ga, K, and Se. A total of 34 countries submitted data on heavy metal concentrations in mosses. In addition, ten countries also submitted data on the nitrogen concentration in mosses. In spite of the growing interest in assessment of the deposition of persistent organic pollutants (PAHs, PCBs, PBDEs, dioxins, PFOS, etc.) using moss, only a limited number of the Western European countries determined POPs. A preliminary assessment of the interlaboratory comparison of moss reference material M2 and M3 will be discussed too. The Sector of Neutron Activation Analysis (NAA) and Applied Research of FLNP JINR (Dubna) continues to support the moss survey programme in some of its member states: Bulgaria, Czech Republic, Mongolia, Poland, Romania, Slovakia and Tadjikistan. Some details are provided on the progress in established DATA MANAGEMENT SYSTEM at the JINR cloud.

References:

- M. V. Frontasyeva, E. Steinnes and H. Harmens. Monitoring long-term and large-scale deposition of air pollutants based on moss analysis. Chapter in a book "Biomonitoring of Air Pollution Using Mosses and Lichens: Passive and Active Approach – State of the Art and Perspectives", Edts. M. Aničić Urošević, G. Vuković, M. Tomašević, Nova Science Publishers, New-York, USA, 2016.
- A. Uzhinskiy, G. Ososkov, M. Frontasyeva. Data management of the Envorinment. Open System Publications (https://www.osp.ru/) No. 4, 2017, c. 42-43, ISSN 1028-7493, https://www.osp.ru/os/2017/04/13053390/
- E. Steinnes, Å. Rühling, H. Lippo, A. Mäkinen. Reference materials for large-scale metal deposition surveys. Accred Qual Assur (1997) 2: 243–249.
- Harmens, H., et al. (2010). Mosses as biomonitors of atmospheric heavy metal deposition: spatial and temporal trends in Europe. Environmental Pollution 158: 3144-3156.

SUMMARY OF ACHIEVEMENTS OF THE ICP VEGETATION IN 2017 AND FUTURE WORKPLAN (2018 – 2020)

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

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

The ICP Vegetation is an international programme that reports on the effects of air pollutants on natural vegetation and crops [1]. It reports to the Working Group on Effects (WGE) of the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP). In particular, the ICP Vegetation focuses on the following air pollution problems: i) quantifying the risks to vegetation posed by ozone pollution and collating field-based evidence of ozone impacts; ii) the atmospheric deposition of heavy metals, nitrogen and persistent organic pollutants (POPs) to vegetation. The ICP Vegetation encourages outreach activities to other regions such as Asia, Africa and South America and has recently established an ICP Vegetation-Asia network.

At the 31st Task Force Meeting we will report on the achievements of the ICP Vegetation in 2017, including:

- Ozone risk assessments: Completion of revision of Chapter 3 of the Modelling and Mapping Manual and associated Scientific Background Documents A and B [1,2];
- Ozone impacts on crops in developing regions and ICP Vegetation-Asia network;
- Heavy metals, nitrogen and persistent organic pollutants (POPs): Progress with data analyses and mapping of the results of moss survey 2015/2016;
- Contributions to workplan items of the WGE and collaboration with the European Monitoring and Evalution Programme (EMEP);
- Contribution to guidance document on ecosystem impacts monitoring as part of the revised EU National Emission Ceilings Directive (Directive 2016/2284).

We will also discuss the future workplan (2018 - 2020), including:

- Further outreach activities in developing countries;
- Evidence of ozone impacts on crops in developing countries;
- Large-scale risk assessment of ozone impacts in soil moisture limited areas (collaboration with EMEP/MSC-West);
- Report on the outcome of the 2015/2016 moss survey;
- Preparations for the 2020 moss survey.

For further details see http://icpvegetation.ceh.ac.uk

Acknowledgement:

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

References:

```
[1] <u>http://icpvegetation.ceh.ac.uk/manuals/mapping_manual.html</u>
[2] <u>http://icpvegetation.ceh.ac.uk/publications/documents/Ozoneflux-basedcriticallevels2017brochure_Mid-res.pdf</u>
```

ICP VEGETATION-ASIA: A NEW POLICY-FOCUSED EVIDENCE COLLECTING AND RISK ASSESSMENT NETWORK FOR OZONE

<u>Kim Oanh</u>^{1*}, Gina Mills², Harry Harmens², Patrick Büker³, Felicity Hayes², Katrina Sharps², Muhammad Adrees⁴, Arti Bhatia⁵, Hanieh Eghdami⁶, Felix Leung⁷, Rebecca Oliver⁸, Durgesh Singh Yadav⁹

*Corresponding author: kimoanh@ait.asia

¹Asian Institute of Technology, Bangkok, Thailand; ²Centre for Ecology & Hydrology, Bangor, UK; ³Stockholm Environment Institute, University of York, UK; ⁴Government College University, Faisalabad, Pakistan; ⁵ICAR-Indian Agricultural Research Institute, Delhi, India; ⁶University of Trier, Trier, Germany; ⁷University of Exeter, Exeter, UK; ⁸Centre for Ecology and Hydrology, Wallingford, UK; ⁹Banaras Hindu University, Varanasi, India

Reporting to the United Nations Convention on Long-Range Transboundary Air Pollution, the ICP Vegetation involves over 250 scientists representing 50 countries. For ozone, the primary objectives are to (i) collate and review evidence of impacts on vegetation and (ii) to assess spatial patterns and temporal trends in the risks of damage from current and future ozone. As part of the Convention's outreach activities, the ICP Vegetation is developing a new Asian network, ICP Vegetation-Asia. The network is being coordinated by Prof. Kim Oanh of the Asian Institute of Technology, Thailand and will initially focus on food security impacts. Assisted by the ICP Vegetation Coordination Centre in the UK, the first phase of activities is on the theme of "seeing is believing", aiming to show policy makers that effects on crops should also be considered along with effects on health. Activities will include a review of evidence presented in the published and "grey" scientific literature and the establishment of a network of sites where sensitive ozone species (SOS) will be used to draw the attention of policy makers, agronomists and the public to the growing ozone problem in Asia. An initial pilot study will be conducted in 2018 at selected sites in S and SE Asian countries, involving ozone-sensitive and -resistant bean varieties grown together with local varieties. The distinctive visible symptoms on the beans will be used to provide "SOS" warnings of the pollutant's potential to damage food crops. Later activities will include expansion of the SOS network, the development of region-specific critical levels and flux-based risk assessments and organising knowledge exchange workshops. Policy makers are involved from the start to ensure the activities of ICP Vegetation are suitably focussed on policy needs. New groups from Asia are very welcome to join the network.

Keywords: ozone, crops, network, field evidence, visible injury, food security, Asia

QUANTIFYING EFFECTS OF OZONE ON CROPS IN DEVELOPED AND DEVELOPING COUNTRIES

Gina Mills¹, <u>Katrina Sharps</u>^{1*}, David Simpson, Håkan Pleijel, Malin Broberg, Johan Uddling, Fernando Jaramillo, William J. Davies, Frank Dentener, Maurits Van den Berg, Madhoolika Agrawal, S.B. Agrawal, Elizabeth A. Ainsworth, Patrick Büker, Lisa Emberson, Zhaozhong Feng, Harry Harmens¹, Felicity Hayes¹, Kazuhiko Kobayashi, Elena Paoletti, Rita Van Dingenen

¹NERC Centre for Ecology & Hydrology, Environment Centre Wales, Bangor, UK *katshar@ceh.ac.uk

Affiliations for remaining co-authors can be found in the paper.

Note: The key results presented here have been submitted to Global Change Biology.

Several of the world's most important crops are negatively affected by ozone pollution, showing decreasing vegetative growth, seed production and root growth, leading to yield reductions. While there is an extensive network of ozone monitoring sites in developed areas of the world (for example, the USA and Europe), monitoring is limited in developing countries.

We have developed a method which allows the quantification of ozone effects on crops around the world. Response functions relating crop yield to stomatal uptake ("flux") of ozone are applied to modelled data on a global scale to predict ozone impacts on crop production. As we have shown that field effects of ozone are more strongly correlated with stomatal ozone uptake than ozone concentration, this analysis is an improvement on previous concentration-based global assessments.

We highlight the regions of the world where important crops are predicted to be most impacted by ozone, in developed countries and also for countries recorded by the Organisation for Economic Co-operation and Development (OECD) Development Assistance Committee (DAC) as receiving Official Development Assistance (ODA).

Overall, ozone effects are highest where irrigation is in use or in areas where rainfall is sufficient to ensure soil moisture is non-limiting to stomatal uptake. We demonstrate the need to consider ozone pollution as a modifying factor in global crop production and show that mitigation of the negative effects of ozone is needed in order to help close current yield gaps.

OZONE SESSIONS

COMBINED EFFECTS OF NITROGEN DEPOSITION AND CLIMATE CHANGE ON SPECIES COMPOSITION OF SUBALPINE GRASSLAND

Bassin S., Volk M.

Agroscope, Reckenholzstr. 191 CH-8046 Zurich, seraina.bassin@agroscope.admin.ch

To investigate the combined effects of increasing temperature, increased nitrogen deposition, and altered water availability, turf monoliths originating from six different alps (2150 m a.s.l.) were transported in 2013 to a common site (Ardez, GR) consisting of six climate change scenarios at different altitudes (1680 – 2360 m a.s.l.) representing approximately 4°C growth period mean temperature difference. NH₄NO₃ solution (equivalent to +3 (N3) and +15 kg N ha⁻¹ yr⁻¹ (N15)) and irrigation with well water (+50% of the annual precipitation sum) were applied bi-weekly in a fully factorial design.

Vegetation composition was recorded yearly at peak vegetation development, following the phenology along the elevation gradient. Cover was estimated for the four plant functional groups (grasses, forbs, sedges, and legumes) as well as for the most abundant individual species.

Vegetation relevées revealed different response patterns of the four functional groups to temperature change and water availability, respectively, and their interactions. Grasses slightly benefitted from the temperature increase, but only in the absence of irrigation. In contrast, the functional group of forbs was consistently negatively affected by the temperature rise, with the effect being much stronger in non-irrigated plots. While in forbs, the positive impact of irrigation was limited to the warmest treatments, the sedges benefitted across the whole temperature range from the water addition. Legumes responded in a similar way, but showing a unimodal temperature response function with a maximum at +0.9°C temperature increase. The functional groups' reactions to the nitrogen addition were unequivocal. Only the sedges showed a clear response, with the effects being positive at cooler temperatures but absent in a warmer climate. Forbs showed a similar, but less pronounced reaction.

Of the individual species *Carex sempervirens* and *Potentilla aurea* were negatively affected by warming, while *Trifolium pratense* showed the same unimodal response as the legume functional group. In contrast, *Sesleria caerulea* was stimulated by higher temperatures. As expected, most species benefitted from the irrigation treatment, except *Nardus stricta*, *Briza media*, *Helianthemum nummularium*, which gained proportion under drought. Of all the species investigated, only *Carex sempervirens* showed a significant reaction to the N addition, with +13% and +28% higher cover in the N3 and N15 treatments, respectively, compared to the control.

In general, the data suggest climatic factors to have a stronger influence on species composition of subalpine pastures than elevated nitrogen deposition. Moreover, the effect of nitrogen addition tends to be alleviated in a warmer climate.

INTERACTIVE EFFECTS OF ELEVATED TEMPERATURE AND OZONE ON SOYBEAN BIOMASS PRODUCTION AND SEED YIELD

Kent O. Burkey, Samuel J. Ray, Walter A. Pursley, and Richard W. Zobel

USDA-ARS Plant Science Research Unit, 3127 Ligon Street, Raleigh, NC, 27607 USA Kent.Burkey@ars.usda.gov

Predicting the impacts of air pollution and climate change on vegetation requires understanding of the interactions between elevated air temperature and atmospheric gases such as ozone. The air exclusion system (AES) developed by our group (see Figure 1) was used to expose soybean plants to combinations of elevated temperature $(+4^{\circ}C)$ and ozone.

Soybean cultivar "Jake" was grown in the AES system in 2017. Season-long treatments were a CF air control, heated CF air (CF+H), elevated ozone (CF+O3), and the combination of heated CF air and elevated ozone (CF+O3+H). Soil moisture was maintained using drip irrigation to account for differences in evapotranspiration demand in heated plots. Biomass was affected only by the combination of high temperature and elevated ozone that resulted in a 21% loss of dry weight (Table 1). Elevated temperature reduced seed yield by 35% (Table 1). Elevated ozone alone reduced yield by 12% for this cultivar-treatment combination. Elevated ozone appeared to minimize the effect of high temperature on seed yield, but the impact was not statistically significant (compare CF+O3+H with CF+H in Table 1).



Figure 1. AES heated field plots use a combination of electrical resistance heat and solar heated water to elevate temperature. Each 3 m x 10 m plot consists of two open-top chamber panels placed in parallel. Modified fan boxes deliver heated, humidified air through each panel into the plant canopy.

Table 1. Effects of elevated ozone and temperature on mid-season biomass and final seed yield for soybean cultivar "Jake" in 2017. Plot means (n=3) followed by the same letter are not significantly different. Percentages indicate relative yield compared to CF. Seasonal means for the ozone 12-hour mean and AOT40 are shown.

| Treatment | Biomass | Seed yield | 12-hour mean | AOT40 |
|-----------|-------------------|-------------------|--------------|-------------|
| | $(g m^{-2})$ | $(g m^{-2})$ | (ppb) | (ppb-hours) |
| CF | 1364 ^a | 797 ^a | 18 | 74 |
| | (100 %) | (100 %) | | |
| CF+O3 | 1407 ^a | 706 ^{ab} | 70 | 42426 |
| | (103 %) | (88 %) | | |
| CF+H | 1274 ^a | 519 ° | 18 | 25 |
| | (93 %) | (65 %) | | |
| CF+O3+H | 1073 ^b | 587 ^{bc} | 62 | 32396 |
| | (79 %) | (74 %) | | |

A COMPARATIVE ANALYSIS OF APOPLASTIC AND SYMPLASTIC ANTIOXIDATIVE RESPONSES TO ELEVATED OZONE IN THE LEAVES OF POPLAR, TOBACCO AND SOYBEAN

Lulu Dai^{1,2}, Zhaozhong Feng^{1*}, Harry Harmens²

¹Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Shuangqing Road 18, Haidian District, Beijing, 100085, China
²Centre for Ecology & Hydrology, Environment Centre Wales, Deiniol Road, Bangor, Gwynedd LL57 2UW, UK

*Corresponding author: Prof. Zhaozhong Feng, E-mail address: fzz@rcees.ac.cn (Z. Feng)

To elucidate whether the apoplastic antioxidants are induced by high O₃ concentrations, three species (tobacco (Nicotiana L), soybean (Glycine max (L.) Merr.), and poplar (populus L)) were exposed to charcoal-filtered air (CF) and elevated O₃ (E-O₃, non-filtered ambient air plus 40 ppb). E-O₃ significantly increased the reduced ascorbate (ASC_{apo}), and redox state_{apo} in the apoplast for all three species, whereas no effect on the apoplastic dehydroascorbate (DHA_{apo}). Total ascorbate (ASC+DHA_{apo}) in the apoplast was increased by E-O₃ for all species although the statistically significance was only found in soybean. On the other hand, E-O₃ significantly increased reduced ascorbate (ASC) and total ascorbate (ASC+DHA) in the leaf tissue for soybean and poplar, but significantly decreased that in tobacco. The dehydroascorbate (DHA) and redox state in the leaf tissue were not affected by E-O₃ for all the species. Only superoxide dismutase (SOD) was detected in the apoplastic space, whereas ascorbate peroxidise (APX), hydrogen peroxidase (CAT) and peroxidase (POD) appeared to be absent in all three species. SOD in the apoplast was increased significantly by E-O₃ in tobacco, whereas significantly decreased that in soybean. SOD in the leaf tissue was increased significantly by E-O₃ in tobacco and poplar. E-O₃ significantly increased malondialdehyde (MDA) in the apoplast and leaf tissue in the species except the MDA_{apo} in soybean. Superoxide anion (O2[•]apo) and hydrogen peroxide $(H_2O_{2 apo})$ contents in the apoplast were significantly increased by E-O₃ in all species. However, E-O₃ only significantly increased O₂⁻ content in poplar and significantly increased H₂O₂ content in the leaf tissues in soybean. The regression analyses further indicated that the ASC_{apo} was more induced by high O₃ concentration rather than accumulative O₃ effects (AOT40), whereas the ASC and SOD_{apo}/SOD may not be induced by high O₃ concentration but result from the antioxidative capacity. The production of H₂O₂ and O₂[•] in the apoplast and leaf tissue was more cumulative O₃ effects than stimulated by high O₃ concentration as suggested by the significant linear correlation between H₂O₂/O₂⁻ and AOT40 but not between them and O₃ concentration. It is indicated that ASC_{apo} and SOD_{apo} play an important role in the detoxification of O₃ as the first defence mechanism when exposed to high O₃ concentration.

Keywords: apoplastic antioxidant, symplastic antioxidant, detoxification, ozone, woody species.

A MULTI-MODEL FRAMEWORK FOR OZONE RISK ASSESSMENT

Anav A.¹, Proietti C.¹, <u>De Marco A.^{2*}</u>, Paoletti E.¹

¹Institute for Sustainable Plant Protection (CNR-IPSP), Via Madonna del Piano 10, Sesto Fiorentino (Florence), Italy ²Italian National Agency for New Technologies, Energy and the Environment (ENEA), C.R. Casaccia, S. Maria di Galeria, Italy

Plant ecosystems play a key role in regulating the concentration of air pollutants in the planetary boundary layer. Among common air pollutants, O_3 is probably the most damaging to forests and crops, frequently reaching high concentrations over large regions of the world and particularly in Mediterranean area. However, O_3 effects on vegetation depend not only on the atmospheric concentrations but also on O_3 uptake through the stomata. Therefore, the quantification of the amount of ozone removed from the atmosphere, and the consequent injuries to vegetation, are particularly relevant for climate, ecological and risk assessment studies.

We developed a regional multi-model framework to be used for integrated risk assessment and for studies on potential risks caused by O_3 pollution on European forests. This framework relies on a mesoscale model that generates climate forcing used offline to run a Chemistry Transport Model (CTM). The O_3 concentrations computed through the CTM (CHIMERE) and the climatic variables computed by a regional weather forecast model (WRF) combined with a stomatal conductance model, allowed us to estimate the stomatal O_3 fluxes using different phenological models and assumptions on the water uptake by plants at different soil depths in the rooting zone and to evaluate the differences between an exposure-based index (i.e. AOT40) and an index based on the effective absorbed O_3 dose (i.e. PODY).

Keywords: O₃, AOT40, POD_Y, DO₃SE, Plant Phenology

*Corresponding author: <u>alessandra.demarco@enea.it</u>

TIME SERIES OF OZONE FLUX IN GERMAN FORESTS - COMPARISON OF DO_3SE AND FO_3REST

Eghdami H., Werner W.

University Trier, Department of Geobotany, werner@uni-trier,

Goal of the presentation is to characterize a risk of German forests by Ozone in a long time series from 1998 to 2015.

We show the temporal and spatial variance of POD_1 for beech and spruce in Germany, calculated with different software (DO₃SE and FO₃REST) and different soil or leaf water (potential) approaches, to characterize the range of POD_1 and their exceedance of critical level.

For the evaluation of ozone-flux hourly datasets without gap for ozone, temperature, global radiation, relative air humidity, wind speed and precipitation as well as geographical coordinates and some structural data of the forest are needed. Such datasets are hard to get, as the consistency of meteorological and ozone concentration is never given and the quality of data for forest objectives is to prove, because the measurement stations for meteorology and air quality are situated often in open land instead in forest canopies.

Only stations in (ICP-Forest)-Level II Plots and some stations in rural areas, for assessment of background ozone concentration are suitable for the assessment of ozone flux in forests. Forest in Germany exists mainly in upper mountains on intermediate or shallow soils, where high ozone concentration were ascertained. Hence forest may be highly endangered ecosystems.

In the Database of the UBA we looked for all available stations which has a time series beginning about 2000 till yet. Depending on data availability and quality we calculated POD₁ with DO₃SE and FO₃REST (Bender at al. 2015) and also with aFO₃REST (an IAM-Model whose input is restricted to temperature and ozone concentration). Main interest was concentrated on spatial and temporal variance of ozone flux as well as on influences of differing quality of input parameters as well as the influence of different soil water budget calculation on POD₁. These investigations shows a dominating influence of soil water to amount of the flux. Without knowledge of the interaction between soil water availability and leaf conductivity the flux and hence POD₁ is overestimated. Otherwise the consideration of soil parameters with sharp boundaries restrict the geostatistical interpretability of the POD₁. Because geostatistical analysis desire isotropic conditions as they exist in meteorological and air pollution but not for soils. The comparison of results from DO₃SE and FO₃REST show only little differences between the different models calculated with same parameterization and soil water influence.

IAM-Model approaches are feasible to characterize spatial differences but not the endangerment against ozone. Exceedance of CL should be interpreted only under consideration of the soil water influence on leaf conductivity. But these results are not interpretable for spatial trends, hence they change abrupt with soil physical conditions (profundity, texture amount of soil skeleton). The model DO₃SE requires most input parameters. The calculation model FO₃REST is available for the receptors beech, spruce (and wheat). It requires the same input parameters as DO₃SE except the LAI. Moreover, DO₃SE and FO₃REST are different in the design of the soil water models.

OZONE EFFECTS ON NITROGEN CYLING IN MEDITERRANEAN ANNUAL PASTURES

Ignacio González-Fernández^{1*}, Susana Elvira¹, Héctor Calvete-Sogo¹, Javier Sanz¹, Rocío Alonso¹, Miguel Quemada², Fernando Valiño¹, Héctor García-Gómez¹, Isaura Rábago¹, Victoria Bermejo-Bermejo¹

¹Ecotoxicology of Air Pollution, CIEMAT, Avda Complutense 40, 28040, Madrid, Spain ²Producción Agraria, ETSIAAB, Universidad Politécnica de Madrid, Avda. Complutense s/n, Madrid, 28040, Spain *ignacio.gonzalez@ciemat.es

Annual herbaceous species are widely present in Mediterranean landscapes and usually represent an important fraction of the biodiversity of Mediterranean ecosystems. Annual Mediterranean pastures are chronically exposed to tropospheric ozone levels above current European air quality regulations for the protection of vegetation and in some areas they are also subject to atmospheric nitrogen deposition levels that exceed empirical critical loads established for the protection of European grassland habitats.

Recent studies on the ozone sensitivity of annual Mediterranean pasture species have shown that indirect effects of ozone, changing the ecosystem functioning, may be as relevant as direct effects, affecting ecosystem services and connecting air pollution issues that are currently approached individually. Ozone has been described to reduce the fertilization effect of nitrogen and to increase soil nitrous oxide emissions of an annual Mediterranean pasture under experimental conditions (Calvete-Sogo et al., 2014, AtmosEnv. 95; Sánchez-Martín et al., 2017, AtmosEnv. 165).

An open-top chamber experiment on the interaction of ozone and nitrogen in a simplified Mediterranean annual pasture community has been used to gain insights on the effects of ozone on nitrogen cycling and how these two pollutants interact at the plant and soil compartments. Ozone effects on the nitrogen use efficiency of component species and on the nitrogen balance of the pasture will be presented.

The interaction between tropospheric ozone and nitrogen, however, needs to be studied in relation with the most important, present and foreseen, environmental driver of annual Mediterranean pastures: drought. Understanding interactions among air pollutants and how these interactions are modified by climate change is one of the main current challenges on the assessment of air pollute effects in Mediterranean ecosystems.

IMPACT OF OZONE ON PHYSIOLOGY AND YIELD OF AFRICAN CROPS

Felicity Hayes^{*}, Gina Mills, Harry Harmens, Katrina Sharps, Ieuan Roberts

Centre for Ecology & Hydrology, Environment Centre Wales, Bangor LL57 2UW, UK

*Corresponding author: fhay@ceh.ac.uk

Ozone pollution is a growing problem in Africa. There is much evidence of adverse effects of ozone on crop yield and crop quality for European crops, but not for crops grown in Africa, or for African varieties of crops also grown elsewhere. We performed two experiments to investigate a) the impact of ozone on African crops and varieties, and b) whether irrigation strategies could be used to reduce the impact of ozone on wheat.

African varieties of wheat (5 varieties), pearl millet (4 varieties) and finger millet (6 varieties), together with 6 varieties of dry (shelling) beans were exposed to ozone in ambient temperature (wheat) or heated (finger and pearl millet, beans) solardomes, with peak ozone concentrations of approximately 30 to 110 ppb. Ozone-induced visible leaf injury was observed on all crops and varieties tested, with a range of ozone-sensitivity between the different varieties. Large reductions in total yield and 1000 seed weight were found for wheat and bean in the highest ozone treatment. The ozone sensitivity of African wheat compared to European varieties based on phytotoxic ozone dose (POD) will be shown, together with flux-based dose response relationships for the other crops.

In a pilot study, one of the ozone-sensitive varieties of wheat ('Kenya Korongo') was exposed to control (30 ppb) or elevated ozone (peaks of 80 ppb) for 3 weeks following anthesis, together with one of three irrigation regimes – well watered, frequent deficit or infrequent deficit irrigation. Reduced visible leaf injury with the deficit irrigation regimes and effects on yield will be described.

TROPOSPHERIC OZONE ASSESSMENT REPORT: PRESENT DAY TROPOSPHERIC OZONE DISTRIBUTION AND TRENDS RELEVANT TO VEGETATION

<u>Gina Mills</u>^{1*}, Håkan Pleijel, Christopher S. Malley, Baerbel Sinha, Owen Cooper, Martin G. Schultz, Howard S. Neufeld, David Simpson, Katrina Sharps, Zhaozhong Feng, Giacomo Gerosa, Harry Harmens, Kazuhiko Kobayashi, Pallavi Saxena, Elena Paoletti, Vinayak Sinha, Xiaobin Xu

¹NERC Centre for Ecology & Hydrology, Environment Centre Wales, Bangor, UK *<u>gmi@ceh.ac.uk</u> Affiliations for co-authors can be found in the paper.

Note: This paper has been submitted to Elementa: Science of the Anthropocene

The Tropospheric Ozone Assessment Report (TOAR) on current knowledge of ozone metrics of relevance to vegetation (TOAR-Vegetation) reports on present day global distribution of ozone at over 3300 vegetated sites and the long-term trends at nearly 1200 sites. TOAR-Vegetation focusses on three metrics over vegetation-relevant time-periods across major world climatic zones: M12, the mean ozone during 08:00 - 19:59; AOT40, the accumulation of hourly mean ozone values over 40 ppb during daylight hours, and W126 with stronger weighting to higher hourly mean values, accumulated during 08:00 - 19:59. The highest values for all three metrics (mean of 2010 - 2014) are in mid-latitudes of the northern hemisphere, including southern regions of the USA, the Mediterranean basin, northern India, north, northwest and east China, the Republic of Korea and Japan. The mean values are higher in East Asia (EAS) than in North America (NAM) and Europe (EUR). For example, the mean AOT40 over 6-months is around 16000, 14200 and 12800 ppb h for EAS, NAM and EUR, respectively (Figure 1). The lowest metric values are in Australia, New Zealand, southern parts of South America and some northern parts of Europe, Canada and the USA. In NAM, the dominant trend during 1995 - 2014 was for a significant decrease in ozone, whilst in EUR it was no change and in EAS it was a significant increase. Several recommendations are made for a future TOAR data collections.



Figure 1: Global distribution of the mean AOT40, 2010 – 2014, for perennial vegetation (6-months). From Mills et al., submitted to Elementa: Science of the Anthropecene

OZONE RISK ASSESSMENT FOR FOREST TREES AS AFFECTED BY SOIL WATER DEFICIT AND NUTRITIONAL AVAILABILITY

Paoletti E.1*, Carrari, E.1, Zhang, L.2, Moura, B.3, Hoshika Y.1

¹IPSP-CNR, Via Madonna del Piano 10, I-50019 Sesto Fiorentino, Italy
 ²College of Horticulture and Landscape Architecture, Northeast Agricultural University, 59 Mucai street, 150030, Harbin, China
 ³Department of Plant Biology, Institute of Biology, University of Campinas (UNICAMP), Campinas SP, Brazil
 *E-mail: elena.paoletti@cnr.it

The level of tropospheric ozone (O_3) concentration has been risen since pre-industrial times in the northern hemisphere, and exceeds the level known to be toxic to forest trees. Ozone risk assessment for forest trees is therefore a crucial issue. Tree sensitivity to O_3 may be affected by other factors such as soil water availability and nutritional condition (e.g. nitrogen (N), and phosphorus (P)). However, studies on the interacting factorial impacts of O₃ and other stressors such as drought and nutrients on risk assessment are still limited. In this presentation, we would like to introduce our recent developments for O_3 risk assessment on: 1) three species of European oaks (Quercus ilex, Q. pubescens, Q. robur) under different soil water availability, and 2) O₃-sensitive poplar clone (Oxford, *Populus maximoviczii* Henry × *berolinensis* Dippel) with different soil N and P conditions. We compared the concentration-based approach (i.e., AOT40, Accumulated Ozone exposure over a Threshold of 40 ppb) with the flux-based approach (i.e, PODy, Phytotoxic Ozone Dose). Studies were carried out in a last-generation O₃ Free Air Controlled Exposure (FACE) system. The results show that soil water availability can significantly affect O₃ risk assessment. In fact, the flux-based approach explained better the dose-response relationships than exposure indices when combining results in different water regimes. In a simplified approach where species were aggregated on the basis of their O_3 sensitivity, the best metric was $POD_{0.5}$, with a critical level (CL) of 6.8 mmol m⁻² for the less O_3 sensitive species Q. *ilex* and Q. *pubescens*, and of 3.5 mmol m⁻² for the more O_3 sensitive species *Q. robur*. Regarding the effects of nutrients, the best O₃ metric for the risk assessment was POD₄. If all nutritional treatments were pooled together, 4.9 mmol m^{-2} POD₄ may be recommended as a CL. The addition of P or N, individually or in combination, increased the CLs for O_3 risk assessment i.e. reduced the sensitivity of poplar to O_3 . This is because high nutritional availability enabled new leaf formation, which may partly compensate the productive decline in injured leaves by O₃. In summary, to explain the O₃ dose-response relationship for forest trees in different soil water availability or nutritional conditions, the fluxbased approach is better than exposure indices. However, the criteria for experimentally selecting the best metrics and Y thresholds still need to be consolidated by discussion within the ICP Vegetation Task Force.

FERTILIZER EFFICIENCY IN WHEAT IS REDUCED BY OZONE POLLUTION

Broberg M.C.¹, Uddling J.¹, Mills G.^{1,2}, Pleijel H.¹

¹Department of Biological and Environmental Sciences, University of Gothenburg, SE 405 30, Gothenburg, Sweden, <u>hakan.pleijel@bioenv.gu.se</u> ²Centre for Ecology & Hydrology, Environment Centre Wales, Deiniol Road, Bangor, Gwynedd, LL57 2UW, United Kingdom

Inefficient use of fertilizers by crops increases the risk of nutrient leaching from agroecosystems, resulting in economic loss and environmental contamination. We investigated how ground-level ozone affects the efficiency by which wheat used applied nitrogen (N) fertilizer to produce grain protein (NEP, N efficiency with respect to protein yield) and grain yield (NEY, N efficiency with respect to grain yield) across a large number of open-top chamber field experiments. Our results show significant negative ozone effects on NE_P and NE_Y, both for a larger data set obtained from data mining (21 experiments, 70 treatments), and a subset of data for which stomatal ozone flux estimates were available (7 experiments, 22 treatments). For one experiment, we report new data on N content of different above-ground plant fractions as well as grain K and P content. Our analysis of the combined dataset demonstrates that the grain yield return for a certain investment in N fertilizer is reduced by ozone. Results from the experiment with more detailed data further show that translocation of accumulated N from straw and leaves to grains is significantly and negatively affected by ozone, and that ozone decreases fertilizer efficiency also for K and P (Figure 1). As a result of lower N fertilization efficiency, ozone causes a risk of increased N losses from agroecosystems, e.g. through nitrate leaching and nitrous oxide emissions, a hitherto neglected negative effect of ozone. This impact of ozone on the N cycle implies that society is facing a dilemma where it either (i) accepts increased N pollution and counteracts ozone-induced yield reductions by increasing fertilization or (ii) counteracts N pollution under elevated ozone by reducing fertilization, accepting further yield loss adding to the direct effect of ozone on yield.



Figure 1. Yield-to-supply ratio of N, P and K in relation to daytime 7h mean ozone concentration (M7) for a Swedish experiment with five different levels of ozone.

EFFECTS OF THE ANTIOZONANT ETHYLENEDIUREA (EDU) ON FRAXINUS ORNUS L.: THE ROLE OF DROUGHT

Salvatori E.*, Fusaro L., Manes F.

Department of Environmental Biology, Sapienza University of Rome P.le Aldo Moro, 5 – 00185 Rome, Italy *elisabetta.salvatori@uniroma1.it

The chemical compound Ethylenediurea, N-[-2-(2-oxo-1-imidazolidinyl) ethyl]-N-phenylurea (abbreviated EDU), is known to protect plants from the phytotoxic effects of tropospheric ozone (O₃). Since the work of Carnhan et al. (1), who firstly reported the antiozonant effect of EDU, it has been largely used for the assessment of O₃ effect on growth and yield of both natural and crop species, as the use of this chemical was also foreseen in the UNECE/ICP Crops (now ICP Vegetation) biomonitoring protocol (2; 3). More recently, many works have also proposed the use of EDU as a research tool for investigating O₃ effects on plants under field conditions, and in developing countries (4, 5). The effectiveness of EDU for these applications, however, depends on its specificity against O₃. Indeed, its mechanism of action remains not fully understood, and it is unclear whether it may also interact with other oxidative stress factors. At this regard, Middleton et al. (6) and Albert et al. (7), have shown that in absence of O₃, EDU substantially ameliorated UV-B damage to foliage in soybean and birch, thus suggesting that EDU can protect plants from other oxidative stresses besides O₃. Aim of this work is to evaluate the applicability of EDU on forest species in the Mediterranean environment where, during summer, vegetation is exposed to multiple oxidative stresses, such as O₃ and drought. The experiment was conducted on *Fraxinus ornus* L. (Manna ash) plants growing in six mesocosms, three kept at full irrigation, while the other three were subjected to drought for 84 days, from June 16 to September 6, 2006. For each mesocosm, three plants were sprayed every 15 days with 450 ppm EDU. Gas exchanges and chlorophyll "a" fluorescence measurements carried out through the experimental period have highlighted that EDU did not affect stomatal conductance, and had an ameliorative effect on functionality of drought stressed plants, thus suggesting that it may act as a generic antioxidant (8). The implications of these findings for the applicability of EDU in field studies are discussed.

References:

- 1. Carnhan, J. E., Jenner, E. L., Wat, E. K. W. (1978). *Phytopathology*, 1225–1229.
- 2. Manes, F., Altieri, A., Tripodo, P., Booth, C. E., Unsworth, M. H. (1990). Ann.Bot. (Roma), 48, 133–149.
- 3. Astorino, G., Margani, I., Tripodo, P., Manes, F. (1995). Plant Sci., 111, 237-248.
- 4. Manning, W. J., Paoletti, E., Sandermann Jr., H., Ernst, D. (2011). *Environ. Pollut.*, 159, 3283–3293.
- 5. Tiwari, S. (2017). Environ. Sci. Pollut. Res., 1-21.
- Middleton, E. M., Kim, M. S., Krizek, D. T., Bajwa, R. K. S. (2005). Photochem. Photobiol., 81, 1075–1085.
- Albert, K. R., Mikkelsen, T. N., Ro-Poulsen, H., Arndal, M. F., Boesgaard, K., Michelsen, A., Bruhn, D., Schmidt, N. M. (2012). *Physiol. Plant.*, 145, 485–500.
- 8. Salvatori E., Fusaro L., Manes F. (2017). Forests, 8, 320; doi:10.3390/f8090320.

DATA AND MODEL EVALUATION TO ESTIMATE O₃ INDUCED CROP YIELD LOSSES IN SWITZERLAND

Schneuwly J.*, Bassin S.

Agroscope Research Institute, Reckenholzstrasse 191, 8046 Zürich, *jerome.schneuwly@agroscope.admin.ch

Not only O_3 peaks, which declined in Switzerland during the last years, but also the mean O_3 concentration of the vegetation period is of importance when assessing the effects of O_3 on crop plants. Elevated O_3 concentrations were reported regularly in the lowland region, which represents the main crop cultivation area, throughout the growing period. Hence, significant crop yield and quality losses have to be taken into account.

Despite the reported negative consequences of O_3 on crops, no further research has been conducted in Switzerland in order to estimate current or future crop yield losses. Assessment whether financial consequences of elevated O_3 concentrations can be predicted accurately is of principal interest in this pilot study. Therefore, the most grown crops and their respective financial importance were identified, as well as the corresponding most relevant varieties. Progress has been made over the last years in the estimation of stomatal O_3 uptake, which enables a more accurate approximation of the ozone-dose relationship for important crop species. We determined the particular O_3 sensitivity of the crops using recent publications. To enhance precision of the predictions, we evaluated whether the existing dose- response functions can be applied for specific Swiss varieties as well. In order to determine if an estimation of crop yield losses will be possible, we will examine different stomatal O_3 flux models. Conclusions will be presented on which model can be best used under Swiss conditions and current data availability. Plant responses to elevated O_3 levels are coupled with several climatic factors and vary between different crops or even between varieties. Therefore, a further step of the study will be to check if Swiss climate data can be implemented in the models.

MOTTLES: A NEW-GENERATION LONG-TERM MONITORING STATIONS ACROSS EUROPE FOR FOREST PROTECTION AGAINS SURFACE OZONE

Sicard P.¹, Anav A.², Badea O.³, Carrari E.², Dalstein-Richier L.⁴, De Marco A.⁵, Fares S.⁶, Giovannelli A.², Hoshika Y.², Leca S.³, Materassi A.², Pitar-Silaghi D.³, Popa I.³, Sabatini F.², Paoletti E.²

 ¹ACRI-HE, Sophia Antipolis, France, <u>psicard@argans.eu</u>
 ²Consiglio Nazionale delle Ricerche - Istituto per la Protezione delle Piante, Sesto Fiorentino, Italy
 ³National Institute for Research and Development in Forestry Marin Dracea, Voluntari, Romania
 ⁴Groupe International d'Etudes des Forêts Sud-européennes, Nice, France
 ⁵Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Roma, Italy
 ⁶Council for Agricultural Research and Economics - Soil-Plant System, Rome, Italy.

Epidemiology is the study of how often and why diseases, injury and other health-related events occur in a defined population, in order to identify risk factors and targets for prevention and control programs. The impact of surface ozone (O_3) on vegetation is under-investigated at regional scale despite worldwide huge areas are exposed to high surface O_3 levels and its concentration is expected to increase in the next future. Epidemiology of O_3 injury may be very helpful in particular when forests are investigated, as large trees require expensive experimental facilities for realistic O_3 simulation and a few individuals can be usually investigated.

A standard for forest protection is considered biologically relevant when it translates into realworld forest impacts. For this reason, epidemiological investigations where large-scale biological responses are compared with ambient data in the field provide useful information for establishing the best standards and thresholds for forest protection from O_3 . The majority of previous epidemiological assessments used ambient O_3 exposure as a metric of injury (e.g. AOT40). However, exposure-based standards for protecting vegetation are not representative of actual field conditions. Ozone effects on vegetation depend on the air concentrations but also on the O_3 uptake through the stomata, i.e. Phytotoxic Ozone Dose above a threshold Y of uptake (PODY).

Unique in the world, the project MOTTLES "*MOnitoring ozone injury for seTTing new critical LEvelS*" (LIFE15 ENV/IT/183) takes place in the main European areas at highest and medium risk of O_3 injury, i.e. Southern and central Europe, and combines field epidemiology with plant responses to O_3 . With the effort of implementing permanent new-generation monitoring stations across Europe, capable to return continuous hourly O_3 concentrations from active monitoring as well as real-time meteorological and environmental parameters (e.g. soil water content, solar radiation, air temperature, relative humidity), PODY will be estimated and correlated to plant responses to O_3 (e.g radial growth, crown defoliation, crown discoloration and visible foliar O_3 injury). Based on real-world flux-effect relationships, derivation of suitable epidemiologically-based O_3 critical levels for European tree species represents a considerable progress in the development of a long-term monitoring strategy and methods for quantifying O_3 effects on vegetation at the regional scale.

Keywords: Critical levels, Epidemiology, Ozone, POD, Visible injury

EVALUATION AND UNCERTAINTY QUANTIFICATION OF THE IMPACTS OF SURFACE OZONE ON GLOBAL PRIMARY PRODUCTIVITY USING A COUPLED ATMOSPHERIC CHEMISTRY-BIOSPHERE MODELING FRAMEWORK

Tai, A.P.K.*, Yung, D.H.Y.

Earth System Science Programme, Faculty of Science, The Chinese University of Hong Kong, Sha Tin, Hong Kong *E-mail: amostai@cuhk.edu.hk

Surface ozone is an air pollutant of significant concerns due to its harmful effects on human health, vegetation and crop productivity. Chronic ozone exposure is shown to reduce photosynthesis and interfere with gas exchange in plants, thereby influencing terrestrial ecosystem productivity, biogeochemical fluxes and surface energy balance, with important ramifications for climate and atmospheric composition. Here we examine the impacts of ozone air pollution on global primary productivity (GPP) using a combination of atmospheric chemistry and biospheric models. We first use the GEOS-Chem global chemical transport model to simulate hourly surface ozone concentration at $2^{\circ} \times 2.5^{\circ}$ latitude-longitude resolution driven by prescribed present-day MERRA-2 meteorology. We then feed the simulated hourly ozone into the Terrestrial Ecosystem Model in R (TEMIR), driven by a consistent set of MERRA-2 meteorology, to simulate the consequent reductions in GPP and canopy conductance under various ozone damage schemes. The current version of TEMIR, developed in-house, is largely an ecophysiological model that reads in prescribed surface meteorology and fluxes to simulate canopy radiative transfer, photosynthesis, conductance as well as biogenic emission rates and dry deposition velocities of atmospheric constituents. TEMIR has been well validated by FLUXNET site measurements of GPP, and we find that the implementation of ozone damage in the model generally reduces the high-biases of simulated GPP from the conventional schemes in comparison with observations. Four dimensions of the full uncertainty space for ozone impacts on global GPP are explored and their relative importance is compared: 1) uncertainty arising from different ozone-vegetation damage schemes and sensitivities, namely, the Sitch et al. (2007) scheme with high and low sensitivity to ozone, and the Lombardozzi et al. (2015) scheme with high, average and low sensitivity to ozone; 2) from interannual variability of climate and ozone concentration spanning a presentday period of five years (e.g., 2008-2012); 3) from the feedback effects of ozone-induced changes in stomatal conductance and thus dry deposition velocity on ozone concentration itself, as determined by asynchronously coupling between GEOS-Chem and TEMIR; and 4) from future rising CO_2 level, which is expected to reduce stomatal conductance and thus ozone uptake.

References:

Lombardozzi, D., Levis, S., Bonan, G., Hess, P. G., and Sparks, J. P.: The influence of chronic ozone exposure on global carbon and water cycles, *J. Climate*, 28, 292-305, 2015. Sitch, S., Cox, P. M., Collins, W. J., and Huntingford, C.: Indirect radiative forcing of climate change through ozone effects on the land-carbon sink, *Nature*, 448, 791-U794, 2007.

THE DOUBLE PUNCH: OZONE AND CLIMATE STRESSES TO SUB-ARCTIC VEGETATION

<u>Vollsnes A.V.</u>^{1*}, Eriksen A.B.¹, Berntsen T.K.², Kauserud H.¹, Büker P.³, Emberson L.³, Stordal F.²

¹Department of Biosciences, University of Oslo, P.O. Box 1066 Blindern, 0316 Oslo, Norway ²Department of Geosciences, University of Oslo, P.O. Box 1022 Blindern, 0316 Oslo,

Norway

³Stockholm Environment Institute, Environment Department, University of York, York, YO10 5NG, UK

*Email: a.v.vollsnes@ibv.uio.no

Vegetation is being hit by a double punch; air pollution and climate change. Tropospheric ozone is a problem reducing yield and growth of plants in natural vegetation all over the world. In Northern Norway the levels of ozone in the air are lower than in more densely populated areas. Nevertheless, the expected daily dose to plants is increased by long periods of light and a moist climate, both factors favouring open stomata. The combined effects of ozone and climate stress on arctic and boreal species are investigated in a new project, including ozone exposure experiments under controlled conditions, field measurements of ozone concentrations, vegetation studies and climate and vegetation modelling. A focus on impacts of the long daylengths, with midnight sun, during the growth season in this region is a novel element, as the lack of darkness may increase ozone sensitivity. Three clover species have been shown to have increased ozone sensitivity in long day conditions (Vollsnes et al 2009, Futsaether et al 2010, Futsaether et al 2015). The project will quantify the impact of 24 h light period on the ozone sensitivity of plant species from the local vegetation.

The subarctic tundra covers a great circumpolar area, with the Eurasian part having its westernmost limit in Northern Norway. New knowledge about the interactions between the vegetation, ozone pollution and the climate is of great importance for the climate modelling and estimates for the future climate, in particular at high latitudes where climate warming is greatly amplified.

Local farmers in Northern Norway clutivate grasses and clovers to feed their livestock. We will include some of these meadow species in our growth experiments and models. New knowledge of plant ozone sensitivity in areas with long daylength in the growth season may be important when farmers are to choose cultivars for use in these areas.

References:

Futsaether CM, Vollsnes A, Kruse OMO, Otterholt E, Kvaal K, Eriksen AB (2009). Effects of the Nordic photoperiod on ozone sensitivity and repair in different clover ecotypes studied using infrared imaging. *Ambio* **38**: 437-442.

Futsaether CM, Vollsnes AV, Kruse OMO, Eriksen AB (2015). Daylength influences the response of three clover species (*Trifolium* spp.) to short-term ozone stress. *Boreal Environmental Reseach* **20**:90-104.

Vollsnes AV, Eriksen AB, Otterholt E, Kvaal K, Oxaal U, Futsaether CM (2009). Visible foliar injury and infrared imaging show that daylength affects short-term recovery after ozone stress in *Trifolium subterraneum*. *Journal of Experimental Botany* **60**: 3677-3686.

MOSS SURVEY SESSIONS

RESULTS OF THE TEN-YEAR STUDY OF THE TERRITORY OF BELARUS

<u>Aleksiayenak Yu.V.</u>*, Frontasyeva M.V.

Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Moscow Region, Russia *beataa@gmail.com

In 2015 for the third time in the Republic of Belarus the moss biomonitoring technique was used to study atmospheric deposition of heavy metals and other trace elements. The moss samples were subject to instrumental neutron activation analysis (INAA) at the IBR-2 reactor of FLNP JINR in Dubna. A total of 36 elements were determined (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Sm, Tb, Yb, Hf, Ta, W, Hg, Th, U). Additionally, in 2017 Cd, Cu and Pb were determined by atomic absorption spectrometry (AAS). The principal component analysis allowed distinguishing soil, plant, and anthropogenic components in the moss, and apportioning the main pollution sources. During this ten-year research in Belarus the local background levels for the range of elements were experimentally established. In general, in comparison with the other European countries, the median concentrations of elements in moss in Belarus are enough low and they are comparable with the Norwegian data, however, some polluted areas were revealed. The main pollution sources in these areas could be attributed to a tractor plant in Minsk, engineering plant in Zhodino, farming, paintworks plants, iron and steel plant. Our results does not show any influence of the transboundary pollution from the neighboring countries.

HEAVY METALS CONCENTRATION IN MOSS SAMPLES IN GREECE

Betsou Ch.¹, Frontasyeva M.², Tsakiri E.³, Kazakis N.⁴, Vasilev A.^{2,5}, Ioannidou A.¹

 ¹Aristotle University of Thessaloniki, Physics Department, Nuclear Physics Laboratory, Thessaloniki 54124, Greece, <u>anta@physics.auth.gr</u>, <u>chbetsou@physics.auth.gr</u>
 ²Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Moscow Region 141980, Russia, <u>marina@nf.jinr.ru</u>
 ³Aristotle University of Thessaloniki, Biology Department, Division of Botany, Thessaloniki, Greece, <u>tsakiri@bio.auth.gr</u>
 ⁴Aristotle University of Thessaloniki, Geology Department, Division of Hydrogeology, Thessaloniki, Greece, <u>kazakis@geo.auth.gr</u>
 ⁵Department of Physics, Sofia University "St. Kliment Ohridski", Sofia, Bulgaria, phys_vasilev@abv.bg

Mosses can be used to investigate and monitor atmospheric deposition of heavy metals. They have the ability to retain particles from the air. Being geographically widespread species they can provide a better understanding of spatial and temporal variations in atmospheric metal deposition (Kempter et al., 2017). Mosses receive most of their nutrients directly from precipitation and dry deposition. The lack of a rooting system means that uptake from the substrate is normally not significant (Harmens et al., 2008). These properties make mosses an ideal way of monitoring and evaluating the concentrations of heavy metals deposited from the air to terrestrial systems in a quite economic way.

Ninety five (95) samples of *Hypnum cupressiforme* Hedw. were collected in Northern Greece in a short time interval during the end of summer 2016, covering a regular grid of 30 km x 30 km. The sampling sites were located from 39.97° to 41.65° North and from 20.97° to 26.26° East. All the samples were collected according to the instructions of the Protocol of the European Survey ICP Vegetation (Harmens et al., 2008) and were analyzed to the content of heavy metals using INAA.

The concentrations of 33 elements were determined. The concentration of Zn is presented higher close to the Bulgarian boarders, indicating a possible transboundary transfer of Zn from the zinc-lead smelter in the region of Kardzhali in Bulgaria. Higher concentrations of Al and V are noticed in areas where metal industries, coal fired power plants and lignite mining exist. Areas with manufacturing, electricity and heat production activities, show an additional increase in concentrations of As, Cr and Ni elements. Therefore, a high sampling density was achieved, providing information for the elemental deposition from the atmosphere to terrestrial systems over the region of Northern Greece.

References:

Harmens, H., Norris, D., Mills, G., and the participants of the moss survey (2013). Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe. ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK, pp 63.

Kempter, H., Krachler, M., Shotyka, W., Zacconee, C., Major and trace elements in Sphagnum moss from four southern German bogs, and comparison with available moss monitoring data, Ecological Indicators 78 (2017), 19–25.

PERSISTENT ORGANIC POLLUTANTS (POP) IN GERMANY: RESULTS FROM THE 2015/2016 MOSS AND TREE SAMPLING

Dreyer A.^{1*}, Nickel S.², Schröder W.², Koschorreck J.³

¹Eurofins GfA GmbH, Air Monitoring, Stenzelring 14b, 21107 Hamburg, Germany *<u>annekatrindreyer@eurofins.de</u> ²Chair of Landscape Ecology, University of Vechta, Vechta, Germany German Environment Agency, 14193 Berlin, Germany

Within the 2015 European moss survey, selected POP have been analysed in eight moss samples from Germany. As sampling sites for these moss samples, areas located in the vicinity of tree sampling sites from the German environment specimen bank (ESB) were chosen in order to allow for a comparison between the different biomonitors of air pollution. These sites were scattered across Germany and covered regions characterized by different land-use types (conurbation areas (Saarland, Halle/Leipzig), forestry areas (Solling), agricultural areas (Belauer See, Scheyern) and background sites (Harz, Berchtesgarden); [1]). Moss samples were taken in fall 2016 using pre-cleaned glass jars. Samples were cleaned of substrate, leaves, or grass and stored refrigerated at -20°C afterwards. Tree samples (deciduous tree leaves, coniferous shoots) were sampled in 2015 or 2016 according to the ESB protocols [1] and stored using liquid nitrogen. Samples were dried, homogenized, spiked with mass-labelled internal standards, solvent-extracted using Soxhlet or ASE and, where needed, cleaned up by suited column chromatography. Overall, 17 polychlorinated dibenzo dioxins and -furans (PCDD/F), 18 polychlorinated biphenyls (PCB), 16 polycyclic aromatic hydrocarbons (PAH), 17 perfluoroalkyl substances (PFAS), 3 isomers of hexabromocyclododecanes (HBCD), 7 polybrominated biphenyls (PBB), 24 polybrominated diphenyl ethers (PBDE), and 21 alternative halogenated flame retardants (HFR) such as Dechlorane Plus were determined by gas chromatography coupled to mass spectrometry (GC-MS), high resolution GC coupled to high resolution MS (HRGC-HRMS), liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS), or GC-atmospheric pressure ionization (API) -MS/MS. Except for PBBs and PFASs, POPs of all substance groups could be quantified, although to different extents. Concentrations of individual PAHs and HFRs were in the same order of magnitude as those observed in coniferous shoots or deciduous tree leaves from nearby located areas [1]. Highest levels of PCDD/F, dl-PCBs, HBCD and PAH in moss were observed at sites close to the Belauer See (Northern Germany, agricultural land-use) and the Harz National Park. Concentrations of PBDEs were highest at the two sampling sites in Saarland (conurbation) and at the Harz site. Concentrations for Dechlorane Plus were highest at the Harz sited followed by sites locates at Solling (forestry) and Schevern (agricultural) and were lowest at the site in the Halle-Leipzig conurbation. Thus, surrounding land-use does not seem to be the (only) driving force determining the POPs burden in moss samples. PBDE moss concentrations observed in this study were similar to those observed at background sites in Spain and lower than those of background/remote sites in Norway [2-4]. Concentrations of Dechlorane Plus were more than a factor of 100 higher than moss concentrations reported for Svalbard (Arctic Norway) [5].

References:

[1] German Environment Agency. Umweltprobenbank des Bundes. www.umweltprobenbank.de (Download: 18.11.2017. 2017). [2] Foan L. et al. *Environ. Pollut.* 2014; 184: 113-122. [3] Mariussen E et al. *Sci. Total Environ.* 2008; 404: 162-170. [4] Wang Z. et al. *Chemosphere.* 2015; 137: 9-13. [5] Na G. et al. *J. Environ. Sci.* 2015; 28: 8-13.

THE USE OF MIXED ARCHIVED MOSS SAMPLES FOR COMPLETING HEAVY METAL DATA IN SWITZERLAND FROM 1990 – 2010

Kosonen Z.K., Thöni L.

FUB – Research Group for Environmental Monitoring, CH-8640 Rapperswil, Switzerland zaida.kosonen@fub-ag.ch, lotti.thoeni@fub-ag.ch

Moss biomonitoring for heavy metal deposition is a well-known and established method, and cross-national surveys on heavy metal deposition using this method have been conducted in Scandinavia since 1980.

Switzerland's first participation in the moss survey was in 1990 when it was expanded to non-Scandinavian countries. Since the beginning the moss material remnants have been archived. These samples, covering six periods between 1990 and 2015, represent a comprehensive countrywide sample set that is potentially a good source for long term deposition data for heavy metals that were not determined in previous studies. Due to missing data during several periods on some heavy metals, we wanted to test the potential of these archive samples for retrospective analyses of deposition across Switzerland. Because of limited resources, archive samples of each geographical region and each period were pooled into a mixed sample. To allow a longterm comparison from 1990-2015 only the study sites sampled in 2015 were included into the mixed samples as they were lower in number than the previous ones. We either prepared the archive samples from scratch using the three-year growth or we mixed already prepared or pulverised samples. To test if mixed samples result in reliable data, we only could compare the concentrations of Ag, Al, Ba, Co, Cs, Mo, Pb, Sb, Se, Tl, U in the mixed samples to the averaged concentrations originally obtained from moss samples in the corresponding period.

For most of the heavy metal concentrations there was no significant difference between sample the mixed and the mean concentration established from single samples (examples are shown in Fig. 1). The only exceptions were Ag and Mo. Ag concentrations were significantly higher in the mixed samples whereas Mo concentrations were significantly lower. We do not have a concluding explanation for these exceptions.

In general the concentrations of the mixed well samples also fitted into the chronological sequence of our existing data and present gaps within the time series could be filled.

properly stored moss samples are a suitable



Fig. 1: Comparison of Ba (circle) and Pb (diamond) concentrations in the mixed samples to the corresponding averaged concentration obtained with single sample at different sampling periods. Each data point represents the concentration within a geographical Based on our results we conclude that region of Switzerland during the period indicated in the labels. The diagonal line indicates the 1:1 line.

source for retrospective information on heavy metal deposition. Therefore, we recommend to archive the moss samples if only possible for future research purposes.

ASSESSMENT OF HEAVY METAL DEPOSITION AND AIR POLLUTION IN THE SOUTHERN PART OF SILESIAN COAL BASIN USING MOSS BIOMONITORING

Krakovská A.^{1,2}, Pavlíková I.^{1,2}, Motyka O.^{1,2}, Svozilík V.^{1,2}, Jančík P.^{1,2}, Frontasyeva M. V.¹

¹Joint Institute for Nuclear Research, Dubna, Russia, email: krakovska@jinr.ru ²VŠB – Technical University of Ostrava, Czech Republic

The main hot spots of air pollution in the central Europe are situated in the coal basins in the northwest and northeast part of the Czech Republic and in the south of Poland. The research is focused on the south part of the Silesian Region, which is highly affected by extraction and processing of black coal and metallurgical industry operation and numerous domestic sources. Sampling area was defined using GIS technology in the Moravian-Silesian region and in the south of Poland in 2015. A network of 41 sampling points was created in the range of 1600 km² (40 x 40 km²). The sampling network was expanded by other 44 sampling points in 2016. Collection of samples was carried out in compliance with the Moss Manual of the UNECE ICP Vegetation. Preferred moss species due to their characteristic and occurrence were *Pleurozium schreberi*, *Hypnum cupressiforme*, *Brachythecium rutabulum*.

The concentrations of 38 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As, Se, Br, Rb, Sr, Mo, Cd, Sb, I, Ba, Cs, La, Ce, Nd, Sm, Tb, Tm, Hf, Ta, W, Au, Th, and U) was determined by neutron activation analysis in both years. The aim of this study was to qualitatively and quantitatively characterize the atmospheric deposition in the study area.

The results indicate dependence of distribution of metals on heavy industry and wind direction. This fact was proved at As, K, Cr, Co, Ni, I, W, U and Fe shown in **Error! Reference source not found.**, where hot spots are located nearby industry sources.

More moss species from same location were taken for comparison of different species. Dependence on moss species was significant in case of biogenic elements (Na, K, Mg).

Hierarchical Clustering on Principal Components (HCPC) was used for the identification of pollution sources. HCPC performed on the isometric log-ratio transformed data revealed existence of four clusters. These clusters were characterizable by the results of the PM_{10} dispersion model that proved them to be grouped according to the prevailing source of pollution, the grouping was most significant in the case of industrial pollution sources.



Distribution of iron.

TEMPORAL AND SPATIAL DISTRIBUTION OF MULTI-ELEMENT ATMOSPHERIC DEPOSITION IN ALBANIA (2010-2015 MOSS SURVEY)

Pranvera Lazo^{1*}, Flora Qarri², Shaniko Allajbeu¹, Lirim Bekteshi³, Trajce Stafilov⁴

¹Department of Chemistry, Faculty of Natural Sciences, University of Tirana, Tirana, Albania ²Department of Chemistry, University of Vlora, Vlora, Albania; ³Department of Chemistry, University of Elbasan, Elbasan, Albania; ⁴Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia *pranveralazo@gmail.com

Abstract: Moss biomonitoring, ICP/AES and AAS analysis were applied to study multielement atmospheric deposition in Albania. Moss samples (*Hypnum cupressiforme*) were collected during the August and September 2015 from 55 monitoring sites (Fig. 1) distributed over the entire country. Sampling was performed in accordance with 2015 LRTAP Convention-ICP Vegetation protocol and European Programme on Biomonitoring of Heavy Metal Atmospheric sampling strategy. 18 elements are analyzed by ICP/AES; As was analyzed by ETAAS and Hg by CVAAS. Concentration data reflect significant differences in spatial distribution of elements. Different statistical analysis was applied for data treatment. Contamination factors are calculated as the ratio of median values of each element to their respective local background level. As, Cd, Cr, Ni and Pb show the 4th category of contamination scale (CCS), moderately polluted scale; Fe, Al, V, Li, Co, Zn and Hg show the 3rd CCS, slightly polluted scale; and Cu, Sr, Ca, , K, Na and Ba show the 2nd CCS, C2, suspended pollution scale.



Fig. 1 Sampling map

By comparing the median values of 2015 and 2010 moss surveys was found it was found that the elements Al (7.8%), Ca (3.3%), Pb (1%), V (5.6%), Sr (9.2%) and Li (4.7%) show a low decline (lower than 105%); and the elements Cd (9.1%), Fe (7.2%), Mn (12.8%) show a low increase (lower than 15%) that indicate a stable situation of these elements for 2015 and 2010 moss surveys. It was found too, that Ba (56.7%), Mg (34%) and K (24.3%) are highly declined. Ba, Mg and K are easy leached from moss samples during wet wether. 2010 was characterized by dry weather for a long time in Albania, while 2015 is characterized by raining weather. On other hand, Cr (95%, Cu (79%), As (39%), Ni (31%) and Na (23%) were highly increased onto the concentrations in moss samples that is probably associated with the scavenging ability of rain in removing pollutants from the atmosphere (Amodio et al. 2014) particularly in high contaminated areas.

The East part of Albania is characterized by high primarily metallogenic mineral deposits (Lazo et al. 2017). Wind blowing mineral dust is an important factor on high concentration of these elements in mosses of Albania, followed by geogenic, mining and metal processing industry. The decline of Hg (about 2-3 times) is linked with different weather conditions during 2015 and 2010 moss surveys. This is explained by a retention process of Hg²⁺ during wet deposition and a considerable supply of Hg⁰ to the moss during the dry deposition (Steinnes et al. 2003) and the effects of temperature to the evaporation of Hg⁰.

References:

Amodio M, et al. Atmospheric Deposition: Sampling Procedures, Analytical Methods, and Main Recent Findings from the Scientific Literature. Advances in Meteorology. Review Article. <u>http://dx.doi.org/10.1155/2014/161730</u> Lazo P, Steinnes E, Qarri F, Allajbeu Sh, Stafilov T, Frontasyeva M, Harmens H (2017) Origin and spatial distribution of metals in moss samples in Albania: A hotspot of HM contamination in Europe. <u>https://doi.org/10.1016/j.chemosphere.2017.09.132</u>

Steinnes E, Berg T, Sjøbakk TE (2003) Temporal and spatial trends in Hg deposition monitored by moss analysis. Sc of Tot Env. 304. 215–219.
INTERSPECIES MOSS COMPARISON IN FRANCE

<u>Leblond S.</u>*, Meyer C.

UMS 2006 Patrimoine Naturel, AFB-CNRS-MNHN, 12 rue Buffon CP39, 75005 Paris *sebastien.leblond@mnhn.fr

To carry out the French moss survey, the diversity of environments makes necessary to sample 5 moss species (species recommended by the original European protocol): *Pseudoscleropodium purum* (Pp), *Hypnum cupressiforme* (Hc), *Thuidium tamariscinum* (Tt), *Pleurozium schreberi* (Ps), *Hylocomium splendens* (Hs). The three species most frequently sampled (Hc, Pp, Tt) represent 99% of the sites of the 2016 survey.

To explain spatial and temporal variations of elements concentrations in mosses, various modeling approach were tested, as spatial autoregressive model or generalized additive mixed model (Lequy et al., 2017a,b). These approaches allow us to test different explanatory variables. Such variables include source (atmospheric deposition and soil concentrations), protocol (sampling month, collector, and moss species), and environment (forest type and canopy density, distance to the coast or the highway, and elevation). For most of elements, the moss species was one of the main explanatory variables of the concentrations in mosses. These results stress the need of research on the effect of the moss species on the capture and retention of trace elements.

In France an inter-species comparison study was conducted, in parallel with the moss survey, in 2006 (15 sites), 2011 (20 sites) and 2016 (32 sites) with 6 sites common to the three surveys. The principle was to collect the 3 species of moss on the same site (2,500 m²) in order to compare their metal contents and to highlight correlations. These studies allowed us to compare the three species survey by survey, or for the whole surveys and to follow the temporal evolution on the common sites. For some elements, there was no significant difference, for others, either a systematic or an occasional (dependent of the survey) difference was observed.

References:

Lequy, E., Saby, N.P., Ilyn, I., Pascaud, A., Sauvage, S. & Leblond, S. 2017. Spatial analysis of trace elements in a moss bio-monitoring data over France by accounting for source, protocol and environmental parameters. Science of the Total Environment, 590-591: 602-610.

Lequy, E., Dubos, N., Witte, I., Pascaud, A., Sauvage, S. & Leblond, S. 2017. Assessing temporal trends of trace metal concentrations in mosses over France between 1996 and 2011: a flexible and robust method to account for heterogeneous sampling strategies. Environmental Pollution, 220: 828-836.

COMPARISON OF POLLEN UPTAKE BY THREE FORESTED MOSSES SPECIES IN FRANCE

Rouillier N.^{1,2,3}, Combourieu-Nebout N.², Leblond S.³, Lebreton V.², Meyer C.^{3*}

¹Ecole Nationale Supérieure des Sciences Agronomiques de Bordeaux Aquitaine, 1 cours du Général de Gaulle, 33170 Gradignan
²UMR 7194 Histoire Naturelle de l'Homme préhistorique, CNRS-MNHN, 1 rue René Panhard, 75013 Paris
³UMS 2006 Patrimoine Naturel, AFB-CNRS-MNHN, 12 rue Buffon CP39, 75005 Paris *caroline.meyer@mnhn.fr

The lack of root system and developed vascular system enables mosses to take up most of their nutrients from dry and wet deposition. Terrestrial mosses have proved to be efficient bio-accumulators of particulate and soluble atmospheric deposition according to many studies. Mosses are also considered as good pollen traps. Analysis of the pollen content in mosses makes possible to calibrate the current pollen / vegetation relationship (Gaillard et al., 1992) and to describe changes in the vegetation cover related to seasonal and interannual climate (Peyron et al., 2013).

To carry out with those various uses and in order to consider the diversity of environments, the sampling protocol may take into account the different species of mosses. However, few studies have been interested in the variability of capture and retention of particles (including pollen) depending on the moss species, often neglected by authors. Up to date, only a few studies have investigated the possible links between the morphology of microscopic particles and their capture by mosses (Boyd 1986).

Our project aims to analyze and to compare the current pollen spectrum trapped by three moss species (*Hypnum cupressiforme*, *Pseudoscleropodium purum* and *Thuidium tamariscinum*). Mosses were collected in 15 forest sites, within the framework of a 2016 French moss survey. After pollen extraction, the pollen grains were identified and counted under microscope. The difference of accumulation was tested according to the morphology of particles.

The main result has showed that the influence of pollen grains morphology on the accumulation by mosses is always to the benefit of *T.tamariscinum*. Such a difference of accumulation among species might therefore be related to the morphology of the mosses. *T.tamariscinum* may have the best accumulation capacity, related to a better ability to capture the whole diversity of particles.

References:

Boyd, W.E., 1986. The role of mosses in modern pollen analysis: the influence of moss morphology on pollen entrapment. Pollen Spores, 28: 243–256.

Gaillard, M.-J., Birks, H.J.B., Emanuelsson, U. & Berglund, B.E., 1992. Modern pollen/land-use relationships as an aid in the reconstruction of past land-uses and cultural landscapes: an example from south Sweden. Vegetation History and Archaeobotany, 1(1): 3-17.

Peyron, O., Magny, M., Goring, S., Joannin, S., de Beaulieu, J.-L., Brugiapaglia, E., Sadori, L., Garfi, G., Kouli, K., Ioakim, C., & Combourieu-Nebout, N., 2013. Contrasting patterns of climatic changes during the Holocene across the Italian Peninsula reconstructed from pollen data. Climate of the Past, 9: 1233-1252.

SPATIAL GENERALIZATION OF CANOPY DRIP EFFECTS ON ELEMENT CONCENTRATIONS IN MOSS BY EXAMPLE OF GERMANY

Nickel S.*, Schröder W.

Chair of Landscape Ecology, University of Germany *<u>Stefan.Nickel@uni-vechta.de</u>

In this study the canopy drip effect on concentrations of 12 heavy metals (Al, As, Cd, Cr, Cu, Fe, Hg, Pb, Ni, Sb, V, Zn) and nitrogen (N) in moss is examined by extensive field measurements and geostatistically modelled for the territory of Germany. The data are on vegetation structure and element concentrations a) in 71 moss samples collected from 25 sites with and without canopy drip effect and at the edge of forest stands in North Western Germany (sample 1, part of German Moss Survey 2015) and b) in 80 moss samples collected 2012 and 79 specimens sampled 2013 at 30 sites in North Western Germany (sample 2); c) from 400 samples collected at a respective number of sites throughout Germany within the moss survey 2015 (sample 3). From the vegetation data of samples 1 and 2 structural measures and their ratios regarding the different sampling fields of the same monitoring site were calculated and correlated with the respective ratios of the element concentrations in moss. For cases with highest correlations regression models were computed. Regression models with $R^2 > 0.5$ (Cu, Hg, Pb, and N) were applied to the 400 sites of the German moss survey 2015 (sample 3) and element concentrations were calculated and geostatistically mapped for open land sites (LAI = 2,96), sites with canopy drip (LAI = 11) and for sites with the arithmetic mean of LAI values of Germany (LAI = 5.1). These modelled data were compared with the maps derived by Kriging interpolation from the pure measurement of element concentrations. The differences between the respective measured element concentrations and those derived by LAI regression models were mapped. The results are given in the Figure.

References:

Nickel, S.; Schröder, W. (2017): Reorganisation of a long-term monitoring network using moss as biomonitor for atmospheric deposition in Germany. Ecological Indicators 76:194-206

Schröder, W.; Nickel, S.; Völksen, B.; Dreyer, A. (2017): Nutzung von Bioindikationsmethoden zur Bestimmung und Regionalisierung von Schadstoffeinträgen für eine Abschätzung des atmosphärischen Beitrags zu aktuellen Belastungen von Ökosystemen. 4. Zwischenbericht, F&E-Vorhaben UFOPLAN 3715 63 212 0, im Auftrag des Umweltbundesamtes, Dessau. Text (82 S.) + 4 Anhänge (212 S.)



Figure. Difference between the concentrations of Cu, Hg, Pb, and N assuming a leaf area index of 5.1 compared to measurements 2015.

VERIFICATION OF THE MATHEMATICAL AIR POLLUTION DISPERSION MODELS USING NEUTRON ACTIVATION ANALYSIS

Svozilík V.^{1,2}, Jančík P.^{1,2}, Krakovská A.^{1,2}, Pavlíková I.^{1,2}, Motyka O.^{1,2}

¹Joint Institute for Nuclear Research, Dubna, Russia, email: svozilik@jinr.ru ²VŠB – Technical University of Ostrava, Czech Republic

Background

The Upper Silesian Basin and its surroundings represent a highly populated region situated in the Czech-Polish borderlands close to the Slovakian border. This region is one of the most polluted areas in Europe [1]. This situation has been influenced by high population density, concentration of heavy industry (especially metallurgical, coal processing, chemical and energetic), transport and natural factors, such as geomorphological and meteorological conditions. Solid fuel for domestic heating is often used due to its accessibility, especially coal. Research institutes, universities, state authorities and private organizations lead several research programs for improvement of the air quality in this region. There are dozens of air pollution monitoring stations located in the area affected by air pollution.

Mathematical modelling

Our research team deals with mathematical modelling of air pollution using Analytic Dispersion Modelling Supercomputer System (ADMOSS). We are able to model the relationship between pollution sources and a concentration at any given point after proper interpolation. These air pollution modelling results are calibrated using the measurements of air pollution monitoring stations. The goal of this modelling is to evaluate the influence of each group of the pollution sources. Consequently, decision makers can propose a better solution of the unsatisfactory situation. The ADMOSS was optimized and expanded by a possibility of modelling the atmospheric deposition of solid pollutants in 2017.

Biomonitoring

A participation on the ICP Vegetation and collaboration with the Frank Laboratory of Neutron Physics (FLNP) was offered to us in 2014. The first moss survey focused on the characterization of air pollution was carried out in the core of the polluted area of the Upper Silesian Basin during the years 2015 and 2016. Preliminary results suggest that the sampling principles for ICP Vegetation [2] are also applicable in a regional scale. Biomonitoring appears as a complementary verification method for mathematical modelling of air pollution. During the year 2017, the area of interest was expanded to Slovakia and Poland in the frame of the international project, AIR TRITIA. Moss samples are processed within the Sector of Neutron Activation Analysis and Applied Research (SNAAPI) in the FLNP. SNAAPI carries out a multi-elemental analysis. Data gained from the NAA is analyzed. Spatial properties, shaped metrics and geostatistical analysis of the data obtained are performed in geographic information systems and classified to clusters according to the influence of different kinds of air pollution sources. The resulting clusters are compared with the mathematical modelling results.

References:

[1] Air quality in Europe: 2017 report [online]. European Environment Agency, 2017 [cit. 2018-01-28]. ISBN 978-92-9213-920-9. Online: https://www.eea.europa.eu/publications/air-quality-in-europe-2017

[2] Monitoring of atmospheric deposition of heavy metals, nitrogen and pops in Europe using bryophytes: monitoring manual [online]. 2015 [cit. 2018-01-26]. Online: https://icpvegetation.ceh.ac.uk/publications/documents/MossmonitoringMANUAL-2015-17.07.14.pdf

STUDYING ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS IN ARMENIA BY THE MOSS BIOMONITORING TECHNIQUE

<u>Tepanosyan G.H.</u>¹, Sahakyan L.V.¹, Yarmaloyan Q.V.¹, Saghatelyan A.K.¹, Strelkova L.P.², Zinicovscaia I.I.², Yushin N.S.², Frontasyeva M.V.²

¹The Center for Ecological-Noosphere Studies, NAS, Yerevan, Republic of Armenia

²Sector of Neutron Activation Analysis and Applied Research, Division of Nuclear Physics, FLNP, JINR, Russian Federation

Moss biomonitoring technique was applied to study the spatial distribution peculiarities of atmospheric deposition of trace elements in the territory of the Republic of Armenia. During the September-December of 2016, 37 moss samples (Homalothecium philippeanum, Syntrichia ruralis, Ptilium crista castrensis, Brachythecium rutabulum, Brachythecium reflexum) were collected and the contents of 42 elements were determined: 39 (Na, Mg, Al, Cl, Ca, K, Sc, Ti, V, Cr, Fe, Mn, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Ta, W, Au, Th, U, and Hf) by instrumental epithermal neutron activation analysis and 3 (Cu, Cd and Pb) using atomic absorption spectrometry. Data statistical treatment including Cluster analysis performed. According to the results K, Ca, Dy and Eu follow normal and Na, Mg, Al, Cl, Sc, Ti, V, Cr, Fe, Mn, Co, Ni, Cu, Rb, Sr, Sb, Cs, Ba, La, Ce, Sm, Tb, Tm, Ta, W, Th, U and Hf lognormal distribution. Abnormal distribution detected for Zn, As, Se, Br, Mo, Cd, Sb, I, Nd and Au indicating the presence of outliers and extreme values. The detailed examination of spatial distribution patterns of these elements showed that the high (>95%) values Mo are spatially allocated near and in city Yerevan area where Mo concentrate smelting plant is operating, as well as in the southern part of Armenia where is located Kajaran Cu-Mo open pit mine. Observed high values of Zn, As, Sb, Nd and Au located in the southern central part of Armenia were linked partially to the geological features of sampling sites characterized by sandstones, limestones and clay facies to the volcanogenic rocks of Palaeogene system. In addition to the natural concentrations of these elements the southern central part are known by the diatomite, marble, limestone, travertine, phosphorite mining, gold extraction plant, as well as deposits of Zn, As and Sb. In the case of Br and I values >75% are spatially located in the northern part of Armenia and supposed to be the results of atmospheric precipitations from the Black Sea and in the southeastern part influenced by the Caspian Sea. According to the Cluster Analysis three distinct groups were observed. Cluster I included La, Ce, Sm, Tb, Hf, Ta, Cs, Th, Ba, Tm, As, Nd, Cr, Eu, Co, Fe, W, Ni, U, Rb, K, Na, Dy, Sr, Mg, Al, Ti, V and Sc which supposed to be associated with the soils mineral particles suggesting that elements in the cluster I are naturally distributed. Cluster II included Zn, Sb, Cu, Pb, I and Cd while cluster III consisted of Cl, Br, Mo, Au, Se and Ca. Elements included in II and III clusters supposed to have a mixed origin as Zn, Sb, Cu, Pb, Cd and Mo are included in the long-range atmospheric transport and Cl, Br, I, Se and Ca in the natural cycling processes categories, as well as may have some contribution from the local sources of pollution.

TEMPORAL TRENDS AND SPATIAL DISTRIBUTION OF TRACE METALS IN MOSSES IN NORWAY

<u>Uggerud H.Th.</u>², Steinnes E.¹, Pfaffhuber K.A.²

¹Department of Chemistry, Norwegian University of Science and Technology, N-7469 Trondheim, Norway. eiliv.steinnes@ntnu.no ²NILU-Norwegian Institute for Air Research, P.O.Box 100, N-2027 Kjeller htu@nilu.no

Commissioned by the Norwegian Environment Agency, NILU-Norwegian Institute for Air Research in collaboration with Norwegian University of Science and Technology (NTNU), collected moss from 230 sites for determination of heavy metals in these. This is the eighth time a moss survey has been conducted in Norway since its inception in 1977. In addition to the ten metals that are prioritized by the European research programme called "International Cooperative Programme on Effects of Air Pollution on Crops", content of 43 more elements are determined. From the results obtained, it is evident that long-range atmospheric transport still significantly contributes to deposition of metals in Norway. Even so, comparison of concentration levels from 2015 with levels obtained in 1977 show that atmospheric deposition of metals has declined substantially. From year 2005 to 2015 a decrease in concentration level is observed only for V and Pb. For Cr, Ni, Cu, Zn, As, Cd, and Sb, there is no appreciable change in deposition in the same period. Maps of geographical distribution of several metals will be shown.

Looking at the geographical distribution maps, there are four areas in Norway that emerge. The area far south (Sørlandet) and the area around the inner part of the Oslo fjord (Indre Oslofjord) have trough all years shown the highest relative levels of atmospheric deposition compared to the rest of the country. The lowest relative levels through all times are found in mid Norway and far north-west. Temporal deposition trends are closer studied at these four different geographical areas. A fifth area in Norway that demands special attention is located far north-east at the Russian border. This area has been influenced by the emissions from two Russian metal smelters. Temporal trends from this area will be shown.

Precipitation for metal analysis are collected at five different sites in mainland Norway. The observatory at Birkenes is a representative measurement site for the region Sørlandet. Moss concentrations of Pb obtained in Sørlandet and Indre Oslofjord were converted to deposition rates by use of regression equations (Berg and Steinnes, 1997). Average deposition rates from Birkenes correlates well with average Pb concentration in moss from Sørlandet. High correlation between Pb concentration in moss from Indre Oslofjord and deposition rates from Hurdal is also found, even though Hurdal is not an especially representative measurement site for the Oslofjord region.

Reference:

Berg, T. and Steinnes, E., (1997) Use of mosses (Hylocomium splendens and Pleurozium Schreberi) as biomotors of heavy metal deposition: From relative to absolute values. Environ.Pollut., 98, 61-71.

DATA MANAGEMENT SYSTEM OF THE UNECE ICP VEGETATION MOSS SURVEY PROGRAM. CURRENT STATUS AND FUTURE PERSPECTIVES

Uzhinskiy A.

Joint Institute for Nuclear Research, 6, Joliot-Curie, str., 141980, Dubna, Moscow Region, Russian Federation

E-mail: <u>uzinskiy@jinr.ru</u>

The Data Management System (DMS) of the UNECE ICP Vegetation consists of a set of interconnected services and tools deployed and hosted at the Joint Institute of Nuclear Research (JINR) cloud infrastructure. DMS is intended to provide its participants with modern unified system of collecting, analyzing and processing of biological monitoring data.

Currently there are sections for management of sampling, intercomparison (M1, M2) and POPs data at the system. Users can create maps, get statistics, check their data, calculate indexes and factors. There are also some analytical tools like mean values comparison between chosen countries. Abilities of DMS and options that will be realized in nearest future are presented.

Possibilities of prediction of heavy metals concentration by a special neural network are considered. Sources for neural network learning are satellite imagery from Google Earth Engine platform and sampling data from DMS.

BIOMONITORING OF THE FOREST AREAS OF SOUTHERN AND NORTH-EASTERN POLAND

Zielińska M.^{1*}, Kłos A.¹, Bochenek Z.², Bjerke J.W.³, Tømmervik H.³, Zagajewski B.⁴, Ziółkowski D.², Rajfur M.¹, Dołhańczuk-Śródka A.¹, Ziembik Z¹

¹Independent Chair of Biotechnology and Molecular Biology, University of Opole, kard. Kominka 6, 45-032 Opole, PL *e-mail: marysia.zielinska@gmail.com ²Institute of Geodesy and Cartography, Warsaw, PL ³Norwegian Institute for Nature Research, Tromsø, NO ⁴Warsaw University, Department of Geoinformatics and Remote Sensing, Warsaw, PL

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

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

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

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

OZONE POSTERS

MONITORING OF AMBIENT AIR POLLUTION AND ITS EFFECTS TO AGRICULTURAL CROPS IN PAKISTAN: A THREAT TO THE FUTURE FOOD SECURITY OF SOUTH ASIA?

Ahmada M.N.*, Ziaa A.

Department of Agricultural Chemistry, University of Agriculture, Peshawar Pakistan *Corresponding Author Email: <u>drnumanahmad@aup.edu.pk</u>, Ph: +92-3329262283

Air pollution has increased rapidly with no knowledge of its effects on agricultural crops in the Northern region of Pakistan. The aim of this study was to assess the impact of hydrogen fluoride (HF) and Ozone (O₃) on agricultural crops in Peshawar through field surveys.

The HF concentrations from about 450 brick kilns around Peshawar, measured using passive samplers were higher in summer than in winter in areas close to brick kiln fields. The mean summer concentration was $0.2 \ \mu g \ HF \ m^{-3}$, with maximum of $0.3 \ \mu g \ HF \ m^{-3}$ in May. Severe HF injuries to mango, apricot and plum leaves, in form of necrotic leaf margins and tipburn, were found near the brick kiln fields. The fluoride content of fruit leaves, wheat grains and spinach was significantly higher in the brick kiln area than at control sites. It was also observed that the local community people were not aware of the toxic effects of air pollution on crops.

Although ozone is well-documented to affect crop yields in the densely populated Indo-Gangetic Plain, there is little knowledge of its effects around cities in more remote areas of south Asia. We surveyed crops around the city of Peshawar, Pakistan for visible injury, linking this to active samplers equipped with remote sensors technology that were used for the first time in this region. Foliar injury was found in the field on potato, onion and cotton when the mean monthly ozone concentration reached 35-55 ppb. The symptoms on onion were reproduced in ozone fumigation experiments, which also showed that daytime ozone concentrations of 60 ppb and above significantly reduce the growth of Pakistani varieties of both spinach (Beta vulgaris) and onion. Aphid infestation on spinach was also reduced at these elevated ozone concentrations. The ozone concentrations in Peshawar are comparable to those through many parts of northern south Asia, where ozone may therefore be a significant threat to sensitive vegetable crops in peri-urban regions. It was concluded that HF and O₃ are significant pollutants in Peshawar, especially for summer crops and can change the climatic conditions for the local crops. Therefore, it is recommended to conduct more detailed studies to determine the magnitude of damage caused by HF and O₃ in the Peshawar and for the whole South Asian region and to educate people about this danger and alerting of the consequences that can jeopardise their future food security.

Keywords: Food security Ozone air pollution vegetable crops Peshawar South Asia

OZONE RISK FOR TREES – PHYTOTOXIC OZONE DOSES AND FUTURE EFFECTS ON TREE GROWTH IN GERMANY

BAUMGARTEN M.^{1*}, GRÜNHAGE L.²

¹Ecophysiology of Plants, Technische Universität München, Hans-Carl-von-Carlowitz-Platz 2, 85354 Freising, Germany

^{*}Corresponding author: <u>manuela.baumgarten1@gmail.com</u> ²Department of Plant Ecology, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 26, 35392 Giessen, Germany

The determination of phytotoxic ozone doses for forest trees is a prerequisite to establish dose response relationships for reliable ozone risk assessment as well as for modelling. To ensure a state-of-the-art basis for future ozone risk assessment in terms of climate change an adjustment of model parametrization is required.

Thus, the main objective of our new research project is to advance ozone risk assessment and modelling for forest trees including future climate scenarios based on the recently established representative concentration pathways (RCP, IPCC 2013) additionally considering tropospheric O_3 and CO_2 -concentrations. The experimental approach of our new research project starting in 2019 is presented.

The experiment will be conducted in newly established phytotrones with 5-8 year-old beech and spruce from natural regeneration, growing in their natural soil monolith (two growing seasons).

Two experimental approaches will be applied:

I - a simulation of an O₃ gradient under standard climate/CO₂ conditions:

Four different O_3 concentrations (pre-industrial, ambient, moderately elevated and high) will be applied in order to develop ozone dose-response-functions adjusted to present conditions and to derive realistic target values for spruce and beech.

II - a sophisticated simulation of a future climate and O₃/CO₂ gradient:

In order to evaluate effects of a changing climate and emission scenarios in the future, daily cycles will be simulated for preindustrial conditions, the present, and the future scenarios RCP2.6 as well as RCP8.5 (2050/2100). The simulation of the corresponding O_3 concentrations and the combination of ozone and CO_2 emission will explain the CO_2 influence and also indicate combined effects, which have to be implemented in future growth modelling.

As a model region for German forests we will select a low mountain range region.

All simulation data will be acquired at a hourly resolution as it is crucial to generate scenarios as "realistic" as possible, especially concerning the concordance of meteorological values with O₃ concentration values within a hourly resolution.

Such kind of simulation database will be at first used in experimental climate impact research. Our experimental concept is open to further collaboration from interested international groups.

Keywords: stomatal ozone uptake, ozone dose-response functions, RCP future scenarios, ozone and CO₂ interactions, beech, spruce

ASSESSMENT OF SURFACE OZONE EFFECTS ON RICE PRODUCTION IN SOUTHERN VIETNAM FOR POSSIBLE ALTERNATIVE CROPPING SYSTEMS

Danh N.T.^{1,2}, Oanh N.T.K.^{1*}

¹Environmental Engineering and Management, Asian Institute of Technology, Pathumthani, Thailand

²Department of Agriculture and Rural Development, Ba Ria, Vung Tau Province, Vietnam (9, Huynh Ngoc Hay Street, Phuoc Hiep Ward, Ba Ria City, Ba Ria-Vung Tau Province, Vietnam)

Increasing trend of ozone has been reported in many developing Asian countries and would continue in near future in the scenario of climate change and higher precursors emissions. This would result in more serious effects on agricultural crop yields and affect the livelihood of farmers. This study aimed to test a hypothesis that it is possible to use suitable cropping systems to minimize O₃ effects in the future emission scenario. O₃ in the Eastern Region of Southern (ERS) of Vietnam were simulated using the WRF-CAMx model for 2010 and evaluated against available monitoring data in the domain. The evaluated CAMx, driven by WRF results of 2010, was used to simulate O₃ in 2030 using the future anthropogenic emissions of RCP8.5 and biogenic emissions in 2010. The CAMx outer domain (Vietnam inland, 12 x 12 km²) for both 2010 and 2030 simulations used the initial and boundary conditions extracted from the Southeast Asia (SEA) simulation which provided the boundary conditions for simulation of the finest ERS domain (4 x 4 km²). The rice yield loss (RYL) was assessed using the flux-based metrics of POD₁₀ and was compared with the loss based on concentration-based metrics of AOT40 and M7 for each of six provinces in ERS which has three rice crop cycles per year. The highest RYL was produced by POD₁₀ that showed the loss for the first crop was the highest in 2010, 25800 tonnes (~ 5.7% of the total rice production), the second highest for the third crop of 21,500 tonnes (~ 3.8%) and the least for the second crop of 6,800 tonnes (~ 1.7%). Higher loss of relevant crop cycles was in the rice production areas located downwind of Ho Chi Minh city. In 2030 the loss would increase and the highest rate would be for the first crop, upto 8.7%.

Alternative cropping systems were considered that could avoid excessive exposure to ozone and minimize the crop production loss in the future high O_3 scenario. Other existing crops in ERS, i.e. soybean and maize, assessed based on AOT40, also have higher loss in 2030 as compared to 2010. The land-use planning of different ERS provinces showed that maize was selected an alternative crop in near future. Therefore, this study recommended to substitute rice by maize only in the water shortage areas during the period of high O_3 , i.e. in the third rice crop cycle, and this would lower the value of agricultural production loss in ERS in the future. Another potential approach was to have earlier rice sowing (by 15 days) to avoid the excessive exposure to O_3 by rice plant during the accumulation period in the third crop. A combination of both approaches may be considered in the future crop planning of ERS.

IMAGE BASED ESTIMATION OF ANATOMICAL OZONE INJURY RESPONSES OF *NICOTIANA TABACUM* L.

Drapikowska M¹., Borowiak K¹., Pagórek C., Lisiak M¹., Byczkowska K¹., Drapikowski P.²

 ¹Department of Ecology and Environmental Protection, Poznań University of Life Sciences, Piatkowska 94c, 61-691 Poznań, Poland, e-mail: <u>mariadra@up.poznan.pl</u>
 ² Institute of Control and Information Engineering, Poznań University of Technology, Piotrowo 3A 60-965 Poznań, Poland

The aim of this study was to evaluate the degree of *Nicotiana tabacum* (L.) leaf tissue injury caused by tropospheric ozone. The study was carried out during growing season of the year 2016. The morphological and anatomical leaf blade injures were analyzed and the degree of damage was estimated using Cell Demmage Analizer Software with the use of preprocessing for remove background. The correlation between morphological and anatomical injures in plants samples was tested. The anatomical and morphological studies have shown that the highest number of dead tissues were recorded in plants in the extramural site. The gradual growth of partially damaged and dead tissues over time was found.

Cell Damage Analyzer Software is a method which identify and calculate the percentage of dead tissue and permit to remove image distortions caused by colored vascular bundles (Drapikowska *et* al. 2016). Thresholding in color spaces is the base method for initial image processing in Cell Damage Analyzer Software, but it does not give the correct results when a color of the image background is identical as a color of the leaf damages. In order to enhance the application of the Cell Damage Analyzer Software, it is added a preprocessing step, for distinguishing the object from the background. Image is contoured and in semi-automated mode the contour of the object of interest is separated. Next binary image of the object (mask) is created. Boolean operation AND between input image and the mask is done in order to remove background.

Reference:

Drapikowska M., Drapikowski P., Borowiak K., Hayes F., Harmens H., Dziewiątka T. 2016. Application of novel image base estimation of invisible leaf injuries in relation to morphological and photosynthetic changes of *Phaseolus vulgaris* L. exposed to tropospheric ozone. Atmospheric Pollution Research. 7: 1065-1071.

15 YEARS OF MEASUREMENTS OF OZONE DEPOSITION FLUXES OVER FORESTS, CROPS AND BARE SOILS IN ITALY

Gerosa G., Finco A., Marzuoli R., Chiesa M.

Catholic University, Dept. of Mathematics and Physics, via Musei 41, Brescia (Italy)

In the last 15 years the research group on ecophysiology and environmental physics of the Catholic University of Brescia performed several measurement campaigns of ozone (O_3) deposition fluxes on different land covers in Italy, including forests, crops and bare soils. The main findings from those campaigns are here summarized:

- The O₃ stomatal fluxes in crops are strongly influenced by water availability. O₃ deposition measurements with eddy covariance technique over different crop fields and in different water limitation conditions showed that O₃ stomatal flux was about 50% of the total O₃ flux in no water stress conditions, with slight variations among different species. Under water limitation, the fraction of O₃ stomatal flux can decrease lower than 20%.
- In a poplar plantation high O_3 stomatal fluxes reduced the maximum CO_2 uptake. An instantaneous flux threshold of 7 nmol m⁻² s⁻¹ of O³ stomatal flux has been found to cause a negative effect on carbon assimilation dynamics and could be suggested for modelling this effect.
- In a mixed oak-hornbeam forest at climax, 30% of O_3 deposited was removed by gas phase reactions with NO emitted from the underlying soil, while only 3% of the O_3 flux removed was attributed to gas phase reactions with biogenic VOCs. The 40% of O_3 deposition was uptaken by leaves stomatas, while the remaining 27% was attributed to destruction on non-living vegetal and soil surfaces.
- Ozone flux measurements over a holm-oak forest and mediterranean maquis ecosystems revealed that higher air humidity and leaf wetness increased the O_3 non-stomatal deposition to the forest
- Ozone fluxes to a forest soil with litter did not show particular variations with the season. The soil resistance to O_3 deposition estimated by automated dynamic chambers in a forest ranged between 400 and 1200 s/m with a clear daily variation. The soil saturation with water increased the soil resistance to O_3 deposition.
- Eddy covariance measurements of soil resistance to O₃ performed in a bare silty-clay agricultural soil under different soil water conditions showed that the bulk soil resistance to O₃ deposition increased from 120 s/m to 375 s/m at increasing soil water content. A simple model parameterisation can be proposed based on the relative soil water content.

These results give evidence of the importance of O_3 non-stomatal deposition as key-factor for a correct and reliable estimation of O_3 stomatal dose in the O_3 risk assessment models.

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

Leung F.^{1,2,3}, Sitch S.¹, Tai A.P.K.³, Wiltshire A.², Gornall J.², Williams K.²

¹University of Exeter, Stocker Road, Exeter, UK EX4 4PY ²Met Office Hadley Centre, Fitzroy Rd, Exeter, UK EX1 3PB ³Institute of Environment, Energy and Sustainability, Chinese University of Hong Kong Email address: <u>F.Leung@exeter.ac.uk</u>

Tropospheric ozone (O₃) is the third most important anthropogenic greenhouse gas. It is harmful to human health and detrimental to plant productivity, causing significant crop production losses. Currently, O₃ concentrations are to increase globally if we are following the business as usual scenario (RCP8.5), which could have a significant impact on food security. The Joint UK Land Environment Simulator modified to include crops (JULES-crop) is used here to quantify the impacts of present-day and future tropospheric O₃ on crop production at the regional scale until 2100 using RCP2.6 and RCP8.5 scenarios. The studied regions include the main crop producing countries. The model will thus contribute to the understanding of the impacts of climate change on food production. With increasing carbon dioxide (CO₂) in the future, models predict CO₂ fertilisation with induced stomatal closure would reduce O₃ damage and increase the productivity of vegetation. Factorial runs of the combination of RCP2.6 and RCP8.5 CO₂, climate and ozone scenarios are performed to investigate the sensitivity of the crops to each climate forcing. The factorial run also explores if climate change mitigation or clean air policy are more important regarding increasing crop yield. The relative impact of CO_2 , O_3 and climate change is quantified and compared in all important agricultural regions. The factorial simulations show that CO_2 has the largest impact on regional yield, followed by climate then ozone. The CO₂ fertilisation and CO₂ induced reduced O₃ damage effect is, however, masked by the negative impacts of tropospheric O_3 in regions with high O_3 concentration such as South Asia and China. The modelled yield in 2050 is compared with Food and Agriculture Organisation (FAO) statistic, and it shows that FAO estimation of future scenario is more conservative than JULES-crop simulation, and it is closer to our JULES-crop RCP8.5 scenario with a combination of ozone and CO₂ and climate.

PROJECTED GLOBAL TROPOSPHERIC OZONE IMPACTS ON VEGETATION UNDER DIFFERENT EMISSION AND CLIMATE SCENARIOS

Sicard P.¹, Anav A.², De Marco A.³, Paoletti E.²

¹ACRI-HE, Sophia Antipolis, France ²Consiglio Nazionale delle Ricerche - Istituto per la Protezione delle Piante, Sesto Fiorentino, Italy ³Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Roma, Italy

The impact of ground-level ozone (O₃) on vegetation is largely under-investigated at global scale despite worldwide large areas are exposed to high surface O₃ levels and concentrations are expected to increase in the next future. To explore future potential impacts of O₃ on vegetation, we compared historical and projected O₃ concentrations simulated by six global atmospheric chemistry transport models on the basis of three representative concentration pathways emission scenarios (i.e. RCP 2.6, 4.5, 8.5). To assess changes in the potential O₃ threat to vegetation, we used the AOT40 metric. Results point out a significant overrun of AOT40 in comparison with the recommendations of UNECE for the protection of vegetation. In fact, many areas of the northern hemisphere show that AOT40-based critical levels will be exceeded by a factor of at least 10 under RCP8.5. Changes in surface O₃ by 2100 range from about + 4-5 ppb worldwide in RCP8.5 scenario to reductions of about 2-10 ppb in the RCP2.6 scenario. The risk of O₃ injury for vegetation decreased by 61% and 47% under RCP2.6 and RCP4.5, respectively and increased by 70% under RCP8.5. Key biodiversity areas in South and North Asia, central Africa and Northern America were identified as being at risk from high O_3 concentrations. To better evaluate the regional exposure of ecosystems to O_3 pollution, we recommend the use of improved chemistry-climate modelling system, fully coupled with dynamic vegetation models. We thank the project MOTTLES "MOnitoring ozone injury for seTTing new critical LEvelS" (LIFE15 ENV/IT/183) for financial support.

* Corresponding author: psicard@argans.eu

EFFECTS OF PLANT PHYSIOLOGICAL RESPONSES TO RISING OZONE AND CO₂ LEVELS ON GLOBAL AIR QUALITY VIA VARIOUS FEEDBACK MECHANISMS

Tai A.P.K.^{*}, Sadiq M., Zhou S., Wong A.Y.H.

Earth System Science Programme, Faculty of Science, The Chinese University of Hong Kong, Sha Tin, Hong Kong *E-mail: amostai@cuhk.edu.hk

Plant physiological functions such as photosynthesis, stomatal activity and terpenoid production play an important role in shaping the Earth's atmosphere. Changes in plant physiology in response to rising CO₂ and tropospheric ozone levels would therefore interfere with land-atmosphere exchange processes (e.g., evapotranspiration, dry deposition, isoprene emission), with ramifications for air quality and climate. Here we first develop and integrate several parameterization schemes for CO₂-ozone-vegetation coupling into the GEOS-Chem chemical transport model to examine how rising CO₂ and ozone damage on vegetation would influence ozone air quality via various pathways. We find that elevated CO₂ for year 2050 under the RCP8.5 scenario can modify surface ozone by -1 to +4 ppb, mostly reflecting compensating effects of reduced isoprene emission (due to CO₂ inhibition effect) and reduced dry deposition velocity (due to lower stomatal conductance). On the other hand, ozone-induced damage on leaf area index (LAI) can lead to an ozone feedback of -1 to +3 ppb, also reflecting compensating effects. In a related study (Sadiq et al., 2017), we integrate a similar parameterization of ozone damage on vegetation into the Community Earth System Model, and find that ozone-vegetation coupling leads to significant increases (up to 4-6 ppb) in simulated ozone concentrations over Europe, North America and China, reflecting a major positive feedback on ozone air quality arising from ozone damage. We also find that ozone-vegetation coupling modifies boundary-layer meteorology including changes in surface temperature, precipitation and humidity. All in all, the changes in surface ozone due to CO₂-ozonevegetation coupling are comparable in magnitude with the effects of climate and land use changes per se, and we therefore suggest that plant physiological changes arising from varying CO₂ and ozone levels are important factors that should be accounted for in historical simulations and future projections of air quality.

Reference:

Sadiq, M., Tai, A.P.K., Lombardozzi, D., and Val Martin, M.: Effects of ozone-vegetation coupling on surface ozone air quality via biogeochemical and meteorological feedbacks. *Atmos. Chem. Phys.*, 17, 3055-3066, 2017.

MESOPHYLL CONDUCTANCE LIMITATION OF PHOTOSYNTHESIS IN POPLAR UNDER ELEVATED OZONE

Xu Y.^{1,2}, Feng Z.^{1*}, Tarvainen L.², Uddling J.²

¹State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Shuangqing Road 18, Haidian District, Beijing 100085, China ²University of Gothenburg, Department of Biological and Environmental Sciences, P. O. Box 461, SE-405 30, Sweden *E-mail: fzz@rcees.ac.cn

Mesophyll conductance (g_m) causes the CO₂ drawdown from CO₂ concentration from the intercellular space (C_i) to the chloroplast (C_c) and constitutes a major limitation of photosynthesis in most tree species studied. However, few studies have investigated if elevated ozone (O₃) affects g_m . In this study, the effects of elevated O₃ on the stomatal, g_m and biochemical limitations of photosynthesis was investigated at four times in the O₃ sensitive hybrid poplar clone ('546') grown in either charcoal filtered ambient air (CF) or non-filtered ambient air with a targeted O₃ addition of 40 ppb (E-O₃). The limitations of stomatal conductance, g_m and biochemical capacity were assessed to quantify the main mechanism affecting photosynthesis in response to elevated O₃. The results indicated that O₃ significantly decreased light-saturated net photosynthesis (A_{sat}), g_m and the maximum carboxylation capacity (V_{cmax}) , and that the effects were more pronounced later in the growing season. However, there were no significant effects of O₃ on stomatal conductance or the maximum rate of electron transport (J_{max}) . The quantification of the contributions of the three relative limitations to decrease A_{sat} in E-O₃ showed that mesophyll conductance limitation (MC_L) was by far the most important (on average 19%) and grew larger over time. Both stomatal limitation (S_L) (on average 1%) and biochemical limitation (B_L) (on average 4%) were rather small and remained roughly stable over time. These findings highlight that g_m plays a key role in limiting photosynthesis of poplar exposed to elevated ozone.



Figs. Light-saturated photosynthesis rate (A), mesophyll conductance (B) and photosynthetic limitations (C) during four sampling times

MOSS SURVEY POSTERS

DISTRIBUTION OF TRACE ELEMENTS INFUENCE FROM SEA COASTAL LINE BY USING MOSS BIOMONITORING

Sh. Allajbeu¹, L. Bekteshi² F. Qarri², S. Kane². P. Lazo¹, T. Stafilov⁴

¹ Department of Chemistry, Faculty of Natural Sciences, University of Tirana, Tirana, Albania
 ² Department of Chemistry, University of Elbasan, Elbasan, Albania
 ³ Department of Chemistry, Faculty of Technical Sciences, University of Vlora, Vlora, Albania
 ⁴ Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia shanikoallajbeu@gmail.com

Distribution of Sr, Ca, Mg, Na, Ba, K, Cr, Cu and Ni is studied by using moss biomonitoring (*Hypnum cupressiforme*) collected from 26 sampling sites of two vertical axes parallel to the sea coastal line of Albania (the average distance of each axis from the coast is respectively 10 and 83 km). The moss samples were collected during the August-September 2015 in wet conditions weathers. Sr, Ca, Mg, Na, Ba and K were analyzed by using *Inductively coupled plasma- atomic emission spectroscopy* (ICP-AES) at *Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia*.

It is generally known that the coastal area is the main source of some chemical elements, such as Mg, Na, K, Sr, Ca and Ba, to terrestrial environments. The aim of the present investigation is the determination of trace elements concentrations in moss samples positioned at the marine coastal area and inland area with different distances from the coast line (Adriatic and Ionian Seas). This study show that the median elements Mg, Na, K, Sr, Ca and Ba are more high in the first axis, near the coastal line (Fig. 1). Similar results were obtained from 2010 moss survey for Cl, I and Br as typical elements of marine sea salt elements.



Fig. 1 Box-Plot diagram of concentration data (mg/kg, DW) (W – western part; E-eastern

part)

The statistical data (mean concentration, median, minimum and maximum values) of Cr, Cu and Ni are compared for to axis, too. The highest concentration of these elements were found in the second axis positioned on eastern part of Albania that is characterized by high deposits of Cr, Cu and Ni ores and mining activity.

These finding prove again that mosses are good bioindicators for trace elements indicating the spatial distribution and differences on their concentration level.

Key words: atmospheric deposition, moss biomonitoring, trace elements, marine coastal area, inland

ENVIRONMENTAL IMPLICATION INDICES BY ELEMENTAL CHARACTERISATION OF THE CO-LOCATED TOPSOIL AND MOSS SAMPLES

Aničić Urošević M.¹, Vuković G.¹, Vasić P.², Jakšić T.², Nikolić D.³, Škrivanj S.⁴, Popović A.⁴

¹Institute of Physics Belgrade, University of Belgrade, 11080 Belgrade, Serbia, E-mail: <u>mira.anicic@ipb.ac.rs</u>; <u>gordana.vukovic@ipb.ac.rs</u>

 ²Faculty of Natural Sciences, University of Priština, 38220, Kosovska Mitrovica, Serbia;
 ³Institute of Meat, Hygiene and Technology, 11000 Belgrade, Serbia;
 ⁴Faculty of Chemistry, University of Belgrade, Belgrade, Serbia, E-mail: apopovic@chem.bg.ac.rs

Pollutants once emitted into the atmosphere are deposited on Earth's surface where they further accumulate in both biota and soil. Hence, it is a challenge to assess a pollutant distribution among different media, and define multiple scaling the pollutant environmental implications. In this study, the content of potentially toxic elements and their environmental implications were estimated through moss (Hypnum cupressiforme) and collocated topsoil (0-5 cm) sampling across the Province of Kosovo and Metohija at 21 sites during June of 2016. The concentrations of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, U, V, and Zn were determined in the samples by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). The increased median Ba, Cd, Cr, Co, Ni, V and maximum As, Cu, Pb, and Zn concentrations were found in the topsoil samples across the study area in comparison to the prescribed values. Furthermore, different formulas for pollution level assessment (enrichment factors-EFs, geo-accumulation-Igeo and pollution load indexes-PLI) were applied to the obtained data and discussed in conjunction. Different pollution scaling testifies about moderate to severe environmental implications (2<PLI<5; 1<Igeo<7, 1<EFs<275) of the potentially toxic elements in the study area. The sampling sites in the northern part of the study area, well-known mineral resource area, are especially under the influence of the toxic element pollution, which is likely a consequence of the exploitation processes and existing dumps. Namely, the comparison of element EFs considering the regional topsoil background with those regarding the average Earth crustal values imply the existence of the strong influence of (resuspended) soil component in the element enrichment of all environmental samples (e.g., the local topsoil and moss). However, EF of Pb, Cu, Zn and U in the moss samples were notably higher than those calculated for the collocated topsoil, which indicates the presence of long-range transported pollution. Finally, both the collocated measurements and multiscale pollution assessment, performed in conjunction, testify about a strong geochemical 'signature' in the studied area [1].

Keywords: air pollution, geochemical background, passive biomonitoring, EF, Igeo, PLI

Reference:

[1] Aničić Urošević M., Vuković G., Vasić P., Jakšić T., Nikolić D., Škrivanj S., Popović A., 2017. Environmental implication indices by elemental characterisation of the collocated topsoil and moss samples, Ecological Indicators, *submitted for publication*.

ATMOSPHERIC DEPOSITION OF RADIONUCLIDES BY MOSS BIOMONITORING TECHNIQUE IN THRACE REGION OF TURKEY

Aslani M.A.A.¹, Haciyakupoglu S.², Belivermis M.³, Kilic O.³, Ileri R.K.², Erenturk Akyil S.²

¹Ege University, Institute of Nuclear Sciences, 35100 Bornova-İzmir, TURKEY, mahmoud.aslani@ege.edu.tr

 ²Istanbul Technical University, Energy Institute, 34469 Maslak-Istanbul, TURKEY, haciyakup1@itu.edu.tr, erenturk@itu.edu.tr, ruveyda_ileri@hotmail.com
 ³Istanbul University, Faculty of Sciences, Department of Biology, Vezneciler, Istanbul, TURKEY, okilic@istanbul.edu.tr, belmurat@istanbul.edu.tr

Moss have been used commonly as bioindicators of fallout radionuclides. Nuclear weapon tests and nuclear reactor accidents are main sources to release artificial radionuclides such as ¹³⁷Cs, ⁹⁰Sr and Pu which have long physical half-lives into the atmosphere. Terrestrial radionuclides such as ⁴⁰K, ²³⁸U and ²³²Th present also in the environment. Part of all radionuclides are deposited in mosses.

Thrace region is located in the northwest of Turkey and the west boundary to Bulgaria and Greece. Most of the Thrace lands are used as agricultural land. The most important subsistence source in two cities (Edirne and Kirklareli) in the region is agriculture and agriculture based industry. In the other province (Tekirdag), which has intensive industrial production, most of the people living in the inner and western part are dealing with agriculture related works again. The intensive industry and large agricultural area and the region have a dual structure.

The present study was undertaken in order to determine the radionuclide activity concentrations in moss samples in Thrace region of Turkey. For this reason, 16 of moss samples were collected from this region. Radiation levels of samples were measured using a gamma multichannel analyser equipped with scintillation gamma spectrometer (3"x3" NaI(Tl) detector). The concentrations of radionuclides were compared with those obtained from similar studies related to Turkey reported in the literature as well as earth's crust average values.

RARE EARTH ELEMENTS IN *TARAXACUM OFFICINALE* COLLECTED IN THREE DIFFERENT CITIES

Borowiak K.¹, Lisiak M.¹, Budka A.², Kanclerz J.³, Janicka E.³, Adamska A.³, Żyromski A.⁴, Biniak-Pieróg M.⁴, Podawca K.⁵, Mleczek M.⁶, Niedzielski P.⁷

 ¹Department of Ecology and Environmental Protection, Poznan University of Life Sciences, Piatkowska 94C, 60-649 Poznan, Poland, klaudine@up.poznan.pl
 ²Department of Mathematical and Statistical Methods, Poznan University of Life Sciences, Wojska Polskiego 28, 60-637 Poznan, Poland
 ³Institute of Land Improvement, Environmental Development and Geodesy, Poznan University of Life Sciences, Piatkowska 94C, 60-649 Poznan, Poland
 ⁴Institute of Environmental Development and Protection, Wroclaw University of Environmental and Life Sciences, Plac Grunwaldzki 24, 50-363 Wroclaw, Poland
 ⁵Department of Engineering and Geodesy, Warsaw University of Life Sciences, Nowoursynowska 166, 02-787 Warsaw, Poland
 ⁶Department of Chemistry, Poznan University of Life Sciences, Wojska Polskiego 38/42, 60-627 Poznan, Poland
 ⁷Analytical Chemistry Laboratory, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznan, Poland

The aim of the study was to evaluate accumulation of rare earth elements (REEs) in dandelion (*Taraxacum officinale*) collected from the different cities in Poland (Poznan, Warsaw and Wroclaw). For this purpose the samples of leaves, roots and soil were collected in each city from 10 research sites. Experimental sites were selected nearby typical facilities for big cities like: airport, train station, old town, motorway, high-density housing areas, low-density housing areas, park, lake, big river and rural areas.

All elements were analysed by inductively coupled plasma optical emission spectrometry followed by microwave-assisted sample digestion by concentrated nitric acid. To characterize the ability of bioaccumulation and translocation of REEs in plants three indicators was calculated: the bioaccumulation factor (BAF), the translocation factor (TF), the contamination factor (CF). For graphical data presentation, GIS tools were used. PCA analysis was applied for visualisation relations between REEs accumulation in plants and research sites.

The spatial distribution of REEs accumulation in *Taraxacum officinale* was varied in the cities. Due to specific features of analysed elements and their occurrence in many modern technologies the difficulties were found to point the direct relations between land use and their accumulation in plants. However, in each of the cities there were areas with increased REEs accumulation. The ability of bioaccumulation and translocation of REEs in plants was also varied.

DISTRIBUTION OF HEAVY AND LIGHT RARE EARTH ELEMENTS IN HERBACEOUS PLANT SPECIES

Anna Budka², Patrycja Mleczek¹, Klaudia Borowiak¹, Przemysław Niedzielski³

 ¹Department of Ecology and Environmental Protection, Poznan University of Life Sciences, Piątkowska 94C,60-649 Poznań, Poland
 ²Poznan University of Life Sciences, Department of Mathematical and Statistical Methods, Wojska Polskiego 28, 60-637 Poznań, Poland
 ³Adam Mickiewicz University in Poznań, Faculty of Chemistry, Umultowska 89B, 61-614 Poznań, Poland

The increase of the use of heavy and light rare earth elements (HREEs, LREEs) in development of new technologies and nanomaterials is a direct cause of a new problem related with contamination of numerous environment components just these groups of elements. For this reason, the aim of study was to estimate accumulation and distribution of REEs in organs of three herbaceous plant species: Artemisia vulgaris L., Taraxacum officinale F.H. Wigg. and Trifolium repens L. All plants were collected form 3 distances (1, 10 and 25 m) from the edge of a busy road in Poland.

There is a high correlation between concentration of REEs in soil and their content in plants (r>0.9300), what points at high potential of these herbaceous plant species to effective phytoextraction especially LREEs. It was confirmed by bioconcentration factor (BCF) values higher than 1, what indicates at effective uptake of this group of elements to plant roots and also their effective transport to aboveground plant parts. In contrary to this, BCF values calculated for HREEs were lower than one, what indicates at exclusion strategy. It is worth to underline that LREEs were the largest proportion of REEs, while HREEs only the marginal portion. The dominant LREEs were Nd and Ce, while Er was dominant element in the HREEs group. The significant differences in REEs concentration, especially between A. vulgaris L. and T. repens L. but also A. vulgaris L. and T. officinale were observed. This relationships for plants growing at all three distances from the road were recorded. Efficiency of REEs and LREEs in studied plant species was as follow: A. vulgaris L. > T. officinale L. > T. repens L., while in case of HREEs only for plants growing at the distance 1 m from the road the same relationship was observed.

Obtained results unambiguously pointed at potential of these herbaceous plant species for removing mainly LREEs from contaminated soil.

Key words: busy road; distribution; heavy rare earth elements; light rare earth elements; herbaceous plants; phytoextraction

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

Bukharina I.L¹., Zhuravleva A.N.¹, Volkov N.A.¹, Vasileva N.A.¹, Bakuleva Y.A.¹, Plotnikova K.V.¹, Frontasyeva M.V.²

¹Udmurt State University, str. Universitetskaya, 1. Izhevsk, 426034, Udmurt Republic, Russian Federation E-mail: <u>buharin@udmlink.ru</u> ²Joint Institute for Nuclear Research, str. Joliot-Curie, 6, Dubna, 141980, Moscow Region, Russian Federation, E-mail: <u>marina@nf.jinr.ru</u>

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



Moss monitoring network in Udmurtia, Wester Urals, in 2017

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, N.A. Vasileva, M.S Shvetsova, M.V. Frontasyeva Moss monitoring of trace elements in the Republic of Udmurtia, Russia // ICP Vegetation 30th Task Force Meeting : 14th-17th February 2017, Poznan, Poland : Programme & Abstracts / ICP Vegetation Programme Coordination Centre, Centre for Ecology & Hydrology. Poznan, 2017. - P. 58.

ATMOSPHERIC DEPOSITION STUDY OF MAJOR AND TRACE ELEMENTS BY THE MOSS BIOMONITORING TECHNIQUE IN GEORGIA: 2014–2016

Chaligava O.^{1,3}, Shetekauri S.¹, Shetekauri T.¹, Kvlividze A.¹, Kalabegishvili T.², Frontasyeva M.V.³, Chepurchenko O.E.³, Tselmovich V.A.⁴

¹I. Javakhishvili Tbilisi State University, Chavchavadze ave 3, Tbilisi 0129, Georgia, E-mail: omar.chaligava@ens.tsu.edu.ge

²I. Javakhishvili State University, E. Andronikashvili Institute of Physics, 6 Tamarashvili str., Tbilisi, 0177, Georgia, E-mail: kalabegi@vahoo.com

³Joint Institute for Nuclear Research, str. Joliot-Curie, 6, Dubna, 141980, Moscow Region, Russian Federation, E-mail: marina@nf.jinr.ru

⁴Borok Geophysical Observatory, a branch of Shmidt's Institute of Physics of the Earth RAS, Russia, 152742, Borok, Nekouz, Yaroslavl region E-mail: tselm@mail.ru

Results of the moss biomonitoring of atmospheric deposition of major and trace elements in Georgia in 2014-2016 are reported. Overall, during these surveys, 111 moss samples were collected nearly over the whole territory of the country. The sampling was performed in compliance with the UNECE ICP Vegetation guidelines [1]. The analysis of moss samples was carried out at the reactor IBR-2 of FLNP JINR by means of epithermal neutron activation analysis: concentrations of 39 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Sr, Zr, Mo, Pb, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Hf, Ta, W, Au, Th, and U) were determined. Concentrations of Cu, Cd and Pb were obtained by atomic absorption spectrometry. Multivariate statistics was applied to find associations of chemical elements and to characterize the sources of element-pollutants determined in the samples. Factor analysis revealed mineral dust, industrial and marine components, as well as vehicle emissions. Scanning electron microscopy and X-ray microanalysis of moss samples collected in the highlands of Georgia showed the presence of clastic, anthropogenic, as well as cosmogenic particles. A comparison of determined concentrations of elements with the data from other Europe countries was carried out. For graphical data presentation, GIS tools were used. The obtained results showed elevated levels of concentrations of heavy metals in the Western Georgia known for industrial and mining enterprises as well as high-traffic roads allocated there.

Reference:

[1] Frontasyeva, M., Harmens, H. (2014) Heavy metals, nitrogen and POPs in European mosses: 2015 survey - Monitoring Manual. Bangor, UK, ICP Vegetation. <u>http://icpvegetation.ceh.ac.uk/publications/documents/MossmonitoringMANUAL-2015-17.07.14.pdf</u>

SPATIAL DISTRIBUTION OF HEAVY METALS AND NITROGEN DEPOSITION IN ROMANIA BASED ON MOSS ANALYSIS IN 2015

Ene A.¹, Stihi C.², Frontasyeva M.³, Radulescu C.², Iacoban C.⁴

 ¹Dunarea de Jos University of Galati, Faculty of Sciences and Environment, 47 Domneasca St., Galati, Romania, e-mail: aene@ugal.ro
 ²Valahia University of Targoviste, Faculty of Sciences and Arts, Targoviste, Romania
 ³Joint Institute for Nuclear Research, Dubna, Russian Federation, e-mail: marina@nf.jinr.ru
 ⁴National Research and Development Institute in Forestry "Marin Dracea", Câmpulung Moldovenesc Station, Suceava County, Romania, E-mail: carmeniacoban@gmail.com

The moss survey, undertaken in 2015/2016 by teams from Targoviste, Galati and Iasi universities, comprised 214 sampling sites over the Romanian territory (Figure). Concentrations of heavy metals and trace elements were determined in mosses in the frame of the JINR-Romania collaborative projects involving Valahia University of Targoviste and Dunarea de Jos University of Galati, Romania. Nitrogen was determined for the first time in the moss surveys in Romania at National Institute for Research and Development in Forestry "Marin Dracea", Campulung Moldovenesc Station, Romania. Maps of distribution of nitrogen and selected heavy metal loads in moss generated by DATA MANAGEMENT SYSTEM (DMS) in the JINR cloud platform are presented in Figure. The calculated concentration factors and geochemical indices evidence high loads of some heavy metals, related to industrial areas in western part of Romania. The data are compared with the values obtained in the previous moss surveys in Romania [1-3] and by other European countries, reported in DMS.



Figure. Sampling points and maps of element concentrations in mosses in Romania (2015).

References:

[1] Harmens, H., Norris, D., Sharps, K., Mills, G., Frontasyeva, M., Ene, A., Stihi, C., et al. (2015), Heavy metal and nitrogen concentrations in mosses are declining across Europe whilst some "hotspots" remain in 2010, *Environmental Pollution* 200: 93-104.

[2] Stihi, C., Popescu, I.V., Frontasyeva, M., Radulescu, C., Ene, A., Culicov, O., Zinicovscaia, I., et al. (2017), Heavy metal air pollution study in Romania using moss biomonitoring, neutron activation analysis and atomic absorption spectrometry, *Analytical Letters* 50(17): 2851-2858.

[3] Harmens, H., Norris, D., Mills, G., and the participants of the moss survey (2013), Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe. ICP Vegetation Programme Coordination Centre, CEH, Bangor, UK.

MERCOX – METROLOGY FOR OXIDISED MERCURY

Fettig I.¹, Horvat M.², de Krom I.³, Douglas D.⁴, Rajamaki T.⁵

¹Umweltbundesamt, Berlin, Germany, ina.fettig@uba.de ²Jožef Stefan Institute, Slovenia ³VSL, Netherlands ⁴LGC, United Kingdom ⁵VTT, Finland

Mercury (Hg) is one of the most toxic metals, and is regulated by the Industrial Emissions Directive (IED) 2010/75/EU, the Air Quality Directive 2004/107/EC, the Waste Incineration Directive 2000/76/EC and the Minamata Convention adopted in 2013; which is a global treaty to protect human health and the environment from the adverse effects of Hg. In addition to its elemental form Hg also exists in oxidised forms (i.e. Hg(II)) that are reactive and can be transformed into organic Hg species such as methylmercury (MeHg), the most toxic Hg species and the one most prone to bioaccumulation in aquatic systems. Half of atmospheric Hg emissions are of natural origin whilst the rest are of anthropogenic sources, primarily from fossil fuel burning and other high temperature industrial processes (cement clinker production, waste incineration, ore roasting, steel production).

Knowledge of Hg speciation both in air and in stack gas emissions is critical when validating models for predicting Hg emissions, transport, deposition and fate at the European level as well as on a global scale. Therefore, atmospheric Hg isotopic signatures that can be used to trace the origin and fate of atmospheric Hg also need metrological support and development.

The overall goal of the EMPIR – MercOx project (Oct 17 – Sept 20) is to develop SI traceable measurements, for the monitoring and control of mercury and its different species in gas emission sources and in the atmosphere. The project will achieve significant improvements in the measurement comparability and uncertainty of Hg measurement results. Currently, traceable calibration methods only exist for elemental mercury, but such measurements are also needed for oxidised Hg species in order to meet the requirements of EU regulation and the implementation of the Minamata Convention. The development of reliable and direct Hg(II) measurement techniques and reliable and traceable Hg(II) standards is needed to solve the traceability problem that currently exists in the measurement of total mercury (Hg^{tot}) and oxidised Hg and for accurately comparing the Hg^{tot} concentration in generated elemental and oxidised Hg reference gas standards are required, as well as improved sampling methods, traceable reference standards, validated methods for the on-line measurement of Hg under field conditions and a comparison of Hg species inter-conversion.

The poster will give an introduction to the project and highlight the main technical objectives. The project is funded by the EURAMET EMPIR initiative. EURAMET is the Regional Metrology Organisation of Europe. The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR participating countries.

CHITIN-COVERED SORBENT SLIDES FOR ACQUIRING DATA ON AIR- OR WATERBORNE POLLUTION, SUBTERRAIN BIOCHEMICAL ACTIVITIES AND SECONDARY CONTRIBUTIONS TO CLIMATE CHANGE

Fränzle S., Retschke D., Erler M., Blind F. IHI Zittau/Dresden Tech

Chitin-based biomonitoring of environmental samples provides more than data which likewise could be obtained by meas of e.g moss-monitoring because chitin "pads" (flakes of shrimp chitin grafted to some glass slide) can be placed at arbitrary sites in an ecosystem (unlike with mosses, there is no requirement for access of daylight or even for conditions which might be endured by "higher" living organisms). Chitin is capable of quickly (≤ 10 min until equilib.) adsorbing analytes from water or moist solids (including minerals, sediments, ground wood, insoluble salts), with little and quantifiable interference by those ligands present in soil water due to biological activity etc.. Almost all (except Mg, Ca, Sr) divalent and all higher-valent metals are adsorbed, as well as complexes and oxoanions such as molybdate or arsenate and biogenic organometals (biomethylation products, homoleptic carbonyls). Placing chitin-modified pads at arbitrary sites means one can intercept flows to some sink or detect introductions by e.g. environmental pollutants. Equilibrium between chitin adsorption at pads immersed into water and underneath sediment, respectively, can be tested for all the elements involved: recently we could show such effects of in- or output along some gradient (sediment column, lake-, pond- or river shore) can be detected by sampling near sediment/water interface only while corresponding processes take place about 50 cm apart (i.e. downward from the very sites of adsorption/measurements), e.g. methanogenesis (giving independent evidence of Ni inputs) or pig iron formation. Thus dynamics of transport can be studied covering processes in both groundwater and flowing rivers besides of airborne deposition. Signals of certain "purely toxic" besides of essential metals (Pb, Al) and of REEs can be attributed to co-precipitation in the framework of the above biological minerogenic processes, cp. removal of REEs from solution by precipitation of Fe(III) in slightly alkalinic conditions during pig iron formation. Access to remote or hazardous sites is planned to be accomplished by means of attaching chitin pads to drones. Aq. detection limit usually is $< 1 \mu g/l$ of ions. Application of achieving vertical "transparency" of sediments detecting processes commencing in deeper layers can be and already are used in studies of secondary effects of climate change in periarctic regions, such as degradation of permafrost. Geochemists also embrace the approach.

Workup of sample is easy, omitting digestion. Chitin surface is simply dissolved by controlled application of a dimethyl formamide solution containing Li⁺, then transferring the chitin-fixed analytes to an acidic ion exchanger (which operates in DMF quite as it does in aq. medium) followed by back-exchange from IX resin to 1% nitric acid (getting all analytes possibly still retained to chitin) and direct injection of elute liquid to ICP-MS or ICP-OES. Electrochemical measurements on the chitin solutions indicate inter-ion interactions among those metal ions/complexes coordinated to chitin strands which may be pertinent in both analysis and catalysis. Preliminary results from different ecosystems including our cooperation with Mongolian environmental scientists are also presented in the talk.



Permafrost/meltwater/biomass dynamics observed by placing chitin around meltdown sites.

CONCENTRATIONS OF NATURAL RADIOACTIVE GAMMA ISOTOPES IN PLEUROZIUM SCHREBERI MOSS

Godyń P., Zielińska M.*, Ziembik Z., Dołhańczuk-Śródka A.

Independent Department of Biotechnology and Molecular Biology, University of Opole, kard. Kominka 6, 45-032 Opole, PL *E-mail: marysia.zielinska@gmail.com

The aim of the study was to describe the process of translocation of radioisotopes among the moss parts, its bedding and soil. The study used epigeic moss *Pleurozium schreberi*, a common species in central Europe.

Samples of moss, bedding and soil were collected in forest areas in Karkonosze Mountains. After manual removal of impurities the collected material was dried to constant mass in temperature of 105 °C. The determinations of activity concentrations of gamma radioisotopes were carried out by means of a gamma-spectrometer with a germanium detector HPGe (Canberra) of high resolution.

The obtained results showed that in most of the studied samples the green parts of the moss were characterized by higher concentrations of natural isotopes than the brown ones. However, only the K-40 isotope occurred in a higher concentrations in green parts of moss in all sampling sites. This phenomenon may be related to their assimilation function and their high intensity of metabolism.

In all studied elements the concentrations of the Pb-210 isotope, of which one of the components may be of anthropogenic origin, is the largest near Szklarska Poręba and south east of Kowary (the largest agglomerations in these areas).

MOSS MONITORING OF ATMOSPHERIC DEPOSITION IN CENTRAL RUSSIA: TULA REGION (2015-2016)

Gorelova S.V.¹, Frontasyeva M.V.², Vergel K.N.², Babicheva D.E.³, Ignatova T.Yu.³

¹Tula State University, Natural Sciences Institute 300012 Lenin Av., 92, Tula, Russia salix35@gmail.com

²Joint Institute for Nuclear Research, 141980 Dubna, Moscow Region, Russia, <u>marina@nf.jinr.ru</u>

³L.N. Tolstoy Tula State Pedagogical University, 300026, Lenin Av., 125, Tula, Russia

Using the method of passive moss biomonitoring air pollution of one of the major industrial regions of Central Russia - Tula region - was studied. A total of 47 elements in 116 moss samples of the Tula region were analyzed by instrumental epithermal neutron activation analysis. A high content of a number of elements of anthropogenic origin V, Fe, Zn, As, Sm, Tb, Hf, W, Th, and U in the air compared to other regions of Russia were revealed. Compared with data of passive moss biomonitoring for the Republic of Belarus and the EU, the air of Tula region contains 1.5-7 times more V, Cr, Fe, Zn, As, Cd. A retrospective analysis of the elements content in the mosses of the region revealed a tendency to increased pollution with such elements as: Fe, Ba, Cr, Co, As, Cd, Sr, Cs, Sm, Tb, Yb, Hf, Ta, W, Th and to decreased the concentration of such elements as Cl, Mn, V in the past 10 years (Fig. 1). Results of the factor analysis revealed four groups of factors: Factor 1 – associates with soils, industrial pollution of soil and weathering processes; Factor 2 (V, Fe, Zn, Se, Mo) can be attributed to air technogenic industrial pollution; Factor 3 - is associated with physiological activity of mosses; Factor 4 is associated with the extraction and processing of ores. The reason for high level of anthropogenic air pollution in Tula region is the activity of enterprises of metallurgical, defense, engineering and chemical industries.



Study was supported by RFBR (Grant 15-45-03252 - r_centre_a)

Figure 1. Comparative of elements content in mosses of Tula region from moss surveys (1999-2000 (Ermakova et al., 2004); 2015-2016 (Gorelova et al., 2016)), mg/kg

References:

Ermakova E.V., Frontasyeva M.V., Steines E. The study of the atmospheric deposition of heavy metals and other elements in the Tula region using the method of moss-biomonitors. Environmental chemistry, 2004; 13: 167-180.

Gorelova S.V., D.E. Babicheva, M.V. Frontasyeva, K.N. Vergel, E.V. Volkova. Atmospheric Deposition of Trace Elements in Central Russia: Tula Region Case Study. Comparison of Different Moss Species for Biomonitoring. Environmental Science, 1, 2016, P. 220-229.

ATMOSPHERIC DEPOSITION OF MAJOR AND TRACE ELEMENTS BY MOSS BIOMONITORING TECHNIQUE IN NORTHWEST OF TURKEY

Haciyakupoglu S., Erenturk S.

Istanbul Technical University, Energy Institute, 34469 Maslak-Istanbul, Turkey

Air pollution is a major environmental and public health problem all over the world caused by different anthropogenic and natural emission sources from industries, traffic, fuel combustion, fires and accidents. Atmospheric pollution with metal, trace elements and radionuclides has been increasingly recognized as a serious threat to human health and ecosystem integrity worldwide. Over the past several decades, biomonitoring has been developed as an alternative method to instrumental air pollutant monitoring. Biomonitoring is regarded as a means to assess trace element concentrations and radionuclide contamination in aerosols and deposition.

The overall aim of the study is to assess the ecological impacts of atmospheric deposition for heavy metals based on moss analysis around Northwest of Turkey called as Thrace Region. Thrace region is located in the northwest of Turkey and the west boundary to Bulgaria and Greece. Most of the Thrace lands are used as agricultural land and intensive industrial area.

Moss sampling sites were selected from different part of Thrace region in Turkey. To measure the element content in the mosses, each sample was dried. Then the samples were digested in acid solution. Digested samples were diluted with distilled water to a total volume of 100 mL. Metal concentrations of Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, V and Zn on the moss samples and standard reference materials was determined by ICP–AES. The air contamination from pollutants was assessed based on enrichment factor, geoaccumulation factors, and ecological risk indices. The results were compared with the data from each site of Istanbul.

ATMOSPHERIC NITROGEN DEPOSITION IN MOSS SAMPLES IN NORTHWEST OF TURKEY

Haciyakupoglu S.¹, Genceli E.², Erenturk S.¹

¹Istanbul Technical University, Energy Institute, 34469 Maslak-Istanbul, Turkey ²Istanbul Technical University, Faculty of Civil Engineering, 34469 Maslak-Istanbul, Turkey

The deposition of atmospheric nitrogen has begun to gain importance as a result of improvements in the field of energy and has become a dominant source for some ecosystems. The global anthropogenic nitrogen reservoir is at the same level as the nitrogen source from natural sources and leads to a doubling of the nitrogen pool for terrestrial organisms in less than a hundred years.

Thrace region is located in the northwest of Turkey and the west boundary to Bulgaria and Greece. Most of the Thrace lands are used as agricultural land. The most important subsistence source in two cities (Edirne and Kirklareli) in the region is agriculture and agriculture based industry. In the other province (Tekirdag), which has intensive industrial production, most of the people living in the inner and western part are dealing with agriculture related works again. The intensive industry and large agricultural area and the region have a dual structure.

The overall aim of the study is to assess the atmospheric nitrogen deposition in Northwest of Turkey called as Thrace Region. The moss samples were dried to constant weight at 40°C. Kjeldahl method for nitrogen analysis were used. Nitrogen concentrations of moss samples were determined and compared with the data for literature.

ACTIVE MONITORING OF AIR POLLUTION IN THE HISTORIC AREA OF THE CITY KALININGRAD USING SPHAGNUM MOSSES

Koroleva Y.¹, Zhurilo D.¹, Ananyan A.¹, Sokhar L.¹, Zegalina L.²

¹Immanuel Kant Baltic federal university, The Institute of Environmental Management, Urban Development and Spatial Planning, Russia, Kaliningrad, Zoologocheskaya, 2, <u>yu.koroleff@yandex.ru</u>

²Immanuel Kant Baltic federal university, Institute of Applied Informatics and Mathematical Geophysics, Russia, Kaliningrad, Proletarskaya, 131, <u>lije@mail.ru</u>

Active moss biomonitoring survey of trace element air pollution in the historic area of Kaliningrad was performed. The main aim was to evaluate possibilities of using *Sphagnum capillifolium* moss bags for investigation of trace elements distribution. The moss bags were placed in the parks, gardens and squares of the central part of town from June to August in 2016 and 2017 years (two-month exposition). The wind situation and quantity of atmospheric precipitation was estimated.

The method of X-ray fluorescence analysis was used to determine such elements as iron, manganese, nickel, zinc, calcium, rubidium, strontium, bromine. Different dynamic of concentration of elements in moss samples were fixed in 2016 and 2017 years. Concentration of such elements as strontium and rubidium has to tendencies to decreasing. The different character of changing probable connected with amount of precipitation (rainfall). In 2016 – 240 mm. 42 rainfall days, and in 2017 - 175 mm. 28 rainfall days.



To identify the relationships (linear dependence) between the elements in *S.capillifolium* samples, a correlation matrix was calculated. Positive significant correlation was found between Ni-Sr, Fe; Zn -Ni, Sr, Fe; Sr-Fe, Br, Rb; and negative between Mn-Br, Sr, Rb, Fe. This may be indicative of a common source of contamination. The special distribution of metals concentration is mapped.



The maximal values of metals concentration were fixed in the heavy traffic areas. Amount of precipitation, air temperature and changing of traffic (for example, during road repair) may be the causes of metals distribution.

RELATIONS BETWEEN LAND USE STRUCTURE AND RARE EARTH ELEMENTS CONCENTRATIONS IN PLANTS

Lisiak M.¹, Borowiak K.¹, Budka A.², Kanclerz J.³, Janicka E.³, Adamska A.³, Żyromski A.⁴, Biniak-Pieróg M.⁴, Podawca K.⁵, Mleczek M.⁶, Niedzielski P.⁷

 ¹Department of Ecology and Environmental Protection, Poznan University of Life Sciences, Piatkowska 94C, 60-649 Poznan, Poland, lismar@up.poznan.pl
 ²Department of Mathematical and Statistical Methods, Poznan University of Life Sciences, Wojska Polskiego 28, 60-637 Poznan, Poland
 ³Institute of Land Improvement, Environmental Development and Geodesy, Poznan University of Life Sciences, Piatkowska 94C, 60-649 Poznan, Poland
 ⁴Institute of Environmental Development and Protection, Wroclaw University of Environmental and Life Sciences, Plac Grunwaldzki 24, 50-363 Wroclaw, Poland
 ⁵Department of Engineering and Geodesy, Warsaw University of Life Sciences, Nowoursynowska 166, 02-787 Warsaw, Poland
 ⁶Department of Chemistry, Poznan University of Life Sciences, Wojska Polskiego 38/42, 60-627 Poznan, Poland
 ⁷Analytical Chemistry Laboratory, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznan, Poland

Rare earth elements (REEs), contrary to their name, are quite common in the environment. They mostly co-exist with other minerals, including lanthanides. These elements are necessary for many industry branches; hence besides conventional sources of pollution connected with activity of factories, an increase of REEs in the environment is observed connected with development of modern technologies.

The aim of the study was to evaluate accumulation of rare earth elements (REEs) in dandelion (*Taraxacum officinale*) collected from the different cities in Poland (Poznan, Warsaw and Wroclaw) and analysis of obtain results in regard to land use of cities. For this purpose the samples of leaves, roots and soil were collected in each city from 10 research sites. Research sites were selected nearby typical facilities for big cities like: airport, train station, old town, motorway, high-density housing areas, low-density housing areas, park, lake, big river and rural areas. The analysis of the land use and landscape structure was carried out for each research sites in aa buffer zone of 500 m.

All elements were analysed by inductively coupled plasma optical emission spectrometry followed by microwave-assisted sample digestion by concentrated nitric acid. GIS tools were used for analysis of the land use structure, landscape metrics and graphical data presentation. PCA analysis was applied for visualisation relations between REEs accumulation in plants, land use structure and landscape.

The spatial distribution of REEs accumulation in *Taraxacum officinale* was varied in the cities. Light rare earth elements (LREEs) were related both the land use structure and selected landscape metrics. Heavy rare earth elements (HREEs), on the other hand, were more related the land use structure than with landscape metrics;

TRENDS OF HEAVY METAL ACCUMULATION IN MOSSES IN SLOVAKIA (1990 -2015)

Maňkovská B.^{1*}, Oszlányi J.¹, Izakovičová Z.¹, Frontasyeva M.V.²

¹Institute of Landscape Ecology, SAS, Štefánikova str. 3, 814 99 Bratislava, Slovakia. <u>bmankov@stonline.sk</u> ²Joint Institute for Nuclear Research, 14180 Dubna, Moscow Region, Russian Federation.

marina@nf.jinr.ru

The use of mosses as biomonitor of atmospheric deposition of heavy metals in Slovakia started more than 30 years ago in connection with the problems of the forest dying in Slovakia.1990s, within the framework of UNECE ICP Vegetation programme, systematic studies using moss were carried on in Slovakia (net 16x16 km), and the results were presented in the European Atlas Atmospheric Heavy Metal Deposition in Europe – Estimations Based on Moss Analysis. It is assumed that in the Slovakia (SK) a large gradient of the atmospheric deposition load of elements exists because part of the SK territory belongs to the most polluted areas in central Europe known as the 'Black Triangle II'. In order to recognise the distribution of element deposition in the SK, the moss monitoring technique, also known as biomonitoring, was applied to the whole territory in 1990, 1995, 1996, 1997, 2000, 2005, 2010 and 2015. In general, the concentration of Cu, Cr, Fe, Ni, Pb, S, Zn in mosses decreased between 1990-2015, but higher for Cd, Mn. Factor analysis was applied to determine possible sources of trace element deposition in SK. In comparison with limit values (Central Norway- as relatively the cleanest region) in SK were exceeded levels for Ag, Al, As, Au, Ba, Br, Ca, Ce, Cd, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Gd, Hf, Hg, I, In, K, La, Lu, Mg, Mn, Mo, N, Na, Nd, Ni, Pb, Rb, S, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn, Zr. In SK was assumed a high gradient of the atmospheric deposition load of elements. The marginal hot spots were revealed in Volovské Mts.(Central Spiš), Kremnické and Štiavnické Mts. (nonferrous ores processing and aluminium factories) and areal Snina, Strážske, Stropkov (border Pl, SK and U). Comparing to average Austrian and Czech values, in SK were found 2-3 times higher values on average, but N decreased.

Keywords: Air pollution, biomonitoring, heavy metals
ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS IN KAZAKHSTAN

Nurgaliyeva D. Zh.¹, Nurkassimova M.U¹, Makhambet A.¹, Omarova N.M.¹, Glushenko V.N², Solodukhin V.P.², Frontasyeva M.V.³, Chepurchenko O³.

¹Department of Chemistry, L.N. Gumilev Eurasian National University (ENU), Mirzoyana Ave., 2, Astana, Republic of Kazakhstan, 010008. omarova_nm@enu.kz, diana.nurgalieva.2012@mail.ru, maha.bilan@mail.ru

²The Institute of Nuclear Physics, Ibragimova st, Almaty, 050032, Republic of Kazakhstan, vik@inp.kz, solodukhin@inp.kz

³Department of Neutron Activation Analysis and Applied Research, Division of Nuclear Physics, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, str. Joliot-Curie, 6, 141980 Dubna, Moscow Region, Russian Federation, marina@nf.jinr.ru, yurchenko0907@mail.ru

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

ATMOSPHERIC DEPOSITIONS OF HEAVY METALS AND RADIONUCLIDES IN IRTYSH AREAS OF KAZAKHSTAN

Nurgalieva D.Zh.¹, Nurkassimova M.U.¹, Omarova N.M.¹, Dalelova A.M.¹, Frontasyeva M.V.², Morzhuhina S.V.²

¹Department of Chemistry, L.N. Gumilev Eurasian National University (ENU), <u>Satpaeva str. 2, Astana, Republic of Kazakhstan, 010008</u>.

E-mail: <u>maha.bilan@mail.ru</u>, <u>tashenov_ak@mail.ru</u>, <u>omarova_nm@enu.kz</u> ²Dubna State University, Department of chemistry, new technologies and materials, Universitetskaya str. 19, Dubna, Moscow Region, Russian Federation, 141980. E-mail: <u>msv@uni-dubna.ru</u>

This article aims to analyze the data obtained by researching the atmospheric depositions of heavy metals and radionuclides in Irtysh areas of Kazakhstan using the method of moss-biomonitors. This method was applied for the Northeastern and Eastern parts of the Republic of Kazakhstan to assess the environmental situation in these regions. In Kazakhstan, due to the current socio-economic development, there are disadvantaged regions by state of the environment, which is a unique urbanistic system saturated with varied companies of very different technological orientation. The presence of large number of enterprises and high levels of radiation in Irtysh area of Kazakhstan determine the urgency of these studies.

The thirty moss samples were collected in autumn and summer of 2015-2016 growth periods. A total of 42 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As, Se, Br, Rb, Sr, Zr, Nb, Mo, Ag, Cd, Sb, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Hf, Ta, W, Au, Th and U) were determined by the epithermal neutron activation analysis, also 14 elements (Ba, Ca, K, Mg, Na, Sr, Cr, Mn, Ni, Co, Zn, Cd, Cu, Pb) were determined by the atomic emission spectrometry with inductively coupled plasma. Multivariate statistical analysis of the obtained results was used to assess the pollution sources in the studied area (Pavlodar, Ust'-Kamenogorsk, and Semey regions).

A comparison of concentrations Kazakhstan-Norway showed the increased values for most of heavy metals (Cd, Sm, Ti, V, As, Mo, Mg, Al, Ca, etc) in the studied samples that apparently are due to the state of the industrial sector of Kazakhstan. The main potential sources of air pollution from the industrial sector of Irtysh area are the Aksu ferroalloy plant, aluminium factory, Kazakhstan electrolysis plant, petrochemical plant in Pavlodar region; Ul'binsk metallurgical plant, titanium-magnesium plant in Ust'-Kamenogorsk region; bus factory, engineering plant, silicate plant in Semey region and etc.; also the production of steel and zinc and etc., coal mining, extraction of natural resources.

The average concentrations of elements are given in table to compare two different methods: NAA and AES with ICP, and was found a correlation coefficient, which is 0,7784.

| The average concentrations of elements, actentified by two affectin methods | | | | | | | | | | | | |
|---|-----|-------|-----|-----|------|------|------|-----|------|-------|------|-------|
| Elements | | Ca | Cd | Co | Cr | Κ | Mg | Mn | Na | Ni | Sr | Zn |
| C(average), mcg/kg by NAA | 170 | 8909 | 0,3 | 4,9 | 19,9 | 8762 | 5716 | 247 | 3178 | 9,1 | 86,6 | 146,2 |
| C(average), mcg/kg by AES | 114 | 12720 | 2,0 | 5,4 | 33,7 | 5316 | 2971 | 473 | 1868 | 172,3 | 76,6 | 225,1 |

The average concentrations of elements, determined by two different methods

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

TRENDS OF ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS IN ALBANIA STUDIED BY THE MOSS BIOMONITORING TECHNIQUE

Qarri F.¹, Lazo P.², Allajbeu Sh.², Bekteshi L³., Stafilov T.⁴

¹Department of Chemistry, University of Vlora, Vlora, Albania ²Department of Chemistry, Faculty of Natural Sciences, University of Tirana, Tirana, Albania ³Department of Chemistry, Faculty of Natural Sciences, University of Elbasan, Elbasan, Albania ⁴Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia

In 2010 and 2015 the moss biomonitoring technique was applied to air pollution studies in Albania in the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) and Convention on Long-Range Transboundary Air Pollution (LRTAP). The main purpose of the study is to investigate the trends of heavy metals deposition and to produce information needed for better identification of contamination sources and improving the potential for assessing environmental in Albania. In autumn 2010 and 2015 samples of the terrestrial mosses Hypnum cupressiforme and Pseudoscleropodium purum were collected at different sites evenly distributed over the territory of the country, in accordance with the sampling strategy of the European moss survey programme.

A total of 19 elements including key toxic metals such as Pb, Cd, As, and Cu were determined by inductively coupled plasma-atomic emission spectrometric (ICP-AES) and atomic absorption spectrometry (AAS). Principal component analysis was used to identify and characterize different pollution sources. The variability of moss metal concentrations reflect the local variation in heavy metal deposition. Distributional maps were prepared to point out the regions most affected by pollution and to relate this to known sources of contamination.

While most European countries reported decreasing trends of elemental content in the mosses that are connected with anthropogenic sources, the data obtained for Albania in 2010 show median values of the elements were high for Al, Cr, Ni, Fe, and V and low for Cd, Cu, and Zn. In comparison with neighbouring countries where similar studies have been made (Bulgaria, Croatia, Kosovo, Macedonia, and Romania), the results obtained for Albania generally were of a similar level.

The results of 2010 are compared with similar survey carried out in 2015 in order to evaluate temporal deposition trends. The level of most toxic elements, such as As, Ni, Cr, Cu, Zn and Cd is increased in 2015 compared to 2010 in moss samples of Albania. Contributions to the trace element concentrations in moss from sources other than atmospheric deposition are identified and discussed.

Keywords: Heavy metals pollution, atmospheric deposition, trend, moss biomonitoring technique, trace elements

POLLUTION EFFECTS ON PAINTED POTTERY OF ROMANIAN CULTURAL HERITAGE

Radulescu C.^{1,2}, Bintintan A.³, Gligor M.³, Ion R.M.^{4,5}, Dulama I.D.², Stihi C.^{1,2}, Teodorescu S.², Stirbescu R.M.²

¹Valahia University of Targoviste, Faculty of Sciences and Arts, 130004 Targoviste, Romania. E-mail: <u>radulescucristiana@yahoo.com</u>

 ²Valahia University of Targoviste, Institute of Multidisciplinary Research for Science and Technology, 130004 Targoviste, Romania. E-mail: <u>dulama_id@yahoo.com</u>
³1 Decembrie 1918 University of Alba Iulia, 510009 Alba Iulia, Romania. E-mail: alina.bintintan@yahoo.com

 ⁴Valahia University of Targoviste, Faculty of Materials Engineering and Mechanics, 130004 Targoviste, Romania, 130004 Targoviste, Romania. E-mail: <u>rodica_ion2000@yahoo.co.uk</u>
⁵National Institute of Research and Development for Chemistry and Petrochemistry – ICECHIM, 060021 Bucharest, Romania

The physical and chemical composition of archaeological ceramics is significantly altered by the life cycle of the artefacts, starting with the production process and use to the post-depositional modification and pollution is a reality. As a wide range of interdisciplinary studies have already shown, in the study of ancient ceramic technology, the traditional archaeological approach based on typology, pattern ornamentation, and context analysis can certainly benefit from the cooperation with the material sciences. In the Transylvanian Neolithic, the Lumea Nouă communities are considered the creators of an elegant painted pottery. The eponym site is Alba Iulia-*Lumea Nouă*, discovered by chance in 1942, while carrying out some town planning works. From the chronological point of view, the Neolithic communities who have produced this type of pottery are included in the time frame 5200-4900 BC. The origins of this type of painted pottery are still controversial.

This study aims to investigate a possible link between the painted pottery from the Alba Iulia-Lumea Nouă settlement and the potential clay sources identified in the proximity of the archaeological site considering the anthropic pollution. In order to establish some correlations between clay source and pottery composition, two analytical techniques (attenuated total reflection - Fourier transform infrared spectrometry and scanning electron microscopy coupled with energy dispersive spectrometry) have been used. The recorded data show similarities for both techniques and give preliminary information regarding the clay composition used for pottery manufacturing in middle Neolithic. Cluster analysis using Average Linkage method correlated the clay sources with the analysed painted pottery. Despite the limited numbers of samples, the archaeometric results indicate that there is an obvious link between the analysed Lumea Nouă painted pottery and two of the selected clay sources from Alba Iulia-*Lumea Nouă* archaeological site. Some of the local clay sources could have been considered the suitable raw material used for the Lumea Nouă pottery type production. However, further determinations performed on a larger set of painted ceramic samples are needed in order to confirm this state of the research.

Acknowledgment: This work was supported by a project of the Romanian National Authority for Scientific Research, UEFISCDI, project number PN-III-PCCDI-2017-0476 "New diagnosis and treatment technologies for the preservation and revitalization of archaeological components of the national cultural heritage".

STATE OF ATMOSPHERIC AIR IN DIFFERENT TERRITORIES OF AZERBAIJAN

Salahova S.Z.¹, Topchiyeva Sh.A.¹, Mehrabova M.A², Humbatov F.Y.²

¹Institute of Zoology, Azernaijan National Academy of Sciences, AZ1073, Azerbaijan, Baku, passage1128, block 50 ²Institute of Radiation Problems, Azernaijan National Academy of Sciences, 1143, Azerbaijan, Baku, B.Vahabzade, 9

salahova.samira@gmail.com, shafiga.topchiyeva@mail.ru, m.mehrabova@science.az, hfamil@mail.ru

Any undesirable change in the composition of atmosphere as a result of the intake of various gases, water vapor and solid particles in it adversely affects the vital activity of living organisms, including human health too. An indicator of air pollution by vehicles is considered carbon monoxide (CO) [2]. According to the World Health Organization (WHO) for 2014, annually in the world approximately 3.7 million people die due to air pollution. According to the International Agency for the Study of Cancer of the WHO, air contamination is the main cause of oncological diseases [3].

Based on the above, the purpose of our researches was to identify the concentration of toxic pollutants of atmospheric air in some regions of Azerbaijan. In the paper presents the data of investigations on air pollution in different territories of Azerbaijan in the periods of 2017.

The quantitative data obtained as a result of monitoring studies and the results of analizys, which carried out on gas chromatographs Agilent GC-7890A with the PFPD, TCD and FID detectors are presented in the table 1.

| | O ₂ | CO | CO ₂ | H ₂ S | CH _{4%} | $C_{5}H_{12}$ | SO ₂ | NO | NO ₂ | O ₃ | Cl ₂ |
|----------|----------------|-------|-----------------|------------------|------------------|---------------|-----------------|-------|-----------------|----------------|-----------------|
| | % | % | % | % | | % | mg/l | mg/l | mg/l | mg/l | mg/l |
| Hachmaz | 17,18 | 0,06 | 0,04 | - | - | 5,95 | | | | | |
| Qaradaq | 20,62 | 0,01 | 0,07 | - | - | | | | | | |
| Surahani | 18,42 | 0,05 | 0,08 | - | 0,22 | 0,15 | | | | | |
| Shikhov | 20.9 | <1.23 | 0.08 | < 0.75 | | | < 0.564 | <1.32 | < 0.20 | < 0.04 | < 0.3 |

Table 1. Air condition in the different territories of Azerbaijan for the period 2012-2013.

The results of the analysis allowed to get a conclusion of local contamination of the territories, as the results of pollution of oil producing and industrial enterprises of Azerbaijan. Based on the obtained results, a complex of necessary measures is proposed to increase the level of environmental safety of the population and marine biota in general.

References:

 [1] Avaliani SL Environment. Assessment of health risks (world experience) / SL Avaliani, MM Andrianova, EV Pechennikova, OV Ponomareva; Advisory Center for Risk Assessment.
- M., 1996. - P. 159.

[2] Denisova, E. L. Influence of environmental factors on the health status of the population (by the example of Orekhovo-Zuevo) / E. L. Denisova, A. I. Gorshkov, N. P. Lyakhova // Hygiene and Sanitation. - 2005. - No. 1. - P. 6-10.

[3] https://en.wikipedia.org/wiki/Anvironmental pollution_Earths

ATMOSPHERIC LEAD DEPOSITION DURING 2011-2014: ESTIMATION BASED ON MOSS ANALYSIS

Dinesh K. Saxena D.K.*, Karuna M.S.

Department of Botany, Bareilly College, Bareilly, UP India *<u>dinesh.botany@gmail.com</u>, dinesh.botany@bareillycollege.org

Mosses are good biomonitor of metals or radioactive pollution because of (*i*) specific biology make them capable to receive and accumulate atmospheric metals from surrounding atmosphere without any selectivity (Glime and Saxena 2001, Ekpo, *et al* 2012), (*ii*) moss does not have a cuticle and epidermis so that its leaves can easily let heavy metal ions in, (*iii*) absence of root system, therefore, possibility of intake of minerals from the soil is eliminated, hence analysis of moss material is a reflection of the atmospheric metal deposition of the area, (*iv*) presence of phenolic compounds, help in preservation of tissues, as a result, a slow degeneration is observed (*v*) besides no microbes attacks and insect chew them, consequently plants can be stored very long period and available for analysis. The present study is aimed at to study the atmospheric lead concentrations using active monitoring approach covering Kumaon, Garhwal and Himachal using acrocarpous moss *Barbul constricta*.

SUMMARY OF THE FINDING

1- Acrocarpous moss *Barbul constricta*, was validated for stress tolerance by measuring Fv and Fm values for photosynthetic efficiency. It was inducted for monitoring, could be its presence even in extreme weather and wide in distribution.

2-Dispersion values of metals Pb revealed high metal load in proximity to the urban habitats studied and crossed permission limit, and concentration decreases while moving away from urban sites.3- Seasonal trend (covering summer, winters and in monsoon) exhibited high Pb values during summer and low for monsoon.

4-Values were crossed checked in another pleurocarpous moss *Thuidium cymbifolium, and Hypnum cupressiformae* had nearly similar trend. Only limitation was low distribution of moss

5- Analysis of moss transplants of *Barbul constricta* showed presence of other metals too i.e. Hg, Cr, Ni, Cu, Cd, Mn, Fe and Zn. Results revealed their levels varied from element to element and from location to location. Seasonal differences in atmospheric metal concentration were also seen. Level of Pb was almost highest in all the locations studied



Ambient lead value measured in moss transplants during 2011-2014 from Kumon (A), Garhwal (B), and from Himachal (C). Financial support is acknowledged from CST, Lucknow.

References:

- Ekpo, B.O., Uno, U. A., Adie, A.P., Ibok, U.J., 2012 Comparative Study of Levels of Trace Metals in Moss Species in Some Cities of the Niger Delta Region of Nigeria., *International Journal of Applied Science and Technology* Vol. 2 No. 3; March 2012
- Glime, J. M., and Saxena, D. K., 2001, uses of Bryophytes, Today & Tomorrow Printers and Publishers,

^{*}Department of chemical engineering, MJP Rohilkhand University, Bareilly

GEOSTATISTICALLY MAPPING SPATIAL STRUCTURES OF MEASUREMENT VALUES AND PERCENTILE STATISTICS OF HEAVY METALS AND NITROGEN ACCUMULATION IN MOSSES SAMPLED 1990-2015 THROUGHOUT GERMANY

Schröder W.^{*}, Nickel, S.

Chair of Landscape Ecology, University of Vechta, Germany *Winfried.Schroeder@uni-vechta.de

Mosses are used to spatially complement the collection of atmospheric deposition by technical samplers and to validate deposition modelling results. Since 1990, the European Moss Surveys have been providing data on element concentrations in moss every five years at up to 7300 sampling sites. In the moss specimens, heavy metals (HM, since 1990), nitrogen (N, since 2005) and persistent organic pollutants (since 2010) were determined. Germany participated in all surveys with the exception of that in 2010. In this study, the spatial structures of element concentrations in moss collected between 1990 and 2015 in Germany were comparatively investigated by use of Moran's I statistics and Variogram Analysis and mapped by use of Kriging interpolation. This is the precondition to spatially join the moss survey data with data collected at other locations within different environmental networks. The calculated maps reveal a clear and statistical significant decrease of concentrations of most heavy metals in moss but not for nitrogen. Whereas Germany wide medians of Fe and Pb decreased continuously, those of Al, As, Cd, Cu, Hg, Ni, and V did not change and those of Cr, Sb and Zn increased between 2000 and 2005. Due to decreasing element concentrations and the unchanged application of the element concentration classification for the mapping, the heavy metals maps for the survey 2015 do not any longer depict much spatial variation. Therefore, this analysis was complemented by calculation HM concentrations a) maps on HM- and survey-specific quantiles (ten percentile classes: $0-10, > 10-20, \dots, > 90-90$); **b**) maps on HMspecific and surveys integrating quantiles (ten percentile classes, see a), where the number of percentiles depends from the decrease or increase of HM concentration across time; c) maps on the spatial structure of a Multi Metal Index (MMI) integrating several HM by transforming their measurement values into 10 scores according to the percentile classes (Figs.).





METAL POLLUTION AROUND NORWEGIAN INDUSTRIES STUDIED BY ANALYSIS OF NATURALLY GROWING MOSS SAMPLES

Steinnes E¹, Uggerud H.T.²

¹Department of Chemistry, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway ²Norwegian Institute for Air Research, NO-2027 Kjeller, Norway

On request from the Norwegian Environment Agency, a survey of atmospheric deposition of heavy metals around industrial enterprises in Norway was carried out. The participation was voluntary and 22 industries located at 17 different sites financed their own participation. The survey is based on analysis of samples of naturally growing moss collected around the enterprises during the summer of 2015 and includes 57 different elements, including those in focus in the ICP Vegetation program. The number of sampling sites around each location varied from 5-20, depending on topography and general pollution level. For most of the sites this survey was a follow-up of corresponding surveys carried out in 2000, 2005, and 2010. In most cases the deposition of heavy metals near the industries depended closely on the industrial processes used as well as the local topographic and meteorological conditions.

The results were evaluated relative to corresponding background levels in moss in parts of Norway with low impact of air pollution. Like in previous surveys, the generally most polluted industrial location was Mo i Rana, where several ferroalloy industries are situated, followed by Odda, were the main air pollution sources are zinc and titanium industries. At most locations where results from repeated surveys are available only minor temporal variations in metal deposition levels are evident.

The observed levels are evaluated relative to background levels in moss at the location concerned. If that ratio exceeds 10 for an element at a given site, obvious pollution is indicated, and in cases where the ratio exceeds the background by a factor of 50, substantial pollution is evident. Some examples of substantial pollution at given sites will be demonstrated in the talk. Metals in focus are Ti, Cr, Mn, Ni, Cu, Zn, Cd, Hg, and Bi, which all show obvious pollution at one or more sites.

Reference:

Steinnes, E. and Uggerud, H.T.: "Metal pollution around Norwegian industries studied by analysis of naturally growing moss samples. 2015 survey". NILU report 1/2017. Norwegian Institute for Air Research, Kjeller, Norway, 82 pp.

TEMPORAL TRENDS OF HEAVY METAL CONCENTRATIONS IN MOSSES COLLECTED FROM ROMANIA IN 2010 AND 2015

Stihi C.¹, Ene A.², Frontasyeva M.³, Radulescu C.¹, Culicov O.^{3,4}, Zinicovscaia I.^{3,5}

¹Valahia University of Targoviste, Targoviste, Romania, e-mail: <u>claudia.stihi@valahia.ro</u>
²Dunarea de Jos University of Galati, Galati, Romania, e-mail: <u>aene@ugal.ro</u>
³Joint Institute for Nuclear Research, Dubna, Russian Federation, e-mail: <u>marina@nf.jinr.ru</u>
⁴National Institute for R&D in Electrical Engineering ICPE-CA, Bucharest, Romania
⁵Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, Romania

The aim of this work was to establish the temporal trends of heavy metal concentrations in moss monitored in a spatial network in Romania, in 2010 and 2015 moss surveys. In both surveys, a total of 29 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) were determined in the large-scale concentration range — from 10000 mg/kg for Al, Fe, Ca and K to 0.001 mg/kg for some rare earths — by two complementary methods: INAA at the IBR-2 reactor in Joint Institute for Nuclear Research at Dubna, Russian Federation, and GFAAS /FAAS* in 2010 and ICP-MS* in 2015 in Institute of Multidisciplinary Research for Science and Technology, Valahia University of Targoviste, Romania. Table 1 depicts descriptive statistical results for some heavy metals (V, Cr, Fe, Ni, Cu, Zn, Cd, and Pb) in moss sampled in 2010 [1-3] and 2015.

| | | Number | | | | | Cton Joud |
|---------|------|---------|---------|---------|---------|----------|-----------|
| Element | Year | of | Mean | Median | Minimum | Maximum | Standard |
| | | samples | | | | | deviation |
| V | 2015 | 214 | 8.87 | 4.32 | 0.72 | 65.10 | 11.79 |
| v | 2010 | 330 | 7.34 | 4.89 | 0.38 | 49.20 | 2.81 |
| Ca | 2015 | 214 | 9.75 | 4.71 | 0.92 | 55.40 | 11.57 |
| Cr | 2010 | 330 | 8.19 | 4.98 | 0.68 | 62.20 | 3.00 |
| E | 2015 | 214 | 3360.32 | 1535.00 | 150.00 | 23900.00 | 4281.16 |
| Fe | 2010 | 330 | 2957.00 | 1670.00 | 237.00 | 29500.00 | 58.36 |
| NI: | 2015 | 214 | 5.16 | 3.10 | 0.67 | 27.80 | 5.25 |
| 1N1 | 2010 | 330 | 4.53 | 3.60 | 0.39 | 35.90 | 2.08 |
| Zn | 2015 | 214 | 7.66 | 40.05 | 10.8 | 393.00 | 33.52 |
| | 2010 | 330 | 56.04 | 42.30 | 0.59 | 1440.00 | 9.35 |
| CI | 2015 | 214 | 0.48 | 0.26 | 0.02 | 3.10 | 0.51 |
| Ca | 2010 | 330 | 2.00 | 1.20 | 0.12 | 101.00 | 2.42 |
| Cu | 2015 | 214 | 11.93 | 5.77 | 0.81 | 122.14 | 13.33 |
| | 2010 | 330 | 38.52 | 17.80 | 0.23 | 627.38 | 8.54 |
| DI | 2015 | 214 | 5.51 | 4.19 | 0.33 | 63.67 | 5.85 |
| PD | 2010 | 330 | 30.63 | 30.80 | 2.20 | 119.93 | 3.82 |

Table 1. Descriptive statistical results for some heavy metals concentrations in moss (mg/kg)

The concentrations of heavy metals in mosses collected in Romania are higher compared to the other (Eastern-) European countries. The temporal trends for median concentration of selected metals revealed a decrease in 2015 for all elements; in the case of mean concentration, there was a decrease in 2015 for Zn, Cd, Cu, and Pb and a slight increase for V, Cr, Fe, and Ni. The obtained results evidence that is a considerable problem in the northern and north-western parts of Romania, named by us historical pollution.

References:

Harmens, H., Norris, D., Mills, G., and the participants of the moss survey (2013), Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe. ICP Vegetation Programme Coordination Centre, CEH, Bangor, UK
Harmens, H., Norris, D., Sharps, K., Mills, G., Frontasyeva, M., Ene, A., Stihi, C., et al. (2015), Heavy metal and nitrogen concentrations in mosses are declining across Europe whilst some "hotspots" remain in 2010, *Environmental Pollution* 200: 93–104
Stihi C., Popescu I.V., Frontasyeva M., Radulescu C., Ene A., Culicov O., Zinicovscaia I., et al. (2017), Heavy Metal Air Pollution Study in Romania Using Moss Biomonitoring, Neutron Activation Analysis and Atomic Absorption Spectrometry, *Analytical Letters* 50(17): 2851–2858

LEAD CONCENTRATION AND STABLE ISOTOPES IN MOSS IN SLOVENIA AND SWITZERLAND

Thöni L.¹, Strok M.², Mazej D.², Schnyder E.¹, Kosonen Z.¹, Jeran Z.², Skudnik, M.³

¹FUB – Research Group for Environmental Monitoring, CH-8640 Rapperswil, Switzerland
²Jožef Stefan Institute Jamova 39, 1000 Ljubljana, Slovenia
³Slovenian Forestry Institute, Večna pot 2, 1000 Ljubljana, Slovenia

Using moss as a biomonitor is an established technique for monitoring atmospheric deposition of trace elements, including lead (Pb). ²⁰⁴Pb is the only primordial stable isotope of Pb, the others are formed due to the radioactive decay of long-lived isotopes of U and Th into stable isotopes: ²³⁸U to ²⁰⁶Pb, ²³⁵U to ²⁰⁷Pb and ²³²Th to ²⁰⁸Pb. The isotopic composition of lead is not affected by anthropogenic activity (e.g. smelting or refining) and therefore the isotopic ratio in Pb can be used to determine sources and pathways of atmospheric Pb pollution.

Results: In Switzerland, the Pb concentration in moss was highest in 1990 and then decreased significantly over time until 2015. In Slovenia, starting 1995 with the moss survey, the decrease in Pb occurred later. This shows that the decrease in Pb emissions started later in Slovenia. In Switzerland no difference between regions (Northern, Central and Southern Switzerland) was found for ²⁰⁶Pb/²⁰⁷Pb isotope ratios (Fig. 1). Differences for ²⁰⁸Pb/²⁰⁶Pb isotope ratios were significant between Northern and Southern Switzerland and between Central and Southern Switzerland but not between Northern and Central Switzerland. In Slovenia, there were no significant differences for ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb isotope ratios between the different regions except for Ljubljana urban forest.

The ²⁰⁶Pb/²⁰⁷Pb isotope ratios increased significantly in Switzerland over time, but the changes were region dependent (Fig. 2). Northern Switzerland showed a strong increase from 1.138 in 1990 to 1.158 in 2015. In the Central Alps, the increase was significant too, but less strong (from 1.148 to 1.159). In the Southern Alps there was no significant change. In general, the ²⁰⁶Pb/²⁰⁷Pb isotope ratios became more similar between regions over time.



Fig. 1: Isotope ratios of all samples in 2015, distribution of isotope ratios within the different regions and countries.



Fig. 2: Changes in ²⁰⁶Pb/²⁰⁷Pb isotope ratios in different regions of Switzerland from 1990 to 2015.

Conclusion: Based on patterns of the Pb isotope ratios in Switzerland and Slovenia in 2015, it seems that the emission sources vary between the different geographical regions and countries. Changes over time can be seen in isotope patterns of Switzerland and thus it can be concluded that since 1990 the emission sources have changed and become more similar between regions. We assume that traffic was the largest contributor for Pb pollution in earlier periods and that the lead deposition is now more influenced by the ratios in bedrock as well as industry and coal and hardly by leaded gasoline.

BIOMONITORING OF HEAVY METALS AND TRACE ELEMENTS IN NORTH RUSSIA: TIKHVIN CASE STUDY 2017

Vergel K.N.¹, Frontasyeva.M.V.¹, Zinicovscaia I.I.^{1,2}, Vikhrova I.M.³, Strelkova L.P.¹

 ¹Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, str. Joliot-Curie, 6, 141980 Dubna, Moscow Oblast', Russian Federation
²Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, 30 Reactorului Str. MG-6, Bucharest - Magurele, Romania.
³School No. 8, 187556, Tikhvin, Leningradskaya Oblast', Russian Federation,

The results of moss analysis by neutron activation analysis and atomic absorption spectrometry – from the 2015/2016 moss survey in Leningradskaya region, undertaken in the framework of the UNECE ICP Vegetation programme are reported. A total of 37 samples of the terrestrial mosses *Pleurozium schreberi* were collected in summer of 2017 around the Tikhvin. The concentrations of 35 elements (Na, Mg, Al, Cl, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Zn, Mo, As, Se, Br, Rb, Sr, Zr, Sb, I, Cs, Ba, La, Ce, Sm, Tb, Hf, Ta, W, Au, Th, and U) were determined in the moss samples by instrumental neutron activation analysis (INAA)and Cd, Pb, Cu by means of atomic absorption spectrometry. Descriptive statistics and distribution maps were prepared. Results obtained for Tikhv in were compared with the data from previous moss survey as well as with data obtained for other Russian regions and European countries.Multivariate statistical analysis helped to reveal the main pollution sources. As in 2010, the main air pollution source in the studied region was ferroalloy plant in the town Tikhvin. The highest content of Al, As, Co, Fe, Cr, Ni and V in moss sampleswas observed in the close vicinity of Tikhvin.

ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN THE MOSS *HYPNUM CUPRESSIFORME* AND TOPSOIL SAMPLED IN SERBIA

Vuković G.¹, Aničić Urošević M.¹, Herceg Romanić S.², Starčević Mendaš G.², Ilić M.³, Milićević T.¹, Frontasyeva M.V.⁴

¹Institute of Physics Belgrade, University of Belgrade, 11080 Belgrade, Serbia, <u>gordana.vukovic@ipb.ac.rs; mira.anicic@ipb.ac.rs; tijana.milicevic@ipb.ac.rs</u> ²Institute for Medical Research and Occupational Health, 10001 Zagreb, Croatia; <u>sherceg@imi.hr; gmendas@imi.hr</u>

³Faculty of Sciences, University of Novi Sad, 21000 Novi Sad, Serbia, <u>marina@nf.jinr.rumilos.ilic@dbe.uns.ac.rs</u>

⁴Joint Institute for Nuclear Research, 141980 Dubna, Russian Federation, <u>marina@nf.jinr.ru</u>

Persistent organic pollutants (POPs), such as intentionally produced polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) currently or once used in agriculture, industry or disease control are highly resistant to degradation. Once POPs have entered the air, they undergo atmospheric transport and subsequently condense onto surfaces such as soil and vegetation in particle-bound form, or deposit via precipitations (rain, snow, and mist). Raised to the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation 2015), this study strived to extend the pilot investigations of POPs in mosses conducted in 2010 in selected countries [1]. The moss Hypnum cupressiforme and surrounding topsoil were collected at 22 sampling sites across Serbia during June and July 2017. Briefly, 5 g of topsoil and 1 g of moss samples were extracted using a mixture of nhexane:acetone (1:1) and assisted by microwave. The fractionation was done using commercial tubes pre-packed with Florisil while the purification was performed with sulphuric acid. Highresolution gas chromatography with electron capture detector(s) was performed on a CLARUS 500 chromatograph using two capillary columns (Restek, Bellefonte, PA, USA) simultaneously: (1) 60 m \times 0.25 mm, Rtx-5 film thickness of 0.25 μ m (column A), and (2) 30 $m \times 0.32$ mm, Rtx-CL Pesticides film thickness of 0.32 µm (column B). We analyzed 17 PCBs: six indicator congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180), eight mono-ortho congeners (PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167, PCB-189), PCB-60, PCB-74 and PCB170; and seven OCPs: hexachlorobenzene (HCB), new POPs (α -, β -, γ -hexachlorocyclohexanes, α -HCH, β -HCH, γ -HCH), 1,1-dichloro-2,2-di(4chlorophenyl)ethylene (p,p´-DDE), 1,1-dichloro-2,2-di(4-chlorophenyl)ethane (p,p´-DDD), and 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (p,p'-DDT). The performance of the analytical procedure was validated through the analysis of referent materials while the method recovery and reproducibility were determined by adding a known quantity of all of the analysed compounds to the aliquots of homogenised moss and soil samples before extraction (method of addition, n = 5). The limits of determination (LOD) were calculated as the average of all determinations based on signal-to-noise ratio and the compounds recovery. The average recoveries for POPs were 72–105% and 73–116% while the LOD for the analyzed compounds were within the range between 0.006 and 0.032 μ g kg⁻¹ and 0.016 and 0.302 μ g kg⁻¹ for OCPs organochlorine compounds and PCB congeners, respectively. The evaluation of the results is in progress.

Reference:

^[1] Frontasyeva M.V., Steinnes E., Harmens H., 2017. Monitoring long-term and large-scale deposition of air pollutants based on moss analysis, in: Aničić Urošević, M., Vuković G., Tomašević, M. (Eds.), Biomonitoring of Air Pollution Using Mosses and Lichens, A Passive and Active Approach, State of the Art Research and Perspectives. Nova Science Publishers, New York, NY.

ATMOSPHERIC NITROGEN INDUCED HEAVY METAL LEACHING

Zia A.¹, Ashmore M.², Nauman Ahmad M.¹

^{1*}Agricultural Chemistry Department, University of Agriculture, Peshawar Pakistan ²Stockholm Environmental Institute, University of York, UK *Corresponding Author Address: <u>afia.zia@aup.edu.pk</u>

Atmospheric nitrogen deposition is linked to increased DOC production, it may be expected that increased nitrogen deposition results in increased heavy metal transport to deeper ground water layers. Especially soils with relative high amounts of heavy metals or soils which are slightly acidified, depleted of base cations and consequently in the aluminium buffer range may be expected to experience elevated levels of heavy metals in solution. A large mesocosm experiment has been specifically designed to test if the differential effects of different dominant nitrogen forms in atmospheric deposition to nutrient poor species rich wet heathlands can be wholly explained by soil acidity and buffering capacity. In a full factorial design, the effects of nitrogen load, nitrogen form and ANC on the floristic and biogeochemical changes has been tested to compare effects of reduced and oxidized Nitrogen deposition specifically same nitrogen deposition with Ammonium and Nitrate ratios from 1:9 and 9:1. Yearly changes in vascular plant and bryophytes cover and composition are recorded and pore water is analyzed monthly. Pore water samples has been analysed for base cations, DOC and ammonium and nitrate. The first results show no relationship between total N load and DOC concentration .However the DOC concentration was significantly higher where nitrate was the dominant nitrogen form in deposition. Application of base cations in the form of lime (Ca and Mg) resulted in an increase of DOC leaching in those treatments where the ammonium was dominant. In contrast ammonium dominance results in acidification of the soil which reduces decomposition and mineralization resulting in low DOC concentrations.

The mesocosms were taken from the Isle of Skye, Scotland in an area with underlying serpentine rock. Serpentine rock is known for its elevated heavy metal concentrations such as copper, nickel, chromium and zinc this provides us with a unique experimental set up to test the hypothesis that nitrogen deposition results in increased DOC leaching and subsequent heavy metal transport. We hypothesized that whether decreasing pH and increasing DOC are associated with higher metal concentrations in soil solutions and to assess whether pH and DOC are associated with the effect of ammonium and nitrate on the partitioning of metals between soil and pore water. Metal mobilisation of Cu and Pb is driven by DOC concentrations and are therefore expected to be high in cores were nitrate in deposition is dominant. .Low pH and high ammonium to be related to Cd and Zn mobility. The metals results are under analysis and the results can be presented in 15 days' time (1st Oct 2011). Since the experiment follows a full factorial design with n=6, GLM statistics are used to analyze the results. The results will provide us with three important fractions: the plant available fraction is quantified by the pore water samples. The potentially available fraction is determined by the exchangeable fration and the total amount present in the soil (and lost due to treatment) will be quantified by the acid digest fraction.

Keywords: Atmospheric Nitrogen, Heavy metals, DOC, Mesocosms