



Centre for  
Ecology & Hydrology

NATURAL ENVIRONMENT RESEARCH COUNCIL



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

28 – 30 January, 2013  
Halmstad, Sweden

*Hotel Tylösand, Tylöhusvägen, Halmstad*

# Programme & Abstracts

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

## Organizers:



### ***ICP Vegetation Programme Coordination Centre***

Centre for Ecology and Hydrology  
Bangor, UK

*Harry Harmens*

*Gina Mills*

*Felicity Hayes*

### *Local organizers*

*Gunilla Pihl-Karlsson, Helena Danielsson, Per Erik Karlsson*

IVL Swedish Environmental Research Institute, Gothenburg, Sweden

*Håkan Pleijel*, Department of Biological and Environmental Sciences,  
University of Gothenburg, Sweden



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GOTHENBURG

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Swedish Environmental  
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SWEDISH ENVIRONMENTAL  
PROTECTION AGENCY

## **Programme 26<sup>th</sup> Task Force Meeting of the ICP Vegetation**

### **Monday 28<sup>th</sup> January, 2013**

**15:00 Ozone workshop expert group on ‘Ongoing ozone flux model development, and AOT40 and flux map validation’**

**18:00 Registration**

**19:00 Welcome buffet**

### **Tuesday 29<sup>th</sup> January, 2013**

**08:00 Registration for late arrivals**

**Session 1: 08:30 – 10:30 (Plenary session) Chair: Gunilla-Pihl Karlsson**

8:30 Welcome: Titus Kyrklund (Swedish Environmental Protection Agency) and John Munthe (Vice president research IVL)

9:00 Harry Harmens et al. – Overview of the achievements of the ICP Vegetation in 2012.

9:20 David Simpson – The EMEP MSC-W model: Recent developments, what to do next?

9:40 Lars Lundin – Report on the ICP Integrated Monitoring activities 2012.

10:00 Ludwig De Temmerman et al. – What about nanomaterials? Future considerations about the deposition of nanoparticles from long range transport.

10:20 General discussion

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

**Session 2: 11:00 – 12:30 Plenary session Chair: Patrick Büker**

11:00 Gina Mills et al. – Impacts of ozone on ecosystem services and biodiversity.

11:20 Jürgen Bender et al. – Introduction of a study to assess the impacts of ozone on biodiversity in terrestrial ecosystems: Database review and analysis of methods and uncertainties in current risk assessment approaches.

11:40 Harry Harmens et al. – Results of the European moss survey 2010/11.

12:00 Eiliv Steinnes et al. - Is terrestrial moss a useful substrate for assessment of the atmospheric deposition of POPs? Implications from the 2010 moss survey in Norway.

12:20 General discussion

**12:30 – 13:40 Lunch**

**Session 3: 13: 40 – 15:00 Plenary session** **Chair: Håkan Pleijel**

- 13:40 Peringe Grennfelt – Update of the recent work under the LRTAP Convention.
- 14:00 Harry Harmens et al. – Medium-term workplan ICP Vegetation: how does it fit in with implementation of the long-term strategy of LRTAP Convention?
- 14:10 Patrick Büker et al. – Collaboration with the Task Force on Hemispheric Transport of Air Pollution.
- 14:25 Antonio Ballerin-Denti – CLRTAP and Alpine Convention: a chance for cooperation on the effects of air pollution on alpine vegetation.
- 14:40 Per Erik Karlsson et al. – S-POD - a simplified ozone index to be used to assess the risk for negative ozone impacts on vegetation at the national level.

**15:00 – 16:00 Coffee/tea and poster session with authors present at posters**

**Session 4: 16:00 – 18:00 (Two parallel sessions: Ozone & Heavy Metals/N/POPs)**

**Session 4a: Ozone: Chair: Felicity Hayes**

- 16:00 Silvano Fares et al. – The effect of ambient ozone on carbon assimilation in trees: estimates using continuous flux measurement.
- 16:20 Zhaozhong Feng – Leaf mass per area elucidates ozone sensitivity of woody species.
- 16:40 Alessandra De Marco et al. – The phytotoxic ozone dose performs well in Mediterranean forests.
- 17:00 Sabine Braun et al. – Reporting back from the working group discussion on further flux based developments and mapping validation.
- 17:15 Patrick Büker et al. – Re-analysis of forest ozone flux-response relationships and some considerations for their application.
- 17:25 Discussion (led by Gina Mills).

**Session 4b: Heavy Metals/N/POPs Chair: Sebastien Leblond**

- 16:00 Jesus Santamaria – Preliminary results of <sup>15</sup>N analyses in mosses.
- 16:20 Mitja Skudnik et al. – Influence of sampling location on nitrogen and trace elements content in mosses.
- 16:40 Lotti Thöni et al. – Relationship between site-specific nitrogen/sulphur concentrations in mosses and atmospheric nitrogen/sulphur deposition rates in selected European countries: preliminary results.
- 17:00 Discussion on the 2010/11 survey report and maps, and the future of the European moss survey (led by Harry Harmens).

**18:30 – 20:00 Dinner at the hotel:**

- 20:00 – 21:00** Discussion on 1) methodology for calculating ozone effects on C sequestration in Europe; 2) further stimulation of participation of EECCA/SEE countries and countries in regions outside the UNECE.

## Wednesday 30<sup>th</sup> January, 2013

**Session 5: 8:30 – 10:15 (Two parallel sessions: Ozone & Heavy Metals/N/POPs)**

**Session 5a: Ozone: Chair: Silvano Fares**

- 8:30 Seraina Bassin et al. – Effect of elevated combined ozone and nitrogen deposition on the species composition of a sub-alpine grassland.
- 8:50 Ignacio González-Fernández et al. – Progress in modelling annual pasture ozone flux.
- 9:10 Jean-Francois Castell et al. – Bio-Economic Assessment of ozone impacts on French farming systems.
- 9:30 Sheikh Saeed Ahmad – Assessing spatial and temporal variability of tropospheric ozone concentration in areas of different scales.
- 9:50 Feedback from Tuesday evening ozone discussion, followed by a general discussion.

**Session 5b: Heavy Metals/N/POPs Chair: Eiliv Steinnes**

- 8:30 Zdravko Spiric et al. – Croatian moss survey 2010 – preliminary results.
- 8:50 Pranvera Lazo et al. – Multi-element atmospheric deposition study in Albania.
- 9:10 Flora Qarri et al. – Middle-term biomonitoring of Vlora-Fier area, Albania.
- 9:30 Sebastien Leblond et al. – Quantifying uncertainty of element concentrations in mosses.
- 9:50 Helena Danielsson et al. – Heavy metals in mosses – what are the advantages of an increased sampling density at the county level?
- 10:10 General discussion.

**10:15 – 10:45 Coffee/tea and poster viewing**

**Session 6: 10:45 – 12:30 (Two parallel sessions: Ozone & Heavy Metals/N/POPs)**

**Session 6a: Ozone: Chair: Jean-Francois Castell**

- 10:45 Kent Burkey et al. – Soybeans from Fiskeby, Sweden - a potential source of tolerance genes for ozone and a broad range of abiotic stresses
- 11:05 Yoshiaki Ueda et al. – Genetic approaches to increase tolerance to ozone in rice.
- 11:25 Anne Repellin et al. – Controlled field ozone fumigation of maize plants: Impact on leaves and grain yield.
- 11:45 Deborah Moura Rebouças et al. – Effects of combined ozone and water stresses on physiology and membrane lipids of two tropical cowpea cultivars.
- 12:05 General discussion.

**Session 6b: Heavy Metals/N/POPs** **Chair: Zdravko Spiric**

- 10:45 Winfried Schröder et al. – Landscape-specific correlation between atmospheric depositions and their concentrations in mosses across Europe?
- 11:05 Erika Hiltbrunner et al. – Enlarged nitrogen availability due to increased atmospheric nitrogen deposition and expansion of N<sub>2</sub> fixing plants: effects on alpine and montane ecosystems.
- 11:25 Stefanie Boltersdorf et al. – Germany-wide comparison of spatial distribution of nitrogen concentrations and stable isotope signatures of bryophytes and lichens.
- 11:45 Hilde Uggerud et al. – PAH in moss from Norway: Spatial distribution and comparison with metal concentrations.
- 12:05 Ludwig De Temmerman – Accumulation of airborne As, Cd and Pb in *Phaseolus* bean.
- 12:25 Discussion.

**12:30 – 13:40 Lunch**

**Session 7: 13:40 – 15:00 (Plenary session) Chair: Ludwig de Temmerman**

- 13:40 Gina Mills et al. – Progress with the European Framework 7 project ECLAIRE.
- 14:00 Gerosa et al. - Photosynthetical response to ozone exposure and nitrogen enrichment of *C. betulus* and *Q. robur* saplings. Results of the first year of experimentation under the ECLAIRE project.
- 14:20 Håkan Pleijel et al. – Ozone risk assessment for the 21<sup>st</sup> century based on ozone and climate change scenarios
- 14:40 Eero Kubin et al. - Nitrogen deposition and leaching in the boreal forest environment.

**Coffee/tea and poster viewing: 15:00 – 15:30**

**Session 8: 15:30 – 17:00 (Plenary session) Chair: Harry Harmens**

- Decisions 26<sup>th</sup> ICP Vegetation Task Force meeting.
- ICP Vegetation work programme for 2013 – 2016.
- Collaboration with other relevant bodies/organizations.
- Any other business.
- Closure of the 26<sup>th</sup> Task Force Meeting.

**17:15 - 18:30. Art exhibition at Hotel Tylösand**

**19:30 Conference dinner**

**Thursday 31<sup>st</sup> January, 2013**

08:30 – 11:00 EU ECLAIRE project meeting – update of C3 data mining and experimental plans for 2013 season.

Participants are to make their own travel arrangements to the airport.

## List of posters

| Pollutant   | Author(s)  | Title   |
|---|--|---|
| Ozone   | Schröder, M., Grünhage, L., Matyssek, R., et al.   | Flux-based ozone risk assessment for adult beech and spruce forests   |
|   | Pierre Sicard, Alessandra De Marco, Camille Renou, Elena Paoletti                          | South European Mediterranean basin: Decreasing in ozone mean concentrations at remote sites and increase in the cities  |
|   | Kent O. Burkey, Amy Burton   | A comparison of the ozone response of two pairs of sensitive and tolerant snap beans  |
|   | Danielsson, H., Karlsson, P.E., Pleijel, H.  | An ozone response relationship for four <i>Phleum pratense</i> genotypes based on modelling of the phytotoxic ozone dose (POD)  |
|   | Melece I., Indriksone I., Frolova M.   | Ground level ozone bioindication on <i>snap bean</i> in Latvia  |
|   | Bermejo, R.; Elustondo, D.; Izquieta, S.; Lasheras, E. and Santamaría, J.M.                | Ozone flux assessment in a Spanish beech stand  |
|   | Gerosa. Finco, Marzuoli, Negri   | Ozone fluxes to a larch forest ecosystem in Italy - results from the MANFRED Project  |
|   | Fumagalli, I., Cieslik, S., Gottardini, E., Cristofolini F., Cristofori, A., De Marco, A., | Ozone effect on grapevine: an open top chamber study  |
| Metals  | Maňkiovská, Oszlányi, Tučeková, Frontasyeva, Andráš, Dubieľ                                | Bryomonitoring in Slovakia, past, present and future  |
|   | Pranvera Lazo, Lirim Bekteshi, Alma Shehu, Flora Qarri                                     | The study of atmospheric deposition of heavy metals in Elbasani urban area, Albania, by active moss biomonitoring technique   |
|   | Flora Qarri, Pranvera Lazo, Denada Kasemi  | Air survey in Vlora area by using honey as bio-indicator  |
|   | Gunilla Pihl Karlsson & Helena Danielsson  | Metal content in mosses continues to decline in Sweden  |
|   | Poikolainen, Jarmo; Piispanen, Juha; Kubin, Eero   | The mining industry grows rapidly in Finland - monitoring of heavy metal deposition?  |
|   | Ludwig De Temmerman, Ann Ruttens, Nadia Waegeneers.  | Transfer of atmospheric arsenic, cadmium and lead to the edible parts of various vegetables   |
|   | Natalia Goltsova   | Moss monitoring as chapter of biomonitoring of air pollution  |
|   | Natalia Goltsova   | The bioindication of radiocontamination at 0-10km-zone after Chernobyl NPP accident . Some results of 1989-1992 years works   |
|   | Pranvera Lazo and Albert Mazhuni   | Preliminary study in atmospheric metal deposition in Kosovo from analysis of moss samples (2010-2011)   |
|   | Dinesh Saxena  | Elemental survey of metals from 2000 to 2010 by using the moss <i>Hypnum cupressiforme</i> L. Ex Hedw. from eastern and north-western part of India                                     |
| Barandovski L., Stafilov T., Šajn R., Frontasyeva M.V., Bačeva K. | Air pollution study in Macedonia by using moss biomonitoring technique, ICP-AES and AAS    |   |
| Nitrogen  | Špirić, Z., Glad M., Kušan V.  | Preliminary results on nitrogen in Croatia moss survey 2010   |
|   | Lina Fusaro, Elisabetta Salvatori, Simone Mereu, Ilaria Bei, Fausto Manes                  | Can nitrogen deposition influence the performance of tree species in Mediterranean forests? Results from a controlled experiment on <i>Quercus ilex</i> L. and <i>Fraxinus ornus</i> L. |
|   | Fumagalli I., Fachinetti D., Gruening C.   | Measurements of soil NO & NO <sub>2</sub> fluxes in subalpine forests: preliminary results  |



**Abstracts**

**Oral**

**Presentations**

# ASSESSING SPATIAL AND TEMPORAL VARIABILITY OF TROPOSPHERIC OZONE CONCENTRATION IN AREAS OF DIFFERENT SCALES

Ahmad S.S.

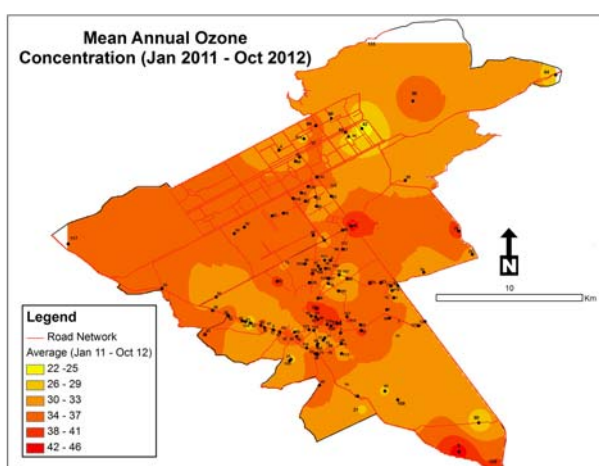
*Fatima Jinnah Women University, the Mall, Rawalpindi, Pakistan, drsaeed@ffwu.edu.pk*

This research article highlights the air pollution scenario of twin cities of Pakistan. The analyses presented in this paper include the concentration levels of ozone measured during two successive years in twin cities (Rawalpindi and Islamabad) of Pakistan from Jan 2011 to Oct 2012. Ozone was determined by continuous ozone analyzer (Model 400E). The average ozone concentration in twin cities of Pakistan was found to be  $37\pm 6$ . Table 1 showed ozone concentration for each category to understand the general trends of ozone concentration levels in among different categories during the course of experimental period.

**Table 1: Average O<sub>3</sub> conc. levels in Twin cities from January 2011 to October 2012**

| Sampling Categories      | No. of Sites | Average Ozone Conc. (ppb) |
|--------------------------|--------------|---------------------------|
| Semi-Rural Area          | 7            | 46.56                     |
| Dual Carriage Ways       | 8            | 42.21                     |
| Bus Stops                | 11           | 35.01                     |
| Major Roads              | 13           | 38.59                     |
| Educational Institutions | 39           | 38.56                     |
| Sub Roads                | 10           | 35.59                     |
| Small Roads              | 6            | 28.56                     |
| Hospitals                | 17           | 34.01                     |

The distribution of the ozone concentration measured in the campaign can be seen in figure 1.



**Figure 1. Spatial Distribution of O<sub>3</sub> concentration in Rawalpindi and Islamabad**

Ozone concentration levels were high in areas of intense traffic flow and congestion. Rawalpindi has more elevated levels of ozone as compared to the Islamabad due to the narrow roads, enclosing architecture of road network and congestion. Climatic variables also influenced the Ozone concentration, Moreover, ozone concentration levels in all sampling points are less than allowed limits of World Health Organization.

## CLRTAP AND ALPINE CONVENTION: A CHANCE FOR COOPERATION ON THE EFFECTS OF AIR POLLUTION ON ALPINE VEGETATION

Ballarin-Denti A (\*), Angelini P (\*\*), Cetara L. (\*\*\*)

(\*) *Catholic University, Brescia, WGE-CLRTAP, AC delegation*

(\*\*) *MATTM - Italian Ministry of the Environment and Land and Sea protection*

(\*\*\*) *EURAC – European Academy, Bolzano (I)*

The *Alpine Convention* is an international treaty binding eight Alpine countries (Austria, France, Germany, Italy, Liechtenstein, Monaco, Slovenia and Switzerland) and the EU itself to protect the environment and to promote a sustainable development in the whole Alpine area. The Convention has been extended by eight protocols aimed at specific agreements in key sectors as Spatial planning and sustainable development, Conservation of nature and countryside, Mountain farming, Mountain forests, Tourism, Energy, Soil conservation and Transport. Climate change and air pollution are two strategic issues which intersect many of these protocols and are especially relevant in the sectors of alpine agriculture, plant biodiversity and forests.

The convention is organized into working groups and platforms which constitute the technical bodies of the convention; they are formed by experts and scientists similarly to the subsidiary bodies of the LRTAP Convention. Moreover, the Alpine Convention interacts with the European Commission's cooperation programme *Alpine Space* which supports, *inter alia*, applied research projects and knowledge advancement on an even larger territorial area (more than 70 million people).

Common thematic areas between the CLRTAP and the Alpine convention are atmospheric depositions and its impact on soil fertility, impact of air pollution on mountain agricultural crops, forests and semi-natural vegetation, climate change and air quality effects on biodiversity, the role of reactive nitrogen in air, water and soil quality and in the animal and human nutrition, ozone and other stressors' effect on plants in relation to their capability to act as carbon sinks, N and C cycles in relation to soil capacity to stock carbon.

Since January 1<sup>st</sup> 2013, Italy has assumed the presidency of the AC and will keep this office for the next two years (2013-2014). This term offers the opportunity to start working in phase with the seven-year time-line of the Alpine Space programme's implementation (2014-2020). Priority issues which will be pursued under the Italian presidency are adaptation strategies to climate change and air pollution impacts on ecosystems which have got so far less attention than others. Efforts will also be devoted to better integrate AS projects with the research strategy of Horizon 2020, bridging basic and applied research, promoting cooperation opportunities, supporting open innovation & technology transfer and favoring growth and exchange of human resources between universities and research centers located into the alpine region.

# EFFECTS OF ELEVATED COMBINED OZONE AND NITROGEN DEPOSITION ON THE SPECIES COMPOSITION OF A SUBALPINE GRASSLAND

Bassin S., Volk M., Fuhrer J.

*Agroscope Reckenholz Research Station ART, Air Pollution/Climate Group,  
Zurich, Switzerland; seraina.bassin@art.admin.ch*

To investigate the effects of elevated ozone (O<sub>3</sub>) and nitrogen (N) deposition on a subalpine pasture, 180 turf monoliths were exposed during seven years at Alp Flix, Switzerland (2000 m a.s.l.) in a free air fumigation system to a combination of one of three O<sub>3</sub> levels (ambient, 1.2 or 1.6x ambient concentration) and one of five N loads (0, +5, +10, +25, +50 kg N ha<sup>-1</sup> yr<sup>-1</sup>). Aboveground biomass of the functional groups of grasses, forbs, sedges, and legumes was recorded annually. The abundance of individual plant species was recorded once each year at peak vegetation development in the first two weeks of July by means of the point-quadrat method with 18 fixed sampling points within a 6 cm grid. Effects of treatments were tested in a repeated measures split-plot analysis using a linear mixed effect model.

N addition caused strong changes in community composition and slightly reduced Shannon diversity: Sedges (*Carex sempervirens* and *Carex ornithopoda*) more than doubled their abundance and triplicated their fractional biomass at the expense of legumes (*Trifolium alpinum*), grasses (*Agrostis capillaris*, *Briza media*, *Festuca* spp.), and forbs, the latter of which responded inconsistently (i.e. *Potentilla aurea* increased, while *Plantago alpina* reduced their proportion). Compositional changes were strong and significant already with +5 kg ha<sup>-1</sup> yr<sup>-1</sup>. At all levels of N however, changes ceased after five years, indicating that a new equilibrium was reached.

Elevated O<sub>3</sub> and the combined O<sub>3</sub> x N exposure had no effect on functional group productivity, but the fraction of dead plant material was increased by 20% in the highest O<sub>3</sub> treatment. Nevertheless, in contrast to earlier assumptions, this O<sub>3</sub>-induced increase in leaf senescence caused no productivity losses or shifts in species abundance, with the exception of *Nardus stricta* which became more abundant. Overall the results reveal high N sensitivity of the subalpine grassland, but low sensitivity to O<sub>3</sub>, singly or in combination with N. Thus, in the longer term any input of N above the current ambient deposition may cause a shift in the plant community composition of these ecosystems which are considered hotspots for biodiversity.

Boltersdorf S. H.<sup>1</sup>, Pesch R.<sup>2</sup>, Schröder, W.<sup>2</sup>, Werner, W.<sup>1</sup>

*1 University of Trier, Department of Geobotany, Behringstr. 21, 54296 Trier, Germany.  
Stefanie.Boltersdorf@gmx.de*

*2 University of Vechta, Chair of Landscape Ecology, PO Box 1553, 49364 Vechta, Germany.  
rpesch@iuw.uni-vechta.de*

Over the past century humans have created immense and all-time changes to the global nitrogen (N) cycle, by converting atmospheric di-nitrogen (N<sub>2</sub>) into many reactive nitrogen (N<sub>r</sub>) compounds. Nowadays, it is clear that these exceeding rates of N deposition are steadily becoming a bigger problem with the growth in the world population (Erisman et al. 2008). This fact urgently calls for a reliable and extensive monitoring system that indicates the N input into ecosystems. Epiphytic lichens and bryophytes have been shown to be outstanding indicator organisms in a wide range of air pollution studies. In the past few years, monitoring of N deposition using lichens and mosses has increased, and diverse studies have confirmed that both organism groups provide a fairly precise picture of the quantity of the atmospheric N deposition in the environment. In order to not just assess N deposition quantitatively, but also identify the qualitative N source, isotope research can be used.

In autumn 2008 epiphytic lichens (*Parmelia sulcata*, *Physcia sp.* and *Xanthoria parietina*) were collected from trees that met the requirements for bioindication with lichens (VDI guideline 3957/13) within a 2-km radius around the 18 deposition measurement field stations of the Federal Environment Agency (Umweltbundesamt, UBA) in Germany. In addition, we used moss samples from the Moss Monitoring Survey 2005/2006. The sampling of mosses (*Pleurozium schreberi*, *Scleropodium prurum* and *Hypnum cupressiforme*) was conducted in accordance with an appropriate UN ECE guideline. Total N concentration and <sup>15</sup>N natural abundance were analysed using an elemental analyser coupled with an isotope-ratio mass spectrometer. Relevant N deposition data were obtained from the responsible institution of the monitoring network (Federal Environment Agency).

The present study focuses on a comparison of both monitoring organism groups and their explanatory power and effectivity as biomonitor organisms. In this regard, we test whether the N accumulation of these different monitor organisms is species-specific, due to an overall increase of N deposition.

Furthermore, we draw a comparison between data obtained from lichen and moss monitoring and data obtained from N monitoring networks based on physico-chemical measurements. Besides, we show that the analysed  $\delta^{15}\text{N}$  signatures of lichens and mosses can identify the main N source of deposition in the environment, despite having different receptor surfaces.

#### **Reference**

J.W. Erisman, M.A. Sutton, J. Galloway, Z. Klimont and W. Winiwarter, How a century of ammonia synthesis changed the world, *Nat. Geosci.* **1**, 636 (2008).

SOYBEANS FROM FISKEBY, SWEDEN - A POTENTIAL SOURCE OF TOLERANCE GENES FOR OZONE AND A BROAD RANGE OF ABIOTIC STRESSES

Kent O. Burkey<sup>1</sup>, Amy Burton<sup>1</sup>, Thomas E. Carter, Jr.<sup>2</sup>, James Orf<sup>3</sup>

<sup>1</sup>USDA-ARS Plant Science Research Unit, 3127 Ligon Street, Raleigh, NC, 27607 USA  
Kent.Burkey@ars.usda.gov, Amy.Burton@ars.usda.gov

<sup>2</sup>USDA-ARS Soybean & Nitrogen Fixation Research Unit, Raleigh, NC, 27607 USA  
Tommy.Carter@ars.usda.gov

<sup>3</sup>Dept. of Agronomy and Plant Genetics, University of Minnesota, St. Paul, MN, 55108 USA  
orfx001@umn.edu

Adapting agriculture to future climates will include development of crops with greater stress tolerance. A first step is to identify germplasm to be used as a source of tolerance genes. In a foliar injury screen of soybean germplasm contributing to North American cultivars, genotypes from Fiskeby, Sweden were found to be ozone (O<sub>3</sub>) tolerant (Burkey and Carter, 2009). The most tolerant genotype tested, Fiskeby III, was compared with an ozone-sensitive genotype, Mandarin Ottawa, to determine whether the tolerance based of foliar injury was translated into protection of seed yield under elevated O<sub>3</sub>. In an open-top chamber study (Table 1), seed yield in Fiskeby III was not affected at elevated O<sub>3</sub> concentrations that reduced yield in Mandarin Ottawa by 40%. Thus, it appears that Fiskeby III is a source of O<sub>3</sub> tolerance genes for soybean improvement.

Other independent screening studies (data not shown) identified Fiskeby germplasm as tolerant to other abiotic stresses including drought, salt stress, iron deficiency chlorosis, and toxic soil aluminum. Such a broad range of stress tolerance is very unusual in a single genotype and provides an opportunity to study potential cross-tolerance genes. A mapping population of 240 random inbred lines has been developed from a cross between Fiskeby III and Mandarin Ottawa. The population has now been assayed for a set of 1500 DNA markers. Screening of the population for O<sub>3</sub> response has been conducted using greenhouse exposure chambers, and the phenotype and marker data are being assembled to identify quantitative trait loci (QTLs) for O<sub>3</sub> response within the soybean genome. Screening of the population for other stresses is underway to look for QTLs that may provide tolerance to multiple stresses.

**Table 1.** Fiskeby III (O<sub>3</sub>-tolerant) and Mandarin Ottawa (O<sub>3</sub>-sensitive) soybean genotypes were subjected to season-long O<sub>3</sub> exposure in open-top chambers using charcoal-filtered (CF) air with elevated ozone treatment targets of 60, 90, and 120 ppb applied as a diurnal profile typical of summer months in Raleigh, NC. Plants were grown in 15-liter pots with Osmocote Plus slow-release fertilizer and routine irrigation to prevent water stress. The experiment consisted of twelve chambers (3 blocks x 4 O<sub>3</sub> treatments) with 3 plants of each genotype randomly assigned in each chamber. Foliar injury at 30 days after planting was estimated as percentage of canopy leaves showing O<sub>3</sub>-induced symptoms. Seed yield was measured at the end of season as g plant<sup>-1</sup>. Values are chamber means ± standard error (n = 3).

| Treatment | AOT40<br>ppbO <sub>3</sub> -hr | Fiskeby III [tolerant] |                | Mandarin Ottawa [sensitive] |                |
|-----------|--------------------------------|------------------------|----------------|-----------------------------|----------------|
|           |                                | % Foliar Injury        | Relative yield | % Foliar Injury             | Relative yield |
| CF        | 256                            | 0 ± 0                  | 1.00           | 1 ± 1                       | 1.00           |
| CF+60     | 16211                          | 0 ± 0                  | 1.15 ± 0.21    | 34 ± 4                      | 0.92 ± 0.17    |
| CF+90     | 44443                          | 22 ± 2                 | 1.02 ± 0.05    | 78 ± 1                      | 0.75 ± 0.01    |
| CF+120    | 74356                          | 55 ± 3                 | 1.02 ± 0.12    | 90 ± 2                      | 0.58 ± 0.07    |

**Reference**

Burkey, K.O. and T.E. Carter, Jr. (2009) Field Crops Research 111: 207-217.

## BIO-ECONOMIC ASSESSMENT OF OZONE IMPACTS ON FRENCH FARMING SYSTEMS

Castell J.-F.<sup>a</sup>, Humblot P.<sup>b</sup>, Leconte-Demarsy D.<sup>b</sup>, Clerino P.<sup>b</sup>, Szopa, S.<sup>c</sup>, Jayet P.-A.<sup>b</sup>

<sup>a</sup>AgroParisTech – INRA UMR 1091 Environnement et Grandes Cultures, 78850 Thiverval-Grignon, France.  
castell@grignon.inra.fr

<sup>b</sup>INRA – UMR Economie Publique INRA-AgroParisTech, 78850 Thiverval-Grignon, France

<sup>c</sup>LSCE-IPSL-CNRS-UVSQ L'Orme des Merisiers, 91191 Gif sur Yvette, France

The impacts of the future ozone concentrations on French agriculture were assessed by the use of the disaggregated farming model AROPAj (Galko and Jayet, 2011) combined with the crop model STICS (Brisson *et al*, 2003), which provides yield functions of the main French crops according to environmental conditions and fertilizer input. These functions were modified by additional AOT40-based response functions (Mills *et al*, 2007) in order to link farming activities and tropospheric O<sub>3</sub> concentrations. Several scenarios of O<sub>3</sub> concentrations and AOT40 for 2030 were computed using two chemistry-transport models, LMDz-INCA (global scale) and CHIMERE (regional scale) (Szopa *et al*, 2006).

In the case of the more pessimistic scenario for 2030, wheat production may decrease by more than 30% and barley production may increase by more than 14%. These variations are due to the direct effects of ozone on yields as well as to modifications in land-use caused by a shift toward more O<sub>3</sub>-resistant crops. Despite economic adaptation of farming systems through changes in land-use and livestock, these changes lead to significant reductions of the agricultural gross margin, which was reduced by more than 1% on average, with a maximum reduction of 7% in some regions. The rise of ozone concentration was also associated with a reduction of agricultural greenhouse gas emissions of about 2%, as a result of decreased use of nitrogen fertilizers.

### References

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# HEAVY METALS IN MOSSES – WHAT ARE THE ADVANTAGES OF AN INCREASED SAMPLING DENSITY AT THE COUNTY LEVEL?

Danielsson H. & Pihl Karlsson G.

*IVL Swedish Environmental Research Institute Ltd., Box 53021, SE-400 14 Göteborg, Sweden, [helena.danielsson@ivl.se](mailto:helena.danielsson@ivl.se), [gunilla.pihl.karlsson@ivl.se](mailto:gunilla.pihl.karlsson@ivl.se)*

Linked to the Swedish national surveys on heavy metals in mosses some counties choose to increase the number of sampling sites in order to obtain more detailed information of the metal load. In some cases, samples were only collected in background areas, in accordance with the terms of the national survey, while others chose to collect mosses in urban areas or in the vicinity of industries.

The aim of this study was to examine how an increased sampling density in three Swedish counties (H, E and U) in 2010, 2000 and 1990 affected the results at the county level. The studied metals were arsenic, cadmium, copper, nickel, lead and zinc.

In Table 1 the median concentrations based on all moss samples, and the corresponding median concentrations based only on the samples included in the national survey for 2010, 2000 and 1990 are shown. The statistical comparison between the medians for 2010 showed no statistically significant difference for any of the metals studied in the two counties with moss samples from background areas only (counties E and U, site type B). For the county with moss samples also from urban and industrial areas (county H, site types B + NB) the addition of samples results, not surprisingly, in statistically significantly different median values for some of the metals in the comparison between values based on only the national survey samples and values based on all samples collected in the county. The corresponding comparison for 2000 shows that significant differences exist for some of the metals for all studied counties in 2000. For 1990 there was no statistically significant difference for any of the metals studied in one of the counties (U) with all moss samples from background areas only. For the other two counties (H and E) there were statistically significant differences between the medians for some of the metals.

**Table 1.** Median concentration of metals ( $\mu\text{g/g}$ , dw) in moss samples from 2010, 2000 and 1990. \* indicates significant differences between the medians of the two samples (all vs. nat.) at the 95.0% confidence level (Mann Whitney U-test). Site type B = Background, site type NB = Non background

| Year | County | Site type | As    |       | Cd    |       | Cu   |      | Ni    |       | Pb   |      | Zn  |      |
|------|--------|-----------|-------|-------|-------|-------|------|------|-------|-------|------|------|-----|------|
|      |        |           | all   | nat.  | all   | nat.  | all  | nat. | all   | nat.  | all  | nat. | all | nat. |
| 2010 | H      | B + NB    | 0.05* | 0.05* | 0.17  | 0.18  | 4.8* | 3.8* | 0.80* | 0.67* | 2.8  | 2.8  | 35  | 35   |
| 2010 | E      | B         | 0.05  | 0.05  | 0.14  | 0.15  | 3.4  | 3.5  | 0.70  | 0.75  | 1.9  | 2.3  | 33  | 36   |
| 2010 | U      | B         | 0.05  | 0.05  | 0.14  | 0.15  | 3.7  | 4.5  | 0.97  | 0.95  | 2.2  | 2.1  | 34  | 38   |
| 2000 | H      | B + NB    | 0.23  | 0.20  | 0.22  | 0.22  | 5.9* | 4.4* | 2.2*  | 1.2*  | 5.2  | 5.1  | 47  | 45   |
| 2000 | E      | B         | 0.19  | 0.17  | 0.19  | 0.18  | 4.7* | 3.5* | 1.7*  | 1.0*  | 4.3  | 4.2  | 39  | 40   |
| 2000 | U      | B         | 0.19  | 0.16  | 0.19  | 0.20  | 4.8  | 4.4  | 2.7*  | 1.7*  | 1.4* | 4.0* | 44  | 44   |
| 1990 | H      | B + NB    | -     | -     | 0.28  | 0.28  | 7.0* | 6.1* | 1.6   | 1.6   | 17*  | 11*  | 49* | 43*  |
| 1990 | E      | B         | -     | -     | 0.43* | 0.23* | 5.6  | 5.4  | 2.2*  | 1.4*  | 18*  | 11*  | 37* | 41*  |
| 1990 | U      | B         | -     | -     | 0.24  | 0.24  | 5.9  | 6.2  | 2.4   | 2.7   | 13   | 12   | 46  | 50   |

**To conclude:** This study indicate that the number of sampling points in the 2010 Swedish national study of metal concentrations in mosses was sufficient to give a good picture of the metal load in the background environment in the counties studied. In earlier years, when the metal concentrations generally were higher, an increase of the sampling density gave a slightly different picture of the metal loads in background areas. The study also showed that the moss method was successfully used to get a more detailed picture of the metal load in urban areas and in the vicinity of industries and other local sources in the studied counties.



## THE PHYTOTOXIC OZONE DOSE PERFORMS WELL IN MEDITERRANEAN FORESTS

De Marco A., Sicard P., Vitale M., Paoletti E.

ENEA, Via Anguillarese 301, 00123 Rome, [alessandra.demarco@enea.it](mailto:alessandra.demarco@enea.it)

In Europe, background ozone levels are gradually increasing, especially in the Mediterranean region. The Mediterranean Basin is expected to be more strongly affected by ongoing global climate change, including ozone pollution, than most of the other regions. At present, the European standard for forest protection is the AOT40 index which is based on the atmospheric O<sub>3</sub> concentrations, although many studies have suggested that stomatal flux-based approach is scientifically-sound and would be an useful tool for O<sub>3</sub> risk assessment. In fact, stomatal uptake is limited by drought during the summer in Mediterranean regions where ozone concentrations are high. Indeed, ozone pollution is more pronounced in regions with strong photochemical activity, combined with the road traffic and industrial emissions, such as the Mediterranean basin, than in the rest of Europe. In conclusion, the Mediterranean basin is at the highest ozone risk in Europe and O<sub>3</sub> levels regularly exceed the critical thresholds for forests. A comparison of maps concerning total stomatal ozone uptake (POD0), threshold-based phytotoxic ozone dose (POD1), and concentrations exceeding 40 ppb (AOT40) for *Pinus halepensis* and *Fagus sylvatica* was conducted in the South-eastern France and North-western Italy regions. Meteorological data (air temperature, relative humidity, soil water content and solar radiation), soil and canopy data and ozone concentrations for 2010 and 2011 were calculated from the coupled MM5-CHIMERE modelling system in order to calculate ozone fluxes. For this work data were provided at 1-h temporal resolution and a spatial resolution of 9×9km across the study area. The comparison of these maps showed the different distributions of AOT40 and fluxes in this Mediterranean area. Moreover, the Canopy Moisture Content (CMC) was used as dependent variable for the assessment of potential impact of ozone on *Fagus sylvatica* and *Pinus halepensis* forests on climatic and ozone metrics variables. Partial correlation analyses demonstrated that AOT40, POD0 and POD1 were negatively correlated to CMC in a significant way only for *P. halepensis* in both years, whereas *F. sylvatica* did not show any linear relationships among these predictors and CMC variable, although POD0 and POD1 were significantly dependent on soil water content. This latter aspect suggested that causal-effect relationships could be mainly indirect rather than direct, which was corroborated by Regression Tree Analysis (RTA) carried out by Random Forest technique. In fact, soil water content and temperature were the most important predictors affecting CMC in *F. sylvatica*. A more complicated pattern was evident in *P. halepensis* being CMC depending on several predictors, although POD0 and relative humidity were the most important predictors especially in 2011. The use of POD1 instead of POD0 did not significantly improve the relationship with CMC, and therefore with plant health. In conclusion, we suggest POD0 as the best index for protecting Mediterranean forests from ozone impacts. This work was made possible with the contribution of the LIFE financial instrument of the European Union (LIFE10 ENV/FR/208) for the FO<sub>3</sub>REST project.

## WHAT ABOUT NANOMATERIALS? FUTURE CONSIDERATIONS ABOUT THE DEPOSITION OF NANO PARTICLES FROM LONG RANGE TRANSPORT

De Temmerman, L.<sup>1</sup>, De Temmerman, P.-J.<sup>2</sup>, Verleysen, E.<sup>2</sup>, Vandermeiren, K.<sup>1</sup>, Ruttens, A.<sup>1</sup>, Waegeneers, N.<sup>1</sup>, Mast, J.<sup>2</sup>

<sup>1</sup>*CODA-CERVA-Unit Trace Elements, Leuvensesteenweg 17 B- 3080 Tervuren*

<sup>2</sup>*CODA-CERVA – Unit TEM, Groeslenberg 99 B-1180 Brussels*

Following the EU Commission recommendation of 18 October 2011 on the definition a nanomaterial (NM), a material is a nanomaterial if it contains particles, in an unbound state or as an aggregate or as an agglomerate, for 50 percent or more of the particles, on a number size distribution and have at least one external dimension in the size range 1-100 nm.

An important shape of NMs is the equiaxial (roughly spherical) particulate form. Other shapes are rod-like (fibers or tubes) and plate-like (flakes or platelets). Natural, incidental or manufactured NMs are used in several industrial and medical applications. NMs are not allowed in food even though they can be present in food additives such as synthetic amorphous silica (E551) added as anti-caking agent and TiO<sub>2</sub> (E171) added as colorant.

The toxicity of NMs depends on their chemical nature, size and shape. NMs can theoretically be taken up by endocytosis and thus cross biological membranes. They can enter the blood stream through the lungs (air pollutants), the intestine (food) and through the skin (skin care products). A prerequisite is that their size and shape allow the transfer through the membranes. Once the NMs are taken up, their chemical nature is important towards human toxicity. Metals and metalloids of nano size that are readily oxidized (Fe, Ag, Au, Al,...) can generate electrons. If captured by oxygen reactive oxygen species can be generated. The biological activity and toxicity of NMs (SiO<sub>2</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>,...) is still under investigation.

Analysis of NMs by ICP-MS, based on the total elemental concentration is not sufficient for risk analysis because their size, shape and elemental composition need to be determined. Transmission Electron Microscopy (TEM) allows to visualize the NMs and with tomography their three dimensional shape can be investigated. An analytical TEM is needed to analyze also the chemical nature of the particles. TEM combined with chemical analysis can also be used. Single Particle ICP-MS allows determining the elemental composition related to the size of the particle, even though this method is limited to NMs with particles that have a uniform and known shape e.g. equiaxial and it is limited by the specific elemental sensitivity of the ICP-MS technique. Unfortunately ICP-MS has a low sensitivity for the analysis of Fe, Ti and Si. Field Flow Fractionation coupled to ICP-MS can resolve some of these problems.

Because NMs occur already in food, research focuses on food analysis in order to determine the nano proportion in food. Less attention is paid to metal or metalloid air pollutants generated by traffic (CeO<sub>2</sub>,...) or by industrial plants. Metal smelters release through their stacks metal vapors that condensate into particles in the nano size range that are transported on a global scale and deposited by precipitation (rain, snow,...). They are absorbed and accumulated by plants. As such they can enter the food chain and NMs are probably more toxic than expected from the total elemental concentration. For air pollutants such as oxides of Pb, Cd, As,... SP-ICP-MS is the most sensitive. Except for Ce that is used as a fuel additive, there are no reference materials (CRMs). Preferably CRMs are used to calibrate the SP-ICP-MS for the measurement of the elemental concentration as well as the size distribution of the particles. These CRMs need to be characterized first with e.g. TEM. A lot of work is still needed to be able to separate the nano particles from a plant matrix in order to quantify and to estimate the size of the particles. In the future not only chemical speciation of trace elements in food will be important but, in the case of particles, probably also their size and shape.

## ACCUMULATION OF AIRBORNE ARSENIC, CADMIUM AND LEAD IN *PHASEOLUS* BEAN

De Temmerman L., Ruttens, A., Waegeneers, N.

CODA-CERVA, Leuvensesteensweg 17, 3080 Tervuren - ludet@coda-cerva.be

Plants accumulate airborne As, Cd and Pb on their above ground parts. The leaves are the best exposed and accumulate very efficiently the atmospheric deposition. As such leafy vegetables are most susceptible to the accumulation of trace elements (1). Also root crops accumulate trace elements, even in their inner tissues (2). In the present work, the effects of airborne trace elements on beans were studied.

Bean plants (*Phaseolus vulgaris*) were grown in containers (3 plants per container) in a reference area with low atmospheric deposition and then exposed in the reference area as well as in a polluted area around a lead smelter. The containers were placed on experimental plots covered with grass near gardens where vegetables are cultivated. The plants were exposed for 42 days for the green harvest and for 70 days for the dry harvest.

At each experimental plot, the containers were exposed in triplicate allowing statistical treatment of the results. After exposure, two plants were harvested and separated in leaves (+ petioles), stems and pods (+seeds). Part of the pods was washed to be able to compare the results with those for the unwashed pods. The leaves and stems were not washed because they are not used for human consumption. Also the unwashed leaves and stems were analyzed. Three plants (one per container) remained on the experimental plots until complete ripening. The dry pods were harvested and beans and pods were analyzed separately. At each site, bulk deposition was measured in order to be able to link the results to atmospheric deposition.

Atmospheric deposition of As, Cd and Pb is accumulating in the leaves (+ petioles) of *Phaseolus* bean. They are well exposed and correlate well with atmospheric deposition. However, there is also an important accumulation in the stems of the plants and also in the green pods with seeds. Both are less exposed as they are covered by the leaf canopy but even then they correlate well with the atmospheric deposition.

Washing the green pods removed 10 % of Cd, 45 % of Pb and 30 % of As. At the dry harvest, an effect of atmospheric deposition on the seeds was noticed. As they have never been exposed directly, their contamination is originating from transport from the leaves to the seeds by the transport of assimilates or the elements are transported from the pods to the seeds.

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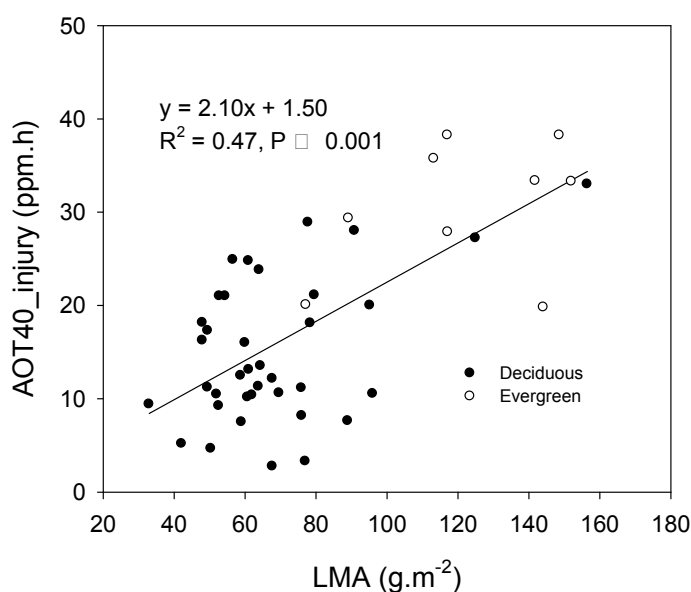
## LEAF MASS PER AREA ELUCIDATES OZONE SENSITIVITY OF WOODY SPECIES

Feng Z.Z.<sup>1</sup>, Buker P.<sup>2</sup>, Pleijel H.<sup>1</sup>, Emberson L.<sup>2</sup>, Uddling J.<sup>1</sup>

<sup>1</sup>Department of Biological and Environmental Sciences, University of Gothenburg,  
P.O. Box 461, 405 30 Gothenburg, Sweden

<sup>2</sup>Stockholm Environment Institute, University of York, York YO10 5DD, UK  
E-mail: zhzhfeng201@hotmail.com (Feng Z.Z.)

We investigated whether consideration of leaf mass per area (LMA) can improve ozone impact assessment in woody plants through a meta-analysis. Results indicated that LMA was positively related with O<sub>3</sub> tolerance (Fig.1). Although no exact LMA threshold for O<sub>3</sub> tolerance could be determined, species with LMA > 100 g m<sup>-2</sup> were usually tolerant to O<sub>3</sub>. Evergreen species had higher LMA and were more tolerant to O<sub>3</sub> than deciduous species. A stomatal O<sub>3</sub> flux-response relationship across seven European forest tree species was strongly improved if flux was expressed per unit leaf mass ( $r^2 = 0.63$ ) compared to per unit leaf area ( $r^2 = 0.34$ ). This study demonstrates that LMA plays a key role in determining O<sub>3</sub> sensitivity of woody plants and that it can be used for improving current O<sub>3</sub> flux-response relationships. Furthermore, it suggests that species with high LMA should be prioritized in afforestation and urban greening in seriously O<sub>3</sub> polluted regions.



**Figure 1.** Relationship between AOT40 at visible injury onset (AOT40\_injury) and LMA of broadleaf woody species grown at Mediterranean, temperate and subtropical regions.

PHOTOSYNTHETICAL RESPONSE TO OZONE EXPOSURE AND NITROGEN ENRICHMENT OF *C. BETULUS* AND *Q. ROBUR* SAPLINGS. RESULTS OF THE FIRST YEAR OF EXPERIMENTATION UNDER THE ECLAIRE PROJECT

Gerosa Giacomo<sup>1</sup>, Monga R<sup>1</sup>, Marzuoli R.<sup>1,\*</sup>

<sup>1,\*</sup> Dept. of Mathematics and Physics, Catholic University of Brescia, via dei Musei 41, 25121 Brescia (Italy) – [riccardo.marzuoli@unicatt.it](mailto:riccardo.marzuoli@unicatt.it)

A manipulation experiment on ozone enrichment and increased nitrogen deposition has been performed in 2012 in Northern Italy on young trees of *Quercus robur* and *Carpinus betulus*, two of the most representative species of forest vegetation of the Po valley and the pre-alpine region. Two hundreds and twentyfour saplings of each species have been potted and placed in 12 Open-Top Chambers following a split-plot design with 3 randomized blocks and two factors: ozone concentration, the main factor, at 4 different levels (CF, AA, AA+35%, AA+70%), and nitrogen irrigation, the nested factor, at 2 different levels (tap water, tap water + 70Kg of N\*ha\*y<sup>-1</sup>).

Saplings growth and physiological have been monitored during the whole growing season from April to the end of September. Gas exchange measurements were performed once a month as well as photosynthetic performance of PSII and stomatal conductance measurements (3 daily cycles).

Moreover A/Ci and A/Light response curves have been made in June and September to assess the maximum carboxylation rate of RuBisCO, the maximum assimilation at non-limiting Ci concentration, photorespiration and dark respiration rates. At the end of the growing season half of the saplings have been harvested in order to estimate the total biomass production and its root/shoot partition.

Preliminary results of the first year of experimentation (ECLAIRE experiment will last two years) reveal significant positive effects of nitrogen and negative effects of ozone at photosynthetic level in both species.

Effects on growth and biomass partition were detected only for nitrogen, particularly for *Q. robur*, while the ozone effects were weak and scattered. The only detectable effect of ozone was a clear reduction of stomatal conductance starting from the mid-season. This fact highlights the need to include a f(O<sub>3</sub>) modifying function in the stomatal conductance models, one of which is proposed for these two species.

The interaction between the two factors shows an antagonistic effects of nitrogen and ozone on the photosynthetic parameters.

The observed incoherence among the ozone effects on photosynthetic parameters and the real plant growth rises a question about the possibility to predict ozone impacts on plant growth with a purely modellistic approach based upon photosynthesis and, once again, highlights the need to set up and support pluriannual experiments on field.

## PROGRESS IN MODELLING ANNUAL PASTURE OZONE FLUX

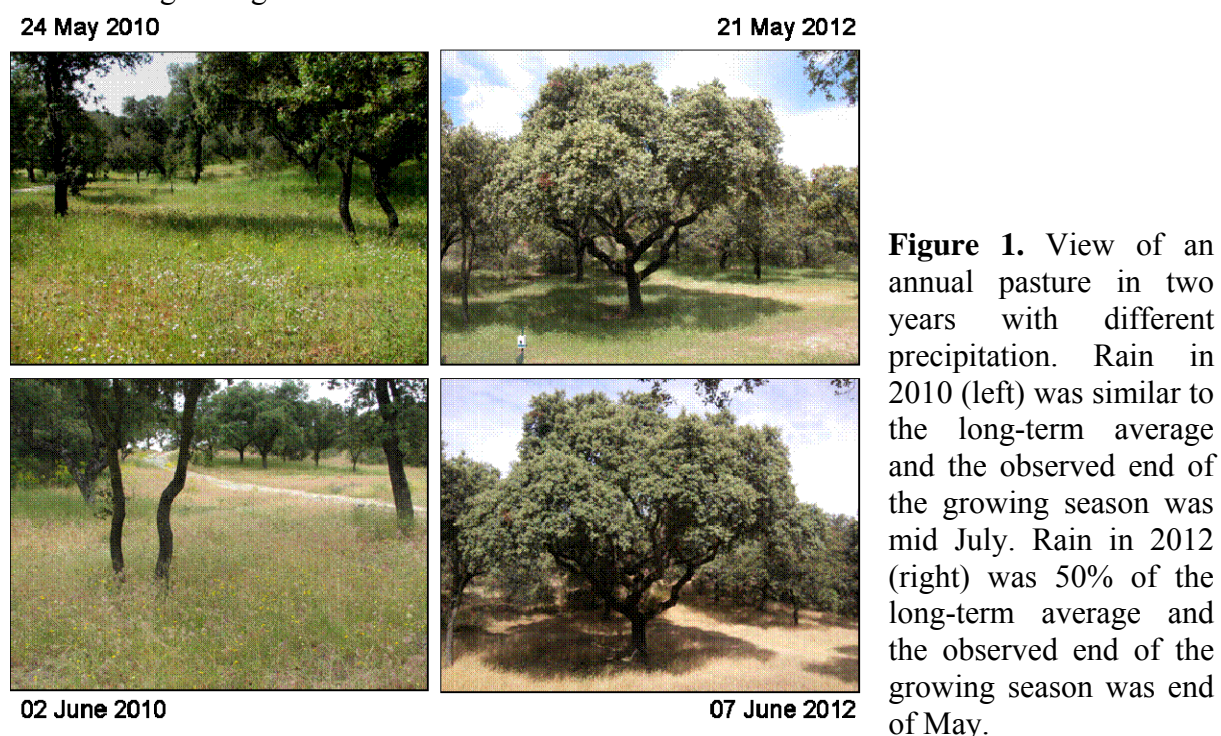
Ignacio González Fernández, Héctor Calvete, Victoria Bermejo, Susana Elvira, Javier Sanz, Héctor García Gómez, Fernando Valiño, Rocío Alonso

*CIEMAT, Avda. Complutense 40, 28040, Madrid. ignacio.gonzalez@ciemat.es*

Dehesas are one of the most characteristic landscapes of the central and Southwestern Iberian Peninsula, typically composed of sparse broadleaf evergreen trees and annual pasture or annual crop cover in the understory. These areas are frequently exposed to phytotoxic ambient ozone ( $O_3$ ) concentrations and are subject to a highly variable climate causing strong inter-annual changes in environmental growing conditions for plants.

Dehesa annual pastures have shown negative responses when exposed to  $O_3$  in open-top chambers including negative effects on above and belowground biomass growth, flower and seed production or forage quality. These effects are strongly related with the amount of  $O_3$  absorbed by the plants through their stomata or phytotoxic  $O_3$  dose (POD). Current EMEP  $DO_3SE$  methodology for modelling the risk of  $O_3$  impacts presents some limitations when describing the inter-annual variability of plant phenology of these plant communities. High inter-annual variations of hydro-meteorological conditions can cause changes in the length of the growing season of annual communities (figure 1) up to one and a half months. This may result into important variations of estimated POD.

This work discusses the influence of inter-annual variations of hydro-meteorological conditions on dehesa annual pasture productivity and the risk of  $O_3$  negative effects under such growing conditions. Soil water availability, plant growth, duration of the growing season and POD were modelled for a dehesa pasture using the MEDPAS model (González-Fernández et al., 2010), which is validated with a new dataset from central Spain with growth data over 3 growing seasons.



González-Fernández I., Bermejo V., Elvira S., Sanz J., Gimeno B.S., Alonso A. 2010. Modelling annual pasture dynamics: Application to stomatal ozone deposition. *Atmospheric Environment* 44: 2507-2517.

## OVERVIEW OF THE ACHIEVEMENTS OF THE ICP VEGETATION IN 2012

Harmens, H.<sup>1</sup>, Mills, G.<sup>1</sup>, Hayes, F.<sup>1</sup>, Norris D.A.<sup>1</sup>,  
and the participants of the ICP Vegetation

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

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

At the 26<sup>th</sup> Task Force Meeting we will report on the achievements of the ICP Vegetation in 2012 [1] and progress made with items to be reported to the LRTAP Convention in 2013 [2], including:

- Supporting evidence for ozone impacts on vegetation, including the 2012 biomonitoring exercise;
- Final report on the European heavy metals and nitrogen in mosses survey 2010/11;
- Report on ozone impacts on biodiversity and ecosystem services;
- Report on the pilot study of mosses as biomonitors of POPs.

In addition, we will report on the contribution of ICP Vegetation to the common work plan items of the WGE for 2013 [2].

Apart from looking back to our achievements in 2012, throughout the Task Force Meeting we will be discussing our future plans, in particular the medium-term work plan of the ICP Vegetation (2013 – 2016).

### **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).

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## RESULTS OF THE EUROPEAN MOSS SURVEY 2010/11

Harmens H.<sup>1</sup>, Norris D.A.<sup>1</sup>, Mills, G.,  
and the participants of the European moss survey 2010/2011

<sup>1</sup> *Centre for Ecology and Hydrology, Environment Centre Wales, Deiniol Road, Bangor, Gwynedd LL57 2UW, UK. hh@ceh.ac.uk*

The European heavy metals and nitrogen in mosses biomonitoring network provides data on the concentration of 12 metals and nitrogen in naturally growing mosses and is currently coordinated by the UNECE ICP Vegetation. The technique of moss analysis provides a complementary, time-integrated measure of elemental deposition from the atmosphere to terrestrial systems. It is easier and cheaper, and allows a much higher sampling density than conventional precipitation analysis. The European heavy metal moss survey has been repeated at five-yearly intervals since 1990 [1]; nitrogen concentrations in mosses were determined for the first time in 2005 [2].

Here we report on the preliminary results of the concentration of Al, As, Cd, Cr, Cu, Fe, Hg, N, Ni, Pb, Sb, V, Zn in mosses in 2010/11. Data were received from 25 countries for heavy metals and 14 countries for nitrogen. In addition, a pilot study was conducted in six countries on the concentration of persistent organic pollutants (POPs), particularly polycyclic aromatic hydrocarbons (PAHs), in mosses. Mosses could be useful indicators of spatial patterns and temporal trends of atmospheric deposition of POPs [3].

Maps were produced of the mean metal and nitrogen concentration in mosses per 50 km x 50 km EMEP grid square, showing the spatial variation across Europe. The spatial variation is generally similar to those reported in previous European moss surveys, i.e. there is an east-west decline in the concentration of metals in mosses. Initial comparison with the previous survey shows that for most metals the concentration in mosses has declined further between 2005 and 2010. The highest decline of median values was observed for Pb (36%) and the lowest decline for Cd and Zn (7%); the decline for Hg was 20%. As reported before, the temporal trends are country- and metal-specific [1] and in several countries increases have been observed for some metals since 2005. On average, the nitrogen concentration in mosses has hardly changed since 2005 (decline of 4%). Results from Norway indicate that mosses may be a useful substrate for indicating the exposure of terrestrial surfaces to POPs (see abstract Steinnes et al.). In Switzerland, good correlations were found between PAHs concentrations in mosses and their concentration in PM<sub>10</sub> and soil.

### **Acknowledgement**

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# ENLARGED NITROGEN AVAILABILITY DUE TO INCREASED ATMOSPHERIC NITROGEN DEPOSITION AND EXPANSION OF N<sub>2</sub> FIXING PLANTS: EFFECTS ON ALPINE AND MONTANE ECOSYSTEMS

Hiltbrunner E., Bühlmann T. and Körner C.

*Institute of Botany, Department Environmental Sciences, University of Basel, Schönbeinstrasse 6, CH-4056 Basel Switzerland, erika.hiltbrunner@unibas.ch*

Montane and alpine grasslands are among the most valuable ecosystems in Europe considering their high biodiversity richness, but also the spatial extension across the European Alps. During the last decades, substantial efforts have been undertaken to characterize the responses of these plant communities to increasing nitrogen (N) deposition and/or in combination with other drivers of global change such as increasing ozone levels, climatic warming, etc. However, land use change which is considered a major driver of global change often has two facets, (1) land use intensification (fertilizer use, industrial activities) is well known to increase the atmospheric nitrogen deposition even in remote alpine areas whereas (2) complete abandonment or inappropriate land use often induces an expansion of aggressive N<sub>2</sub> fixing plant species. Such N<sub>2</sub> fixing invaders can act like a consistent, massive atmospheric N depositional input, which significantly threatens biodiversity.

We evaluated the empirical critical nitrogen loads for alpine grasslands by adding NH<sub>4</sub>NO<sub>3</sub> in solution at rates of 0, 2.5, 5, 10, 15, 20, and 25 kg N ha<sup>-1</sup> a<sup>-1</sup> to plots in a calcareous grassland at 2450 m a.s.l. in the Swiss Alps during seven years. The location receives on average a wet ambient N deposition of 3.1 kg N ha<sup>-1</sup> a<sup>-1</sup>. We determined plant species composition changes, above and belowground biomass after four and seven years of N treatments. Species richness and diversity indices did not change significantly in response to the N additions, but the dominant sedge *Carex firma* responded significantly by increased cover and biomass at N rates of 5 and 10 kg N ha<sup>-1</sup> a<sup>-1</sup>, respectively.

In the Swiss Alps, besides the expansion of forests, c. 1000 ha of montane, often species rich grasslands are currently lost every year because they are invaded by the native, N<sub>2</sub> fixing green alders (*Alnus viridis*) as a consequence of reduced land use. Green alder shrubs fix enormous amounts of N<sub>2</sub>, exceeding the N input by atmospheric N deposition by up to ten times, causing nitrate leaching, soil acidification and losses in soil basic cations. Consequently, plant diversity -when transformed to shrubland- commonly drops by half. In addition, preliminary results indicate that seasonal emission of nitrous oxide (N<sub>2</sub>O) from alder stands is c. 35 times higher than in adjacent grazed grassland.

While increased atmospheric nitrogen deposition is a widely accepted threat to different ecosystems, we advocate here an additional, so far less approved avenue of “N pollution“. Land use change induced invasion of N<sub>2</sub> fixing plants alters rapidly and at large scale the N cycle, thus jeopardizing biodiversity.

**Acknowledgement:** This work was financed by the Federal Office for the Environment (FOEN), Air Pollution Control and Chemicals Division (E. Hiltbrunner) and the PSC-Mercator PhD Fellowship Program (T. Bühlmann)

# S-POD - A SIMPLIFIED OZONE INDEX TO BE USED TO ASSESS THE RISK FOR NEGATIVE OZONE IMPACTS ON VEGETATION AT THE NATIONAL LEVEL

PER ERIK KARLSSON (1), DANIELSSON, H.(1), HÅKAN PLEIJEL (2), GUNILLA PIHL KARLSSON (1), DAVID SIMPSON (3)

(1) Swedish Environmental Research Institute, P.O. Box 53021, SE-40014 Göteborg, Sweden

(2) Department of Plant and Environmental Sciences, University of Gothenburg, P.O. Box 461, SE-40530 Göteborg, Sweden

(3) The Norwegian Meteorological Institute, P.O. Box 43 Blindern, 0313 Oslo, Norway

Corresponding author: pererik.karlsson@ivl.se; tel +46 31 7256207; fax +46 31 7256290

In this study we introduce a new possibility to assess ozone impacts on vegetation in Sweden based on a simplified ozone flux concept, the “Simplified Phytotoxic Ozone Dose”, S-POD. The concept is similar to the “Modified AOT” concept (Pihl Karlsson et al., 2004) that is already in the LRTAP Mapping Manual. However, here we introduce more modifying factors. Still, the ambition is that it should be possible to estimate the ozone exposure based on relatively few *in situ* measurements.

The S-POD is estimated from measured hourly ozone concentrations according to:

$$\text{S-POD}_x; \sum \text{daylight } ([\text{O}_3] * f) > x; \quad f = \max [f_{\min}, (f_{\text{phen}} * f_{\text{temp}} * f_{\text{VPD}} * f_{\text{gmax}})]$$

The functions used are the same as in the LRTAP Mapping Manual for the specific plant species. The  $f_{\text{gmax}}$  is introduced as a possibility to normalize between different plant species based on  $g_{\text{max}}$ .  $[\text{O}_3]$  corrected to the top of canopy of the relevant vegetation.

We tested the S-POD concept on experimental data from Sweden and Finland on wheat and young Norway spruce and Silver birch and compared dose-response relationships (D-R) with those using POD and AOT40.

For both crops and trees the strongest dose-response relationships were still obtained with POD. However, the D-R derived from S-POD was almost as good as for POD and far better than for AOT40. By using proper values for  $f_{\text{gmax}}$ , it was possible to use the same threshold for both crops and trees, S-POD15.

S-POD15 was estimated for ambient air at three different sites in Sweden based on hourly measurements of  $[\text{O}_3]$  and air temperature and humidity and the estimated ozone impacts on crops and trees were estimated from D-R. Maps for S-POD15 were also produced for Sweden.

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Pihl Karlsson, G., Karlsson, P.E., Soja, G., Vandermeiren, K. & Pleijel, H. 2004. Test of the short-term critical levels for acute ozone injury on plants – improvements by ozone uptake modeling and the use of an effect threshold. Atmospheric Environment, 38, 2237-2245.

## NITROGEN DEPOSITION AND LEACHING IN THE BOREAL FOREST ENVIRONMENT

Kubin E.,<sup>1</sup> Poikolainen, J.,<sup>1</sup> Lindroos, A.-J.<sup>2</sup> and Piispanen, J.<sup>1</sup>

<sup>1</sup>Finnish Forest Research Institute, Paavo Havaksen tie 3, FI-90014 University of Oulu.  
Email: Eero.Kubin@metla.fi, Jarmo.Poikolainen@metla.fi, Juha.Piispanen@metla.fi

<sup>2</sup>Finnish Forest Research Institute, P.O.Box 18, FI-01301 Vantaa.  
Email: Antti.Lindroos@metla.fi

The suitability of boreal forest mosses has been investigated as bioindicators of nitrogen deposition in Finland. It has also been studied, how the growing environment, composition of nitrogen deposition and factors related to the mosses themselves, affect the measured nitrogen concentration in mosses *Hylocomium splendens* and *Pleurozium schreberi*. The research supports 5-year intervals carried out national surveys in Finland as a part of the pan-European ICP Vegetation programme. Since 1990 nitrogen concentrations in mosses have decreased all over the country (Fig. 1).

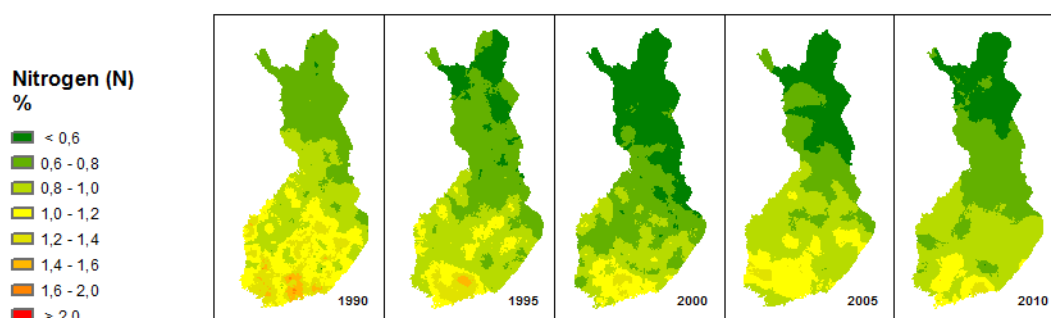


Fig. 1. Nitrogen concentrations in mosses 1990 – 2010.

The results measured in the sites of ICP-Forest Level II indicate that the total nitrogen deposition in Finland varies between 0.98 – 5.56 kg/ha/year depending on the site and the stand. There is less nitrogen deposition in Northern Finland but differences between Pine and Spruce stands are small. Nitrogen content of mosses varies between 0.51 – 1.18 %, and again the smaller concentrations are measured in the Northern part of the country.

Areal differences in deposition and concentrations can be utilized in determining critical loads for nitrogen. Low levels of deposition are known, in the long term, to change the abundance relationships between the understorey vegetation, to increase the susceptibility to fungal pathogens and to affect the structure of the microbial communities in forest soils.

Moss species are especially sensitive in the case of increasing nitrogen deposition. In the boreal environment forestry practise and especially clear cutting also change the ground vegetation structure and the ecosystem function. According the long term-monitoring nitrate nitrogen seems to be the foremost nutrient leached into the groundwater as a consequence of forestry operations. The effects of clear-cutting on nitrate nitrogen leaching and concentrations in surface water have been shown to last only a few years, but the long-term property of increasing groundwater concentrations have persisted 25 years up to the recovery of mosses and other vegetation. In the Task Force Meeting the role of mosses as a part of boreal forest ecosystem will be discussed.

# MULTI-ELEMENT ATMOSPHERIC DEPOSITION STUDY IN ALBANIA

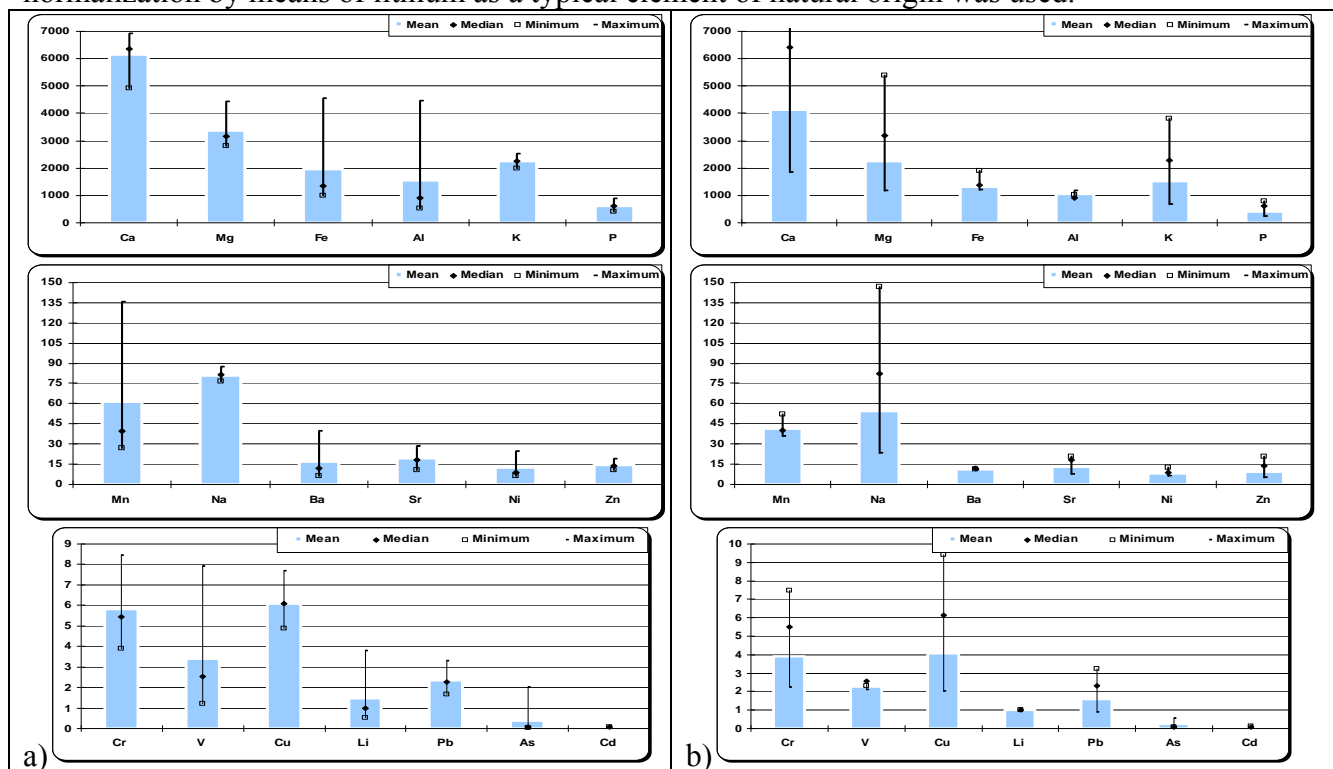
Pranvera Lazo<sup>1</sup>, Trajce Stafillov<sup>2</sup>, Marina Frontasyeva<sup>3</sup>, Lirim Bekteshi<sup>1</sup>,  
Katerina Baceva<sup>2</sup>, Zoya Goryainova<sup>3</sup>, Flora Malaj<sup>1</sup>

<sup>1</sup> Department of Chemistry, Faculty of Natural Sciences, University of Tirana, Albania.  
pranveralazo@gmail.com

<sup>2</sup> Institute of Chemistry, Faculty of Science, Ss. Cyril and Methodius University, Skopje, Macedonia

<sup>3</sup> Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia

**Abstract:** For the first time the moss biomonitoring technique and two complementary analytical techniques (AAS and ICP/AES) were applied to study multi-element atmospheric deposition in Albania. Moss samples (*Hypnum cupressiforme*) were collected during the summer of 2011 from 30 sites evenly distributed over the East part of the country. Sampling was performed in accordance with the LRTAP Convention-ICP Vegetation protocol and sampling strategy of the European Programme on Biomonitoring of Heavy Metal Atmospheric Deposition. ICP/AES analysis made it possible to determine concentrations of 19 elements including key toxic metals such as Pb, Cd, As, and Cu. Cluster and Factor analysis (PCA with Varimax rotation) was applied to distinguish elements mainly of anthropogenic origin from those predominantly originating from natural sources. Geographical distribution maps of the elements over the sampled territory were constructed using GIS technology. The median values of the elements were generally found around the average median values observed in Europe through the European programme. This study was conducted in order to provide a reliable assessment of air quality throughout Albania and to produce information needed for better identification of pollution sources and improving the potential for assessing environmental and health risks in Albania, associated with toxic metals. For studying natural or anthropogenic origin of the elements, geochemical normalization by means of lithium as a typical element of natural origin was used.



**Figure 1** The box plot of the statistical parameters: a) by using the gradient of concentration, b) after geochemical normalization by using Li as reference element

Different results were obtained by comparing the gradients of element's concentration and the values obtained after normalization.

## REPORT OF THE ICP-IM ACTIVITIES 2012 FROM THE CHAIRMAN

Lundin L.

*CLRTAP, WGE, International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems, ICP IM  
Swedish University of Agricultural Science, Department of Aquatic Sciences and Assessment,  
P.O. Box 7050, SE-750 07 Uppsala, Sweden. Lars.Lundin@slu.se*

The integrated monitoring of ecosystems refers to the simultaneous measurement of physical, chemical and biological properties of ecosystems over time and across compartments at the same location using a cross-media flux approach furnishing possibilities for cause-effect explanations. The new strategies of the CLRTAP have now taken a direction on multi-media content and the ecosystem concept turning similar to the ICP IM long-term approach.

The monitoring network presently (1997-2012) includes fifteen countries; four stopped monitoring but Poland and Switzerland show intentions to re-join. In total, data exists from 70 mostly European sites but active in recent years are 43 sites in 15 countries. Future and on-going work priorities relate to WGE common item such as guidelines for reporting, outreach and joint report, and revision of the protocols. Specific work are Heavy metals budgets and critical loads; Budgets, trends and acidification recovery related to sulphur, nitrogen and base cations; Site specific dynamic modelling; Nutrient nitrogen loads and effects; CL for acidification and eutrophication for terrestrial and aquatic sites; Biodiversity indicators; Air pollution effects in relation to climate change.

Current issues of the CLRTAP has been revision of protocols and to the Gothenburg protocol WGE contributed with a joint report on scenario analysis for 2020 and further, a summary report on ICP results and their policy implications was presented. Outreach for ICP IM relates very much to cooperation with EC-projects such as LTER Europe and EnvEurope but includes also east European countries. Participation in the European biodiversity monitoring system should be noted.

The scientific work in priority topics in 2012 focused especially on the three items;

- i) Report on relations between biodiversity indicators and CL-exceedances should be prepared by the national focal points of Austria and Sweden,
- ii) Update report on mass balances for S and N to be prepared by the ICP IM PC,
- iii) Progress report on dynamic modelling to be prepared in cooperation between the NFP of UK and the JEG.

Results are presented in the 21<sup>th</sup> ICP IM Annual Report submitted to WGE in Sept. 2012.

For 2013 the tasks concern: 1) Changes in catchment retention of N and S; 2) Report on VSD modelling; 3) CL exceedances and links to indicators; 4) New HM approaches.

An ad-hoc group assessment, related to the long-term strategy of the LRTAP Convention, was carried out with possible intentions for an evaluation of the Convention structure in 2013.

The ICP IM carried out its 20<sup>th</sup> Task Force in Kaunas, Lithuania on May 22-25, 2012 and will have the 21<sup>st</sup> ICP IM TF in Moscow, May 21-23, 2013.

## IMPACTS OF OZONE ON ECOSYSTEM SERVICES AND BIODIVERSITY

Mills, G.<sup>1</sup>, Wagg, S.<sup>1,2</sup>, Harmens, H.<sup>1</sup>, Jones, L.<sup>1</sup>, Power, S.<sup>2</sup>,  
and participants of the ICP Vegetation

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

<sup>2</sup> *Imperial College London, Silwood Park Campus, Ascot, Berkshire SL5 7PY. s.power@imperial.ac.uk*

Earth's ecosystems provide an array of services upon which humans depend for food, fresh water, disease management, climate regulation, aesthetic enjoyment and spiritual fulfilment (Millennium Ecosystem Assessment, 2005). Such 'Ecosystem Services' are currently grouped according to the benefits they provide to humans, distinguishing between provisioning, regulating, supporting and cultural services. Although humans are an integral part of ecosystems, the increased global population along with increased standards of living and other socio-political, economic and technological and societal changes, mean that our interventions can have profound negative effects on the quality of the services provided by ecosystems.

The ICP Vegetation Programme Coordination Centre, in collaboration with some participants of the ICP Vegetation, has been conducting a literature review on the impacts of ozone on ecosystem services and biodiversity. In the spring of 2013, this review will be published as a glossy report and during the 26<sup>th</sup> Task Force meeting we will present and discuss progress so far.

The following topics will be presented in the report:

- The growing threat of ozone to ecosystem service provision;
- Effects of ozone on water cycling and consequences for water-related ecosystem services;
- Effects of ozone on primary productivity and associated ecosystem services;
- Effects of ozone on nutrient cycling and associated ecosystem services;
- Impacts of ozone on air purification;
- Impacts of ozone on biodiversity;
- Impacts of ozone on cultural services including leisure, recreation and amenity.

A summary of the results presented in the report will also be included in a report on impacts of air pollution on ecosystems services and biodiversity, prepared by the Working Group on Effects of the LRTAP Convention in 2013.

### **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).

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## EFFECTS OF COMBINED OZONE AND WATER STRESSES ON PHYSIOLOGY AND MEMBRANE LIPIDS OF TWO TROPICAL COWPEA CULTIVARS

Moura Rebouças D.<sup>1,3</sup>, Bagard M.<sup>1</sup>, Maia Y.<sup>2,3</sup>, Costa J.H.<sup>3</sup>, Jolivet Y.<sup>2</sup>, Fernandes De Melo D.<sup>3</sup>, Repellin A.<sup>1</sup>

<sup>1</sup> UMR 7618 Bioemco, Université Paris Est Créteil, 94010 Créteil, France

<sup>2</sup> UMR 1137 EEF, Université de Lorraine, 54506 Vandœuvre-lès-Nancy, France

<sup>3</sup> Department of Biochemistry, Federal University of Ceara, Fortaleza, Brazil

Corresponding author: [matthieu.bagard@u-pec.fr](mailto:matthieu.bagard@u-pec.fr)

Drought and elevated tropospheric ozone (O<sub>3</sub>) concentrations are growing issues related to climate change, which can occur simultaneously to reduce plant growth and biomass production. The objective of this work was to investigate the interacting effects of drought and ozone in two tropical cowpea cultivars: EPACE (drought-tolerant) and IT83 (drought-susceptible). Cowpea (*Vigna unguiculata* L. (Walp.)) is an edible legume widely grown in semiarid regions. The physiological responses of the two cultivars to the combination of stresses were studied. In addition, we focused on membrane lipid content and composition, as well as on the expression of genes related to membrane lipid biosynthesis. Cell membranes are primary targets of damage induced by environmental stresses and the preservation of cell integrity through stable membrane lipid composition is essential to plant survival.

Drought and ozone stress (120 ppb ± 10 ppb) were applied on three-week-old seedlings under controlled conditions during two weeks. The two cultivars were strongly and equally affected by the drought treatment alone or in combination, with significant reduction in biomass production, relative water content and stomatal conductance. Despite the strong impact of drought on both cultivars, only the drought-sensitive one (IT83) showed a decrease in photosynthesis and in plastidial galactolipid contents (MGDG and DGDG). The ozone treatment alone had a very limited impact on EPACE plants: fumigated plants showed typical necrotic spots on the upper surface of mature leaves but no significant effects on physiological parameters were measured. Nonetheless, specific responses were observed and identified as potential features of ozone tolerance. In contrast, O<sub>3</sub>-fumigated IT83 plants showed a higher level of leaf injury than EPACE plants. In addition, significant reductions in biomass production and total fatty acid, MGDG and DGDG contents were noticed, as compared to the controls.

Under our experimental conditions, no difference could be observed between the two cultivars in terms of drought tolerance. However, the two cultivars were differentially susceptible to ozone. The relative tolerance of EPACE could result from O<sub>3</sub>-induced regulation of stomatal conductance, which limited uptake of O<sub>3</sub> and its detrimental impact on leaf tissues. Conversely, IT83 received higher doses of ozone, which could explain the stronger effects on leaf tissues and physiological parameters. The two stresses in combination led to results similar to those observed in response to the drought treatment alone. This likely reflected the severe restriction of O<sub>3</sub> uptake resulting from drought-induced stomatal closure.

# OZONE RISK ASSESSMENT FOR THE 21<sup>st</sup> CENTURY BASED ON OZONE AND CLIMATE CHANGE SCENARIOS

Pleijel H.<sup>1</sup>, Klingberg J.<sup>1</sup>, Engardt M.<sup>2</sup>, Karlsson P.E.<sup>3</sup>, Langner J.<sup>2</sup>

<sup>1</sup> *BioEnv, University of Gothenburg, P.O. Box 461, SE-40530 Göteborg, Sweden*

<sup>2</sup> *Swedish Meteorological and Hydrological Institute, SE-60176 Norrköping, Sweden*

<sup>3</sup> *Swedish Environmental Research Institute, P.O. Box 53021, SE-40014 Göteborg, Sweden*  
Corresponding author: [hakan.pleijel@bioenv.gu.se](mailto:hakan.pleijel@bioenv.gu.se); tel +46 31 7862532; fax +46 31 786 2560

The impact of climate change and changes in ozone precursor emission on growing season ozone concentrations and AOT40 in Europe was studied. In addition, meteorological factors affecting stomatal uptake of ozone were investigated to find out if climate change is likely to enhance or reduce the risk for ozone damage to vegetation by influencing plant gas exchange. Climate simulations based on the IPCC SRES A1B scenario were combined with ozone precursor emission changes suggested by the RCP4.5 scenario and used as input the eulerian Chemical Transport Model (CTM) MATCH from which ozone data were derived. Details of the model setup can be found in Langner et al. (2012).

Provided that the climate projections are realistic and the emission reductions suggested by the emission scenario are undertaken, the ozone concentrations over Europe will be significantly reduced between 1990-2009 and 2040-2059. Since the frequency of exceeding hourly concentrations above 40 ppb declines strongly, the reduction in AOT40 between 1990-2009 and 2040-2059 is more pronounced than the reduction in average ozone concentrations. In an earlier study, Klingberg et al (2011) showed that, at constant emissions, climate change will result in higher ozone concentrations, especially in southern Europe, partly because of less ozone deposition to vegetation. The large reductions of ozone concentrations and AOT40 obtained in the present study are driven by the emission reductions assumed by the RCP4.5 scenario.

As expected, higher temperatures in a future climate will lead to a longer growing seasons over Europe and larger temperature sums during the growing season. Temperature may be an important limiting factor for gas exchange in colder parts of Europe. Both the extended growing season and higher temperatures could thus lead to enhanced ozone uptake by plants in these areas. The future climate, as suggested by the regional climate model, will be characterised by dryer conditions in terms of higher vapour pressure deficit (VPD) and lower soil moisture in south and south-east Europe, to an extent which may have profound effects on vegetation. This would lead to less ozone uptake by vegetation. VPD and soil moisture was not indicated to change in north and north-west Europe in a way that would influence ozone uptake by vegetation positively or negatively in the period between 1990-2009 to 2040-2059.

This study shows that substantial reductions of ozone precursor emissions, if implemented, have the potential to strongly reduce the risk for ozone effect on vegetation over Europe, even if concurrent climate change to some extent promotes ozone formation. Ozone uptake by vegetation is likely to be reduced by dry conditions in south Europe over the next 40-50 years, while higher temperatures may enhance ozone uptake in north Europe.

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## MIDDLE-TERM BIOMONITORING OF VLORA-FIER AREA, ALBANIA

Qarri F.<sup>1</sup>, Lazo P.<sup>2</sup>

<sup>1</sup> University "I. Qemali", Vlora, <sup>2</sup> University of Tirana, e-mail: [flora.qarri@gmail.com](mailto:flora.qarri@gmail.com)

The aim of this survey is the comparison of air pollution in the different sites of Vlora-Fier area, Albania. The use of mosses as biomonitors of heavy metal deposition has been extensively applied in numerous studies in the last years. This study is presently being implemented, where samples are collected in the south of Albania and a comparison is made between the results of the two cities. Samples of *Hypnum cupressiforme* were collected in 10 sites in this area, and the concentration of Cd, Cr, Cu, Fe, Mn, Ni, Pb, Hg, K, Na and Zn was determined for each sample. Heavy metals (Cu, Pb, Zn, Mn, Fe and Cd) were determined by atomic absorption spectrometry by using flame/and or electrothermal system. CVAAS was used for mercury determination and atomic emission spectrometry for K and Na determination. Contamination factor (CF) was calculated to point out the contamination level of the area. Some differences in trace metal concentration was found in Vlora area caused by coastal factors, expressed by the negative correlation coefficients between Na and Al, Ba, Fe, Cr, Li and Ni in Vlora coastal area. We have been tried to categorize different places on the basis of metal concentrations in the mosses and data statistical treatment.

**Key words:** biomonitor, heavy metals, air pollution, moss survey, AAS method, statistical analysis.

THE EARLY WARNING SYSTEM SAT-O<sub>3</sub> IN CUBA:  
THE PROTECTION OF CROPS AND EFFECTS ON FOOD SECURITY

Ramírez Almogueva Jesús\*. García Trapaga Cesar\*\*. Valdés Valdés Lourdes\*.  
Ramírez Valdés Susej\*.

\* *Institute of Meteorology;*

\*\* *Institute of Applied Technology*

Ozone is an air pollutant that causes more damage to forests, crops and vegetation in general, has a strong influence on the occurrence of pests and diseases. This phenomenon was initially attributed to highly industrialized countries, now extends to other less developed countries such as Cuba and other countries of the "Fourth Region Meteorological". This region presents great contrasts between the degree of economic and ozone levels.

Ranked third among the pollutants involved in global warming as a result of the greenhouse effect, for all these reasons has a direct impact on climate change.

#### MATERIALS AND METHODS.

The economies of most Latin American countries depend heavily on agriculture, the food situation is precarious in many of these countries, but little progress has been made in protecting crops against damage that produces the pollutant Ozone.

Data were collected in different provinces of Cuba, in crops of garlic, onion, and potato.

The basis of this work is an early warning system that lets you know when ozone limits reach harmful to five days in advance

**RESULTS** Cuba: The period of maximum concentrations (from October to March) is the most important for ensuring national food security, because then the principal agricultural crops mature (Ramírez et al. 2010). During this stage, levels of ozone can reach 120 ppb. During March 2010, ozone concentrations were quite evident in the three study sites. In all these sites it was observed that ozone exceeded the permissible limit established in Cuba as hazardous for agricultural crops (40 ppb), when the region was influenced by continental air masses as a consequence of the arrival of cold fronts and high-pressure centers. Although levels of ozone high enough to produce severe crop damage were observed throughout the month, in the first ten days of observation levels rose above 70 ppb, coinciding with hazardous meteorological phenomena. Throughout the country damage to garlic, onions, and potatoes was observed, but in certain places where projections of ozone from the meteorological institute enabled counter-measures to be taken by the agricultural.

In agricultural areas of Cuba have observed severe impacts on agricultural crops caused by ozone, which have threatened the food supply to the population, as in the case of garlic cultivation, where in 1992, 73 were lost % of crops, also the tobacco industry, which is one of the main economic lines in the country, suffered severe damage, these impacts reached in 2500 has seen.

We demonstrated the need for an early warning system for rural areas that can alleviate the damage that produces ozone, as a way of adapting to current climate change at local and regional levels.

## QUANTIFYING UNCERTAINTY OF ELEMENT CONCENTRATIONS IN MOSSES

Sauvage S.<sup>1,2</sup>, Leblond S.<sup>3</sup>, Laffray X.<sup>4</sup>, Coddeville P.<sup>1,2</sup>

<sup>1</sup> *Université de Lille Nord de France, F-59000, Lille, France;*

<sup>2</sup> *Ecole des Mines de Douai, Dpt. Chimie et Environnement, 59508, Douai, France;*

<sup>3</sup> *Muséum national d'Histoire naturelle, SPN / UMR 7205 (OSEB); CP39, 57 rue Cuvier, 75005 Paris, France ; sleblond@mnhn.fr*

<sup>4</sup> *Muséum national d'Histoire naturelle; CP39, 57 rue Cuvier, 75005 Paris, France*

France takes part in the European heavy metals in mosses biomonitoring network (UNECE-LRATP). Four surveys in France were carried out (1996, 2000, 2006 and 2011), covering approximately 500 sampling sites located throughout the country; 13 elements were monitored (Al, As, Cd, Cr, Cu, Fe, Hg, N, Ni, Pb, Sb, V, Zn).

The concentration of an element in a moss sample is used to estimate the exposure of the moss towards air contaminants. However, the use of data from moss survey is based on a relative method of comparing the results between them: spatial comparison between sites or temporal comparison on the same site. Therefore, in order to interpret objectively the results, it is necessary to associate a confidence interval to each concentration value by the measurement uncertainty.

A decomposed approach has been used to estimate the uncertainty following the ISO/GUM: (1) clearly define the measurand, (2) identify exhaustively the sources of uncertainty, (3) quantify these components thanks to several experiment results from previous campaigns (4) combine them to obtain the relative uncertainty. Beside, the final result tacks into account the detection limit of the method and the relative uncertainty.

The relative uncertainty varies from 22% (Cu) to 54% (Cr) for metallic elements while it is 14% for Nitrogen. For most of the elements, the inter-species component remains the main part of the uncertainty except for Cr, Sb and Hg for which analytical method is most important. The spatial variability is found to be significant mainly for Cr and Sb. Nevertheless, additional field results are expected to better estimate this component.

This work gives a first order of magnitude for each element to examine the reliability of results. Therefore it allows to analyze the whole process to identify the main influencing factors and their contribution and finally provide objective improvements for future campaigns.

# LANDSCAPE-SPECIFIC CORRELATION BETWEEN ATMOSPHERIC DEPOSITIONS AND THEIR CONCENTRATIONS IN MOSSES ACROSS EUROPE?

Schröder W<sup>1</sup>, Pesch R<sup>1</sup>, Hertel A<sup>1</sup>, Harmens H<sup>2</sup>, Fagerli H<sup>3</sup>, Ilyin I<sup>4</sup>.

<sup>1</sup> Chair of Landscape Ecology, University of Vechta, PO Box 1553, D-49356 Vechta, Germany, wschroeder@iuw.uni-vechta.de

<sup>2</sup> Centre for Ecology and Hydrology, Bangor, UK, hh@ceh.ac.uk

<sup>3</sup> EMEP-MSC/West, Norwegian Meteorological Institute, Oslo, Norway, h.fagerli@met.no

<sup>4</sup> EMEP-MSC/East, Moscow, Russian Federation, ilia.ilyin@msceast.org

**Background and Aim.** Recent studies corroborated that, across Europe, 1. heavy metal and nitrogen concentrations in mosses are primarily determined by the total deposition of these substances. 2. Correlations between the respective concentrations in mosses and modelled atmospheric depositions vary according to country and substance. 3. Spatial patterns and temporal trends agree well between metal and nitrogen concentrations in mosses and depositions.

**Materials and Methods.** Based on these findings, the statistical association between the concentrations of cadmium, lead, mercury, and nitrogen in mosses and corresponding depositions within ecologically defined land classes across European were investigated. To this end, measurements from the 2005 European moss survey and modelled atmospheric depositions 2005 were intersected with a map depicting the spatial pattern of 40 ecologically defined landscapes across Europe. This map was calculated from data on vegetation, elevation, climate and soil texture using GIS and decision tree techniques. The minimum number of sampling sites required within the landscapes was statistically analyzed. Subsequently, the correlations between the concentrations of cadmium, lead, mercury, and nitrogen in mosses and corresponding depositions were calculated for each of the 40 landscape units.

**Results.** Positive correlation coefficients amounting for Cd up to 0.77, for Hg up to 0.53, for Pb up to 0.67 and for N up to 0.8 were classified and mapped. The next step was to calculate decision tree models allowing for investigating the multivariate interactions between moss concentrations and, amongst others, modelled atmospheric depositions, land use, elevation or moss species within landscapes. This study proved that the number of sampling sites within all participating countries as well as within most of the landscapes covering Europe is sufficient. Additionally, it could be shown that spatial patterns of the correlation between the atmospheric bioaccumulation and deposition vary by substance and landscape.

**Keywords:** Bioaccumulation; biomonitoring; ecological land classification; minimum number

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## INFLUENCE OF SAMPLING LOCATION ON NITROGEN AND TRACE ELEMENT CONTENT IN MOSSES

Skudnik M.<sup>1,\*</sup>, Batič F.<sup>2</sup>, Kastelec D.<sup>2</sup>, Mazej D.<sup>3</sup>, Simončič P.<sup>4</sup> & Jeran Z.<sup>3</sup>

<sup>1</sup> *Department of Forest and Landscape Planning and Monitoring, Slovenian Forestry Institute, Večna pot 2, 1000 Ljubljana, Slovenia. mitja.skudnik@gozdis.si*

<sup>2</sup> *Department of agronomy, Biotechnical faculty, University of Ljubljana, Jamnikarjeva 101, 1000 Ljubljana, Slovenia*

<sup>3</sup> *Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*

<sup>4</sup> *Department of Forest Ecology, Slovenian Forestry Institute, Večna pot 2, 1000 Ljubljana, Slovenia*

In 2010 the fourth national moss survey was performed in Slovenia. As some discrepancies from previous surveys were found in the results, a systematic sampling approach was performed in 2010 aiming to test the influence of sampling site characteristics on element levels in mosses. Moss samples (*Hypnum cupressiforme*) were collected at 113 locations that were regularly distributed throughout the country on a 8 x 16 km grid which is also part of the national forest inventory sampling grid, including 18 locations near plots of the Intensive Monitoring Programme (UN-ECE ICP-Forest) in Slovenia and neighbouring countries. At each sampling plot two types of samples, namely below the canopy and in the gap were taken and analysed for selected elements (trace elements, nitrogen and sulphur). Additional explanatory variables collected in the field or later by GIS were moss variables (distance to nearest tree, distance to nearest shrub), forest variables (tree types, tree height, basal area, canopy closure, age of stand), relief variables (elevation, slope, exposition, type of bedrock), climate variables (yearly averages of precipitation, air temperature, sunshine duration, snow cover and average wind speed), and land use within a radius of 500, 1000 and 5000 m (% of forest land, crop land, grassland, settlement land and waterland).

Statistical analyses showed that there was a statistical significant linear correlation between element concentration in mosses in the gap and below the canopy for all measured elements, and that the significant higher element concentrations were found for all elements below the canopy. The highest ratios between element concentration below canopy and in the gap were for Cu (1.38), N (1.33), Pb (1.29), S (1.28), V (1.25), Mo (1.25), Ni (1.22) and As (1.21).

In the next step we tried to find linear models for the estimation of element concentrations in the gap on the basis of the element concentration below the canopy and on the basis of additional explanatory variables mentioned above. For the elements Cu, Ni, Pb, Sb, Zn, S and N there were significant influences of some of the chosen explanatory variables on the concentration of the elements in the gap. Influential variables differed between elements and comprised: yearly average of precipitation, type of bedrock (carbonate or non-carbonate soils), distance to nearest tree canopy, growing stock of surrounding trees, age of surrounding trees and canopy closure. Linear models did not explain high enough fraction of the total variation, to be used for good prediction of the element concentration in the gap on the basis of the element concentration below the canopy and other explanatory variables for a particular location ( $0.49 < R^2 < 0.72$ ). For other elements As, Cd, Co, Cr, Fe, Mo and V there was no significant influence of the chosen additional explanatory variables on the concentration of the elements in the gap.

## CROATIAN MOSS SURVEY 2010 - PRELIMINARY RESULTS

Špirić, Z.<sup>1</sup>, Stafilov T.<sup>2</sup>, Kušan V.<sup>1</sup>, Vuckovic I.<sup>2</sup> and Frontasyeva M.<sup>3</sup>

<sup>1</sup> OIKON Ltd. – Institute for Applied Ecology, Trg senjskih uskoka 1-2, 10020 Zagreb, Croatia, zspiric@oikon.hr

<sup>2</sup> Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, Skopje, Macedonia

<sup>3</sup> Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Moscow, Russia

For the second consecutive time, Croatia participated in moss 2010 survey within the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops heavy metals in Europe. Moss samples were collected during the summer/autumn 2010, from 121 locations evenly distributed across the country with additional samples in/around urban/industrial areas (with a total of 161 locations). The map of 2010 sampling points is shown in Fig. 1.

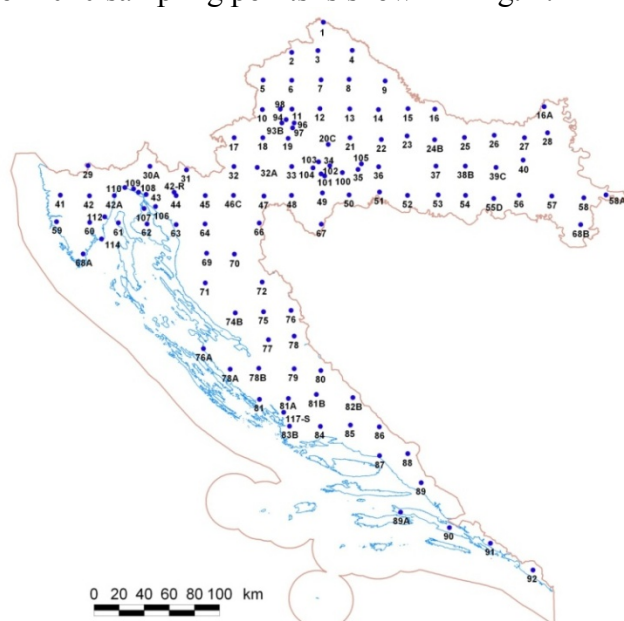


Fig. 1. CRO 2010 moss sampling points

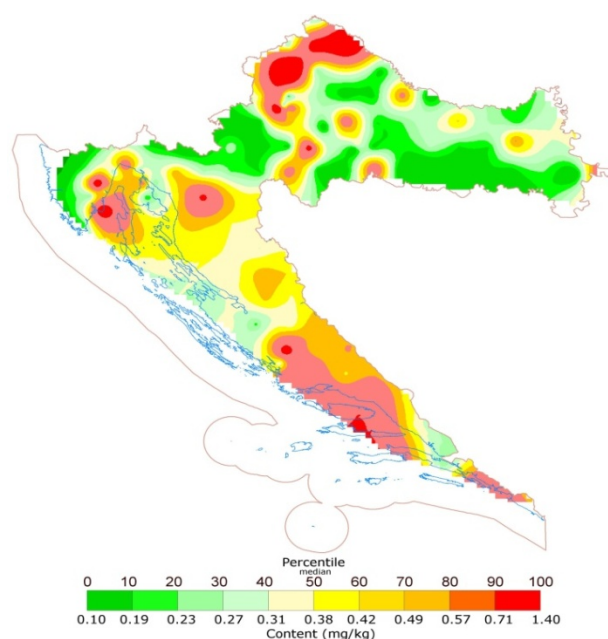


Fig. 2. Distribution of Cd in CRO 2010 moss samples

The content of 21 elements was determined by ICP-AES and AAS. From data obtained in 2010, it can be concluded that the median values and ranges of all elements obtained in this study are very similar to the median values and ranges obtained in the previous study in 2006 (Špirić *et al.*, 2012). Only a few elements have slightly higher values for medians. Median value for Cd (Fig 2 Distribution map) is 1.4 times higher, for Cu 1.13, for Mg 1.44, for Ni 1.17, and for Pb 1.3 times higher. For some typical anthropogenic elements such as Cr, Hg, V and Zn, lower median values have been recorded. For these elements in 2006, median values of 2.8 mg kg<sup>-1</sup>, 0.064 mg kg<sup>-1</sup>, 3.1 mg kg<sup>-1</sup> and 29 mg kg<sup>-1</sup> respectively have been measured, while in the present study for the same elements median values of 1.94 mg kg<sup>-1</sup>, 0.043 mg kg<sup>-1</sup>, 2.55 mg kg<sup>-1</sup> and 24.8 mg kg<sup>-1</sup>, have been measured. According to this comparison, it is obvious that the state of anthropogenic pollution in the last five years has not changed significantly, although it is obvious that the anthropogenic influence is decreasing.

**Reference.** Špirić Z, Frontasyeva M, Steinnes E, Stafilov T. (2012): Multi-element atmospheric deposition study in Croatia, *International Journal of Environmental Analytical Chemistry*, *International Journal of environmental analytical chemistry*, 92:10, 1200-1214.

IS TERRESTRIAL MOSS A USEFUL SUBSTRATE FOR ASSESSMENT OF  
THE ATMOSPHERIC DEPOSITION OF POPs?  
IMPLICATIONS FROM THE 2010 MOSS SURVEY IN NORWAY

Steinnes, E.<sup>1</sup>, Schlabach, M.<sup>2</sup>, Schuster, J.K.<sup>3</sup>, Jones, K.C.<sup>3</sup>

<sup>1</sup> *Dept. of Chemistry, Norwegian Univ. of Science and Technology, Trondheim, Norway*

<sup>2</sup> *Norwegian Institute for Air Research, Kjeller, Norway*

<sup>3</sup> *Lancaster Environment Center, Lancaster University, Lancaster, UK*

During the 2010 moss survey in Norway samples were collected at 20 different sites all over the country in order to assess the feasibility of the moss technique for studying atmospheric deposition of some frequently studied groups of POPs. 3-litre samples of *Hylocomium splendens* were collected in pre-cleaned glass jars and stored at -20°C until analysis. The following compounds/groups were determined: PCB, DDT and metabolites, HCB and PeCB, HCH, PBDE, and PAH. This presentation is concentrated on the observed geographical distributions of persistent chlorinated and brominated compounds and their relation to previous data for the same substances in surface soil and SPMDs (semi-permeable membrane devices). The concentrations in surface soil are presumably related to the integrated atmospheric deposition of slightly volatile compounds, whereas their contents in SPMDs rather reflect their relative air concentrations. Some of the most prominent trends observed were as follows:

- Most of the substances showed the highest levels in moss in the far south, indicating input from trans-boundary pollution. This is the case for the DDT group, most of the PAHs, HCB, PeCB, PBDE, and the heavier PCBs.
- Fractionation of lighter PCB congeners relative to heavier ones with northern latitude is evident in moss in a similar way as previously shown for SPMDs.
- PCB in moss is not correlated with PCB in surface soil.
- The data for PBDE are generally consistent with previous data from the same sites based on moss samples collected in 2003.

Although there are no over-all strong correlations between the studied POPs in moss samples and their levels in either organic-rich surface soils or SPMDs, the results indicate that moss may be a useful substrate for demonstrating the exposure of POPs to terrestrial surfaces.

# RELATIONSHIP BETWEEN SITE-SPECIFIC NITROGEN/SULPHUR CONCENTRATIONS IN MOSSES AND ATMOSPHERIC NITROGEN/SULPHUR DEPOSITION RATES IN SELECTED EUROPEAN COUNTRIES: PRELIMINARY RESULTS

Thöni L.<sup>a</sup>, Harmens H.<sup>b</sup>, Leblond S.<sup>c</sup>, Mohr K.<sup>d</sup>, Poikolainen J.<sup>e</sup>, Santamaria J.M.<sup>f</sup>, Skudnik M.<sup>g</sup>, Zechmeister H.<sup>h</sup>

<sup>a</sup> FUB – Research Group for Environmental Monitoring, Alte Jonastr. 83, CH-8640 Rapperswil, Switzerland (lotti.thoeni@fub-ag.ch)

<sup>b</sup> Centre for Ecology and Hydrology, Bangor, Gwynedd LL57 2UW, UK. (hh@ceh.ac.uk)

<sup>c</sup> Muséum d'Histoire Naturelle, 57 rue Cuvier, F-75005 Paris (sleblon@mnhn.fr)

<sup>d</sup> Landwirtschaftskammer Niedersachsen, FB.3.12, Mars-la-Tour Str. 1-13, D-26121 Oldenburg, Germany (Karsten.Mohr@LWK-Niedersachsen.de)

<sup>e</sup> METLA – Finnish Forest Research Institute, Muhos, Kirkkosaarentie 7, FI-91500 Muhos, Finland (jarmo.poikolainen@metla.fi)

<sup>f</sup> Universidad de Navarra, Departamento de Química y Edafología, LICA c/ Irunlarrea 1, E-31008 Pamplona, Spain (chusmi@unav.es)

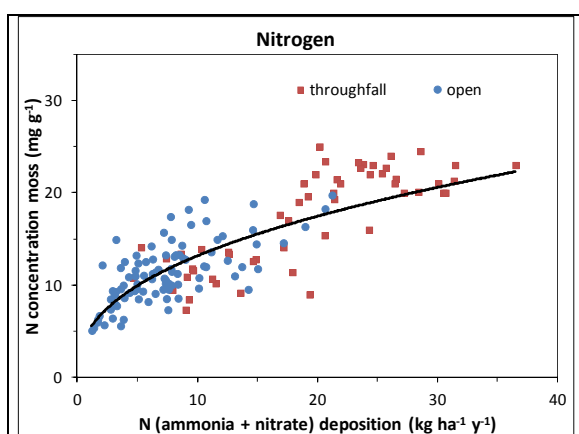
<sup>g</sup> Slovenian Forestry Institute, Department of Forest and Landscape Planning and Monitoring, Vecna pot 2, SI-1000 Ljubljana, Slovenia (mitja.skudnik@gozdis.si)

<sup>h</sup> University of Vienna, Faculty of Life Sciences, Rennweg. 14, A-1030 Vienna, Austria (harald.zechmeister@univie.ac.at)

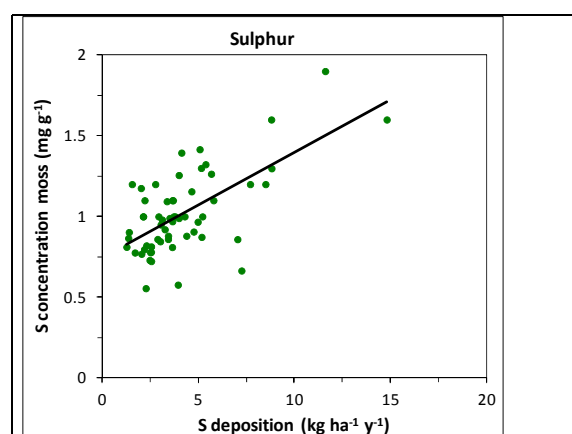
Previously, an asymptotic relationship was found between EMEP modelled total nitrogen deposition rates and total nitrogen (N) concentrations in mosses (each averaged per 50km x 50km EMEP grid; Harmens et al., 2011). In the current study we compared measured N deposition with the total N concentration in mosses at sites not more than 1 km distance from each other. Initial data analysis also confirms a non-linear relationship between the measured parameters (Fig. 1). Generally, higher N deposition rates and concentrations in mosses were observed at ‘throughfall’ deposition sites in forests.

Although a linear relationship was found between sulphur deposition and concentrations in mosses (data from Austria, Germany, Slovenia, Switzerland; Fig. 2), it should be noted that this is primarily driven by a few sites with high sulphur deposition.

Points for further analysis and discussion include (i) overall variability of the measured parameters, (ii) statistical analyses and curve fitting, (iii) inter-species variation, (iv) definition of “open” and “throughfall” sites, (v) N from nitrate/ammonia vs. total N (incl. organic) in deposition, and (vi) country-specific variation.



**Fig. 1.** Relationship between nitrogen in moss and deposition (nitrate + ammonia).



**Fig. 2.** Relationship between sulphur in moss and deposition (sulphate).

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## GENETIC APPROACHES TO INCREASE TOLERANCE TO OZONE IN RICE

Ueda Y.<sup>1</sup>, Wang Y.<sup>2</sup>, Wissuwa M.<sup>3</sup>, Frei M.<sup>1</sup>

<sup>1</sup> *Institute of Crop Science and Resource Conservation (INRES) – Plant Nutrition, University of Bonn, Germany, ueda@uni-bonn.de*

<sup>2</sup> *Key Lab of Crop Genetics & Physiology of Jiangsu Province, Yangzhou University, China*

<sup>3</sup> *Crop Production and Environment Division, Japan International Research Center For Agricultural Sciences, Tsukuba, Japan*

Due to anthropogenic gas emission, the concentration of tropospheric ozone is increasing. Since the industrial revolution tropospheric ozone concentrations have significantly increased along with industrial development, and they will increase further in the future. Ozone has high oxidative capacity and therefore is highly toxic to humans and plants. It is known that ozone decreases photosynthetic rate and plant growth, leading to decreased crop yields. Considering the food security in the 21<sup>st</sup> century, it is essential to identify the possible mechanisms to increase ozone tolerance of crops. In our investigation we focus on the effect of ozone on rice, which is the major staple crop in Asia, where the strongest increases in future ozone concentration have been projected.

To dissect genetic factors associated with ozone tolerance in rice, we first conducted genotype screening followed by a QTL mapping study, in which chromosomal regions associated with ozone tolerance were identified. Experiments with chromosome segment substitution lines confirmed that these chromosomal regions affected ozone tolerance. Season long exposure to different ozone levels did not lead to clear differences in grain yield, but significant differences were seen in plant composition and quality between tolerant and intolerant lines. Transcriptome analyses using contrasting genotypes with chromosomal introgressions at QTL positions led to the identification of a gene potentially involved in ozone tolerance, namely an ascorbate oxidase (AO). AO expression was highly induced by ozone stress, and the tolerant and the intolerant lines showed significantly different expression patterns. Current experiments using gene knockout and over-expression lines aim at further characterizing the involvement of this gene in ozone tolerance. Knockout lines were less responsive to ozone in terms of tiller number, visible symptoms, and grain yield. Vice versa, an AO over-expression line showed higher susceptibility to ozone.

In order to enlarge the genetic pool for ozone tolerance screening, we are currently preparing a Genome-Wide Association Study (GWAS) using an association panel consisting of around 350 different genotypes representing the entire genetic diversity in rice. Loci associated with ozone tolerance will be mapped using available marker data for currently around 40 000 single nucleotide polymorphisms (SNP). With additional marker data becoming available soon (up to 700 000 SNP) this project may allow to map ozone tolerance genes at very high resolution, thus contributing substantially to the advancement of breeding for ozone resistance.

PAH IN MOSS FROM NORWAY: SPATIAL DISTRIBUTION AND COMPARISON  
WITH METAL CONCENTRATIONS.

Uggerud H.<sup>1</sup>, Steinnes, E.<sup>2</sup>, Schlabach, M.<sup>1</sup>, and Berg, T.<sup>2</sup>

<sup>1</sup>*NILU(Norwegian Institute for Air Research), P.O.Box 100, N-2027 Kjeller. htu@nilu.no*

<sup>2</sup>*Department of Chemistry, Norwegian University of Science and Technology, N-7469  
Trondheim, Norway.*

The geographical distribution of atmospheric deposition of heavy metals in Norway has been monitored every fifth year since 1977 by analysis of moss samples (*Hylocomium splendens*) from sites distributed all over mainland Norway. In 2010, determinations of selected persistent organic pollutants were included in the survey as a contribution to the evaluation of terrestrial moss as a sample medium for these compounds. In the time period May to September 2010, samples were collected from 20 sites from all parts of the country. PAH concentrations were determined by high resolution gas chromatography in combination with low resolution mass spectrometry. In the present talk concentrations and spatial distribution of 16 PAH will be presented. In addition, results from statistical treatment of PAH concentrations with heavy metal data from 2010 will be shown.

**Abstracts**

**Posters**

# BRIDGING THE GAP: INCORPORATING A CANOPY EXCHANGE PROCESS MODEL IN A DYNAMIC GLOBAL VEGETATION MODEL

Ashworth K.<sup>1</sup>, Ganzeveld L.<sup>2</sup>, Arneth A.<sup>1</sup>

1. *Ecosystem-Atmosphere Interactions, Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research-Atmospheric Environmental Research, Kreuzeckbahnstrasse 19, 82467 Garmisch-Partenkirchen, Bayern, Germany; kirsti.ashworth@imk.fzk.de; almut.arneth@kit.edu*

2. *Department of Environmental Sciences, Wageningen University and Research Centre, Lumen, Droevendaalsesteeg, Netherlands; Laurens.Ganzeveld@wur.nl*

Currently, the overwhelming majority of coupled land-surface-atmosphere models, regardless of resolution and overall complexity, do not include a representation of the canopy. Furthermore, the bottom-most layer of the atmosphere is often 10s of metres in height, with physical and chemical processes within that layer assumed to take place at mid-height. This may, depending on the nature of the vegetation, be well above or below the canopy surface. This results in a decoupling of the atmosphere and biosphere within the model with implications that are not understood but which may significantly affect model projections, particularly regarding interactions between the biosphere and atmosphere under future global change. This project seeks to address this issue by coupling a canopy exchange model (MLC-CHEM - Multi-Layer Canopy-Chemistry Exchange Model) into the LPJ-GUESS DGVM. MLC-CHEM incorporates all aspects of physical and chemical processes within the canopy, while LPJ-GUESS simulates the biological processes within the terrestrial biosphere. Coupling the two models will result in a detailed 1D model of canopy exchange processes that will enable us to explore and evaluate the significance of such processes on atmospheric chemistry and composition, and hence air quality and climate. The results of our investigations will inform the conditions (environmental, chemical, physical and biological) under which such exchange processes are important enough to be fully included in 3D regional and global modelling, when they could be parameterised without loss of detail in larger scale simulations, and when they could be safely ignored. Here, I present an overview of the potential of such an exciting and ambitious development project, which encompasses many of the objectives of ICP and LRTAP. Specifically, the project will address the scientific question that bVOCs protect plant cells from oxidative damage caused by the deposition and uptake of atmospheric (ground-level) ozone, taking the hypothesis that high bVOC-emitting species have a competitive advantage over co-located low bVOC-emitting species in a world of increasing atmospheric ozone concentrations. The coupled model will be evaluated, developed and utilised across the full range of spatial scales from single point through regional to global. The project will encompass a variety of techniques, approaches and studies; from highly specific model-measurement comparisons to speculative “what if?” scenarios. The project builds on previously highly successful work of both individual models to simulate biosphere-atmosphere interactions (see e.g. Ganzeveld and Lelieveld, 2002; Sitch et al., 2003), as well as novel data-mining techniques developed for use at ICP Forest sites within Europe (see e.g. Laubhann et al., 2009; Solberg et al., 2009). The performance of the coupled model will first be evaluated against long-term forest growth data from the ICP Forest Level II sites in Europe. Evaluation against fluxes of bVOCs, N-compounds and ozone will be carried out using data from the ECLAIRE flux network as it becomes available. It is hoped that this presentation will provide a springboard for discussion and invite ideas, suggestions and contributions from the wider ICP and LRTAP communities.

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## AIR POLLUTION STUDY IN MACEDONIA BY USING MOSS BIOMONITORING TECHNIQUE, ICP-AES AND AAS

Barandovski L.<sup>1</sup>, Stafilov T.<sup>2</sup>, Šajn R.<sup>3</sup>, Frontasyeva M.V.<sup>4</sup>, Bačeva K.<sup>2</sup>

<sup>1</sup> *Institute of Physics, Faculty of Natural Sciences and Mathematics, Ss Cyril and Methodius University, POB 162, 1000 Skopje, Macedonia.*

<sup>2</sup> *Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss Cyril and Methodius University, POB 162, 1000 Skopje, Macedonia; trajcest@pmf.ukim.mk*

<sup>3</sup> *Geological Survey of Slovenia, Dimičeva ul. 14, 1000 Ljubljana, Slovenia.*

<sup>4</sup> *Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Moscow Region, Russian Federation.*

In the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops under the auspices of the United Nations Economic Commission for Europe (UNECE-ICP Vegetation) Convention on Long-Range Transboundary Air Pollution (LRTAP), in 2002 and 2005 moss biomonitoring technique was applied to air pollution studies in the Republic of Macedonia. The third moss survey took place in August and September 2010 when 72 samples of the terrestrial mosses *Homalothecium lutescens* and *Hypnum cupressiforme* were collected over the territory of the Republic of Macedonia, using the same sampling network grid as for the previous surveys. Using inductively coupled plasma - atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS), total of 18 elements (Al, Ba, Ca, Cd, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Ni, P, Pb, Sr, V and Zn) were determined. To reveal hidden multivariate data structures and to identify and characterize different pollution sources Principal Component Analysis was used. Distributional maps were prepared to point out the regions most affected by pollution and related to known sources of contamination. As in the previous surveys, the regions near the towns of Skopje, Veles, Tetovo, Radoviš and Kavadarci were found as most affected by pollution, even the median elemental content in the mosses in 2010 for Cd, Cr, Cu, Ni, Pb and Zn are slightly lower than the previous surveys. For the first time P content in the moss samples was analyzed and the higher content of this element as well as K in the mosses was observed in the agricultural regions of the country.

## OZONE FLUX ASSESSMENT IN A SPANISH BEECH STAND

Bermejo R.(\*), Elustondo D., Izquieta S., Lasheras E. and Santamaría J.M.

LICA, University of Navarre. Irunlarrea 1, 31080 Pamplona, Spain. (\*)[rberord@unav.es](mailto:rberord@unav.es)

Widespread evidence on the deleterious effects of O<sub>3</sub> on vegetation and crops in Europe has been extensively documented during the last decades. The DO<sub>3</sub>SE model constitutes a feasible tool for the estimation of the dose absorbed by plants and is thus extensively used for the assessment of O<sub>3</sub> risk to vegetation and crops within the framework of the LRTAP Convention (Mills et al. 2011).

This communication presents preliminary sap flow data, obtained during the 2012 growing season from old-growth beech trees growing in the western Pyrenees in Spain. The study aims at inferring the O<sub>3</sub> dose absorbed by the trees and providing data from mature trees growing in field conditions to contrast with DO<sub>3</sub>SE estimations.

The experimental site is an active ICP IM network site since 2007 and is located within the Señorío de Bertiz Natural Park, where forest management activities were suspended over a century ago. Sap flow was estimated using the THB approach (Čermák et al. 2004; Fig.1) from the leaf sprout in April to the leaf drop in mid November. Soil water content, meteorological parameters and O<sub>3</sub> concentrations were also registered at the site. The AOT40 critical level for the protection of forests was exceeded in May; the O<sub>3</sub> levels scored an hourly maximum of 158 µg m<sup>-3</sup> (Fig.2). Mean temperature was 17.5°C and ranged from 0°C to 41°C. There were 89 days of rainfall that totalled 828 mm of precipitation. Maximum solar radiation values were over 1200 W m<sup>-2</sup>.

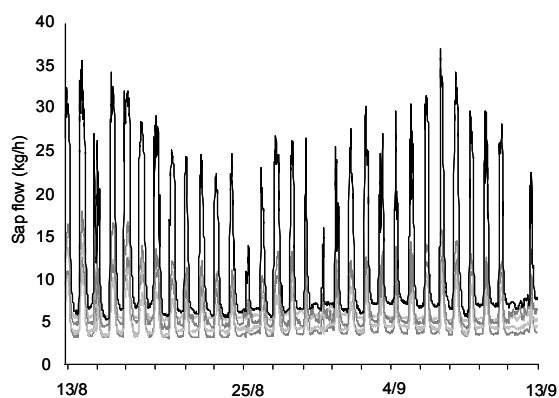


Fig.1. Raw sap flow data in beech trees at Bertiz ES02.

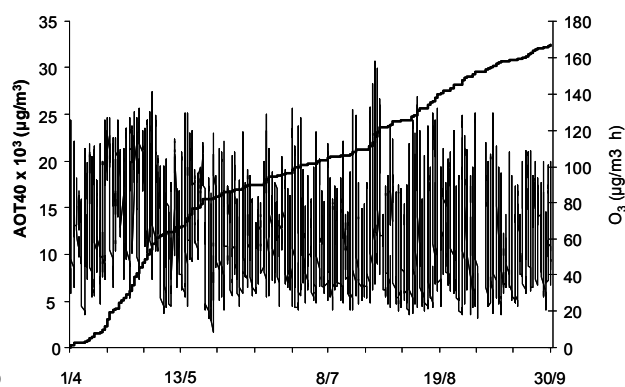


Fig.2. Evolution of O<sub>3</sub> levels and AOT40 at Bertiz ES02.

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## A COMPARISON OF THE OZONE RESPONSE OF TWO PAIRS OF SENSITIVE AND TOLERANT SNAP BEANS

Kent O. Burkey, Amy Burton

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

Snap bean random inbred lines derived from a cross between ozone (O<sub>3</sub>)-sensitive and tolerant parents (Reinert and Eason, 2000) are being tested as an O<sub>3</sub> bio-indicator system. Two pairs of O<sub>3</sub>-sensitive (S) and tolerant (R) snap bean genotypes, S156/R123 and S129/R331, were originally established based on similar yield under clean air conditions and differential yield responses reflected in declining yield ratios when grown in elevated O<sub>3</sub> environments. The S156/R123 pair has been tested previously in open-top chambers (Burkey et al., 2000) and is currently being utilized in the ICP-Vegetation snap bean project.

In a 2012 open-top chamber study, S156/R123 and S129/R331 yield ratios declined as expected with increasing O<sub>3</sub> exposure (Table 1). However, pod yields for R123 were lower in the CF controls than in the AA treatment. This phenomenon was associated with elevated numbers of undeveloped pods in open-top chamber plots (Table 2), suggesting that the differential yield potential of R and S lines may be affected by factors other than O<sub>3</sub> under certain conditions. High temperature effects on reproductive growth are one critical factor to consider. Daytime temperatures averaged 3°C higher in 2012 than in the previous open-top chamber study during the critical July period of pollination and pod development.

**Table 1.** Snap bean genotype pairs, S156/R123 and S129/R331, were compared under charcoal-filtered (CF) or non-filtered (NF) air treatments in open-top chambers as well as ambient air (AA) plots during the summer of 2012. Plants were grown in 15-liter pots of Sunshine MVP mix with Osmocote Plus slow-release fertilizer following the ICP-Vegetation snap bean protocol. The experiment consisted of twelve plots (4 blocks x 3 O<sub>3</sub> treatments) with 4 plants per genotype randomly assigned in each plot. Pod yield was measured as g plant<sup>-1</sup> and included both mature pods with seeds and small, undeveloped pods without seeds. Values are chamber means ± standard error (n = 4).

| Treatment | AOT40<br>ppbO <sub>3</sub> -hr | S156<br>pod yield (g plant <sup>-1</sup> ) | R123<br>pod yield (g plant <sup>-1</sup> ) | S156/R123<br>yield ratio | S129<br>pod yield (g plant <sup>-1</sup> ) | R331<br>pod yield (g plant <sup>-1</sup> ) | S129/R331<br>yield ratio |
|-----------|--------------------------------|--|--|--------------------------|--|--|--------------------------|
| CF        | 968                            | 72 ± 7                                     | 49 ± 10                                    | 1.57 ± .20               | 74 ± 6                                     | 69 ± 3                                     | 1.08 ± .09               |
| NF        | 6216                           | 49 ± 4                                     | 40 ± 2                                     | 1.23 ± .11               | 57 ± 4                                     | 66 ± 8                                     | 0.92 ± .16               |
| AA        | 7005                           | 39 ± 1                                     | 68 ± 4                                     | 0.58 ± .05               | 50 ± 1                                     | 74 ± 9                                     | 0.71 ± .09               |

**Table 2.** Assessment of undeveloped pods in the S156/R123 and S129/R331 snap bean pairs for the experiment described in Table 1. Values are chamber means ± standard error (n = 4).

| Treatment | Undeveloped Pods (number plant <sup>-1</sup> ) |          |        |          |
|-----------|--|----------|--------|----------|
|           | S156   | R123     | S129   | R331     |
| CF        | 26 ± 8   | 306 ± 26 | 40 ± 5 | 235 ± 20 |
| NF        | 47 ± 4   | 337 ± 11 | 47 ± 7 | 234 ± 23 |
| AA        | 13 ± 2   | 71 ± 3   | 16 ± 4 | 75 ± 11  |

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OZONE EFFECTS ON GRAPEVINE:  
AN OPEN TOP CHAMBER STUDY

Fumagalli, I.<sup>1</sup>, Cieslik, S.<sup>1</sup>, Gottardini, E.<sup>2</sup>, Cristofolini F.<sup>2</sup>,  
Cristofori, A.<sup>2</sup>, De Marco, A.<sup>3</sup>, Paoletti, E.<sup>4</sup>;

<sup>1</sup>Joint Research Centre, Ispra, Italy. [ivan.fumagalli@jrc.ec.europa.eu](mailto:ivan.fumagalli@jrc.ec.europa.eu);  
[stanislaw.cieslik@jrc.ec.europa.eu](mailto:stanislaw.cieslik@jrc.ec.europa.eu)

<sup>2</sup>Fondazione Edmund Mach, S. Michele all'Adige, Italy. [elena.gottardini@fmach.it](mailto:elena.gottardini@fmach.it);  
[fabiana.cristofolini@fmach.it](mailto:fabiana.cristofolini@fmach.it); [antonella.cristofori@fmach.it](mailto:antonella.cristofori@fmach.it)

<sup>3</sup>ENEA, Rome, Italy. [alessandra.demarco@casaccia.enea.it](mailto:alessandra.demarco@casaccia.enea.it)

<sup>4</sup>CNR/IPP, Florence, Italy. [e.paoletti@ipp.cnr.it](mailto:e.paoletti@ipp.cnr.it)

An open top chamber (OTC) study has been conducted during the growing seasons of 2010 and 2011 over a vineyard located in Angera, northern Italy. Four OTCs were used. Two of them were fumigated with air from which ozone had been partly eliminated, and two others were fumigated with ambient air. Ozone concentration was monitored in both filtered and non-filtered chambers, as well as in outside air. At harvest time, grapevine bunches grown inside and outside the OTCs were cut and investigated for various ponderal and chemical parameters. Results were compared with ozone exposure (AOT40) and phytotoxic ozone dose (POD) as calculated by the DO<sub>3</sub>SE model.

Grapes exposed to enhanced ozone doses or concentrations showed sensitivity towards weight per bunch, degree Brix (related to sugar content), malic acid and polyphenol concentrations. Ozone thus seems to affect both yield (volume of wine production) and quality of the final product.



AN OZONE RESPONSE RELATIONSHIP FOR FOUR *PHLEUM PRATENSE*  
GENOTYPES BASED ON MODELLING OF THE PHYTOTOXIC OZONE DOSE (POD)

Danielsson, H.<sup>\*a</sup>, Karlsson, P E.<sup>a</sup> and Pleijel, H.<sup>b</sup>

<sup>a</sup> IVL Swedish Environmental Research Institute, P.O. Box 53021, SE-400 14 Göteborg, Sweden

<sup>b</sup> Department of Biological and Environmental Sciences, University of Gothenburg, P.O. Box 461, SE-405 30 Göteborg, Sweden

\*[helena.danielsson@ivl.se](mailto:helena.danielsson@ivl.se)

In the last decade extensive research has focussed on the development of dose-response relationships based on stomatal plant ozone uptake (Phytotoxic Ozone Dose, POD). So far most work has concentrated on crops and forest trees. This study provides a flux-based dose-response function for timothy (*Phleum pratense*), a widespread grassland species, which can be used in risk assessment for ground-level ozone. In 1996 and 2001 timothy was exposed in open-top chambers to ozone concentrations ranging from around 10 nmol mol<sup>-1</sup> in the charcoal filtered treatments up to 60 nmol mol<sup>-1</sup> in the fumigated treatments (08:00 – 20:00). In 1996 there was a negative effect of ozone on biomass production in the non-filtered treatment while in 2001 no such ozone effect in the non-filtered treatment could be seen. Measurements of stomatal conductance on four timothy genotypes in 2001 were used to calibrate a Jarvis-type multiplicative stomatal conductance model. The maximum conductance varied between the genotypes, from 477 to 589 mmol O<sub>3</sub> m<sup>-2</sup> s<sup>-1</sup> (projected leaf area). The model includes functions describing the reduction of stomatal conductance of senescing leaves and the direct effects on stomatal conductance by light, temperature and water vapour pressure deficit. A function describing ozone induced senescence of the leaves was included since exposure to ozone is known to cause premature senescence. The function for ozone was applied when it suggested ozone to be more limiting to stomatal conductance than phenology. To avoid overestimation of stomatal conductance in days with high VPD, a function reflecting the effect on leaf water potential on stomatal conductance was included. Comparison between modelled and measured conductance for the four timothy genotypes resulted in an r<sup>2</sup> value at 0.57 and a very small average deviation of observed from modelled values. The calibrated stomatal conductance model was used to estimate the accumulated POD, i.e. the accumulated stomatal flux of ozone, of the plants in the 1996 and 2001 experiments. The strongest relationship between ozone relative effects on biomass was obtained when POD was accumulated from 105 degree days after emergence to 1000 degree days after emergence, and integrated using an uptake rate threshold of 7 nmol m<sup>-2</sup> s<sup>-1</sup> (POD<sub>7</sub>). The response relationship between biomass and POD<sub>7</sub> resulted in an r<sup>2</sup> value of 0.71 over all four genotypes. This r<sup>2</sup> value was somewhat higher than for the corresponding relationship based on the accumulated ozone exposure over 40 nmol mol<sup>-1</sup> (AOT40; r<sup>2</sup> = 0.66). With an uptake rate threshold at 7 nmol m<sup>-2</sup> s<sup>-1</sup>, ozone concentrations above ~20 nmol mol<sup>-1</sup>, contribute to reduce the biomass production of timothy if meteorological conditions promote maximum stomatal conductance.

# TRANSFER OF AIRBORNE ARSENIC, CADMIUM AND LEAD TO THE EDIBLE PARTS OF VARIOUS VEGETABLES

De Temmerman L., Ruttens, A., Waegeneers, N.

*CODA-CERVA, Leuvensesteensweg 17, 3080 Tervuren - ludet@coda-cerva.be*

Exposure of vegetable crops for biomonitoring purposes is suitable to study the impact of air borne trace elements. Leafy vegetables accumulate large amounts of trace elements and correlations between atmospheric deposition of Cd and Pb and their accumulation in leafy vegetables were calculated (1). Leafy vegetables accumulate most efficient deposited trace elements on their exposed leaf blades and only part of it can be removed by thoroughly washing. To meet the conditions referring to the maximum tolerable values in the European legislation (3;4) it is better to correlate washed instead of unwashed leafy vegetables with deposition whereas unwashed crops are more suitable for biomonitoring.

The leafy vegetables studied were spinach (*Spinacia oleracea*), lettuce (*Lactuca sativa*), endive (*Cichorium endivia*), lamb's lettuce (*Valerianella locusta*), celery (*Apium graveolens* var. *secalinum*), leek (*Allium porrum*) and curly kale (*Brassica oleracea* convar. *acephala* var. *laciniata*). Even root crops and bulbs can be used for biomonitoring but they are less suitable (2). However, the applied biomonitoring techniques appear to be suitable to study the transfer of atmospheric deposition to the consumable parts (peeled storage organs) of root and bulb crops. Carrots (*Daucus carota*), celeriac (*Apium graveolens* var. *rapaceum*) and onion (*Allium cepa*) were tested. Even bean (*Phaseolus vulgaris*) was used for green and dry harvest.

The test plants were grown in a reference area with low atmospheric deposition and then exposed in a polluted area around a lead smelter for 14 days (spinach and lettuce), 28 days (endive, green beans and lamb's lettuce), 1.5 months for green beans and 2.5 months for the dry harvest, 2 months (onion celery, curly kale and carrots), 3 months (leek) or 4 months (celeriac). In most cases the containers were placed near gardens where vegetables were cultivated. At each experimental plot, the containers were exposed in triplicate allowing statistical treatment of the results. After exposure, the edible parts, leaves, fruits, bulbs were cleaned, washed, dried and analyzed. Also the unwashed leaves were analyzed for comparison reasons. The storage organs of carrot and celeriac were cleaned, washed thoroughly and peeled. At each site, bulk deposition was measured in order to be able to link the results to atmospheric deposition.

Leafy vegetables accumulate most efficiently air borne trace elements and primarily the late season vegetables are showing the highest accumulation rate due to their reduced growth and biomass increase. The storage organs of celeriac and carrot accumulate airborne Cd, Pb and As but in the inner part only a significant accumulation of As and Cd was observed. For lead there is no significant increase. Results for green beans revealed a clear impact of airborne As, Cd and Pb on the green pods + seeds and even on the ripened dry seeds. For onion bulbs, however, there is a clear impact of As and Cd deposition but no effect of Pb deposition was noticed.

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## MEASUREMENTS OF SOIL NO & NO<sub>2</sub> FLUXES IN SUBALPINE FOREST: PRELIMINARY RESULTS

Fumagalli I., Fachinetti D., Gruening C.

*Joint Research Centre, Ispra, Italy, [ivan.fumagalli@jrc.ec.europa.eu](mailto:ivan.fumagalli@jrc.ec.europa.eu)*

In the framework of the FP7 project ECLAIRE (Effects of Climate Change on Air Pollution and Response Strategies for European Ecosystems) a forest flux station on the JRC Ispra site has been equipped recently with new facilities.

In this context, an automated dynamic chamber system for measure NO & NO<sub>2</sub> fluxes from the soil has been installed during 2012 at the JRC. The setup consists of 5 replicate chambers measuring soil fluxes and one chamber that is closed to the ground and thus serves as a measurement blank. The analysers, pumps, control and data acquisition systems are installed in a small trailer.



*Pic. 1: Chamber system to measure NO & NO<sub>2</sub> fluxes from soil at the JRC Ispra forest site.*

During a measurement cycle, the lids of one chamber are closed and the chamber is flushed with approx. 55 l/min for 6 minutes. At the same time, the concentrations of NO, NO<sub>2</sub> are measured at the outflowing air of chamber. To account for concentration changes due to the reaction  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$  in the chamber and sampling lines, the concentration of O<sub>3</sub> is measured as well. Combining the measured concentrations, air flow and chamber size, raw soil fluxes of NO and NO<sub>2</sub> are calculated.

The NO and NO<sub>2</sub> soil flux data from several weeks of measurements are showed and discussed. First results already indicate that the soil is a source for NO and a sink for NO<sub>2</sub> with significant differences between the different chamber positions.

CAN NITROGEN DEPOSITION INFLUENCE THE PERFORMANCE OF TREE SPECIES IN MEDITERRANEAN FOREST? RESULTS FROM A CONTROLLED EXPERIMENT ON *QUERCUS ILEX* L. AND *FRAXINUS ORNUS* L.

Fusaro L.<sup>1\*</sup>, Salvatori E.<sup>1</sup>, Mereu S.<sup>2</sup>, Bei I.<sup>1</sup>, Manes F.<sup>1</sup>.

<sup>1</sup> *Sapienza University of Rome, Department of Environmental Biology, P.le Aldo Moro, 5 – 00185 Rome (Italy)*

<sup>2</sup> *DipNeT-Department of Sciences for Nature and Environmental Resources, University of Sassari, via E. De Nicola 1- 07100 Sassari (Italy)*

\**lina.fusaro@uniroma1.it*

The emissions of ammonia (NH<sub>3</sub>) and nitrogen oxides (NO<sub>x</sub>) have strongly increased in Europe in the second half of the 20th century (Volk et al., 2011). Because of short- and long range transport of these nitrogenous compounds, atmospheric nitrogen (N) deposition is increased in many natural and semi-natural ecosystems (Bobbink et al., 2011). Serious gaps in knowledge exist on the effects of enhanced nitrogen deposition on Mediterranean forests (Ochoa-Hueso et al., 2011). In this area, where the nutrient limitation and drought stress are among the major factor controlling the vegetation functionality, physiological and structural effects of enhanced nitrogen availability can influence biodiversity (Bobbink, 1998), structural composition of ecosystems and also their stress responsiveness. In a controlled open environment experiment, we have evaluated the response to nitrogen addition (30 Kg ha yr<sup>-1</sup>), on two Mediterranean woody species differing for leaf habitus (the evergreen *Quercus ilex* vs the deciduous *Fraxinus ornus*). For the first experimental period (97 days) all plants were watered at field capacity and N was added weekly. After this period, for half plants for each species, the irrigation was suspended, thus simulating summer drought stress conditions. Biomass allocation and photosynthetic properties (leaf gas exchange and photosystems functionality) were measured, in order to evaluate how these species with different nutrient uptake strategies and stress response, are influenced. It's interesting to notice that the N addition didn't have large influence on biomass allocation, but the interaction between the two stress factors had opposite effects on physiology of the two considered species.

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# ATMOSPHERIC DEPOSITION OF HEAVY METALS IN ELBASAN CITY, ALBANIA

Pranvera Lazo<sup>1</sup>, Lirim Bekteshi<sup>1</sup>, Alma Shehu<sup>1</sup>, Flora Qarri<sup>2</sup>

<sup>1</sup> University of Tirana, Faculty of Natural Sciences, Dept. of Chemistry, Tirana, Albania.  
pranveralazo@gmail.com

<sup>2</sup> University "Ismail Qemali", Faculty of Natural Sciences, Department of Chemistry, Vlora, Albania

**ABSTRACT:** The effects of industrial activities associated with ferro-chromium metallurgy and cement production of Elbasan urban area, Albania, were investigated by using the moss-bag technique. Samples of *Hypnum cupressiforme* were collected from a remote unpolluted area (Llogora, N: 40° 12' 31.1"; E: 19° 35' 6.7") in south-west part of Albania.

Metal concentrations in the pre-exposed bags were measured (i.e. background levels). Metal levels determined from moss bags at 14 sites of Elbasan city were exposed for 6 months (September 2011-March 2012) without irrigation. Heavy metals (Cu, Pb, Cd, Zn, Cr, Mn, Ni, Co and Fe) were determined by AAS technique, using flame and/ or electrothermal system. CVAAS was used for Hg as well as AES technique for K and Na determination. For a better interpretation of data, elements, such as K, Na, Ca and Mg, were also included. Concentrations of trace levels of heavy metals (Cu, Pb, Zn, Ni, Co, Cd, Hg), especially in the sites close to the pollution sources, were elevated during the period of exposure. However, examination of the biological state of the exposed mosses indicated that contamination existed near to the pollution sources, with elevated concentrations of Pb, Zn, Mn, Co and Hg. Some cities result to be highly polluted with Mn, Pb, Zn and Hg, emitted from cement industry and metallurgy operation on this area, as well as moderately polluted, due to the vehicular emissions and city dust. Therefore, we have tried to categorize different places of the city on the basis of the metal concentrations in the mosses and data statistical treatment. The comparison of the results with unexposed moss samples allowed us assessing the enrichments factors in exposed moss samples for all determined elements.

Correlation analysis was carried out in order to distinguish different geochemical mobility of the elements.

Most of the analyzed heavy metals were significantly accumulated in *Hypnum cupressiforme* dry moss bags exposed for 6 months in 14 sites of Elbasani urban area, Albania. The range of variation of Pb, Zn, Mn and Hg in moss bag samples is the highest one. Generally, the area was classified to be highly/and or moderately polluted by heavy metals. The main source of these elements is ferro-chrome and steel industry as well as cement industry activity present in this area. By the study of accumulation factors, the elements can be divided into 3 groups. The first group of elements (Zn, Fe, Cu, K and Na) shows low accumulation factors (mean  $AF < 3$ ), the second one (Zn, Fe, Cu, K and Na) moderate accumulation factors (mean  $3 < AF < 10$ , which means moderately polluted), while Pb, Zn and Mn show high accumulation factors (mean  $AF > 10$ , highly polluted).

After a 6-months exposure period, the appearance of moss samples was investigated. The mosses exposed at stations K-5, K-6 and K-10 were dry, brown and dead. The contents of Cu, Cr, Ni, Zn and Pb in these mosses were high or extremely high, particularly the Pb content in K-10 moss bag sample.

**Keywords:** Active biomonitoring, dry moss bag, urban area, heavy metals, accumulation factor, multivariate analysis, highly polluted.

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PRELIMINARY STUDY IN ATMOSPHERIC METAL DEPOSITION IN KOSOVO  
FROM ANALYSIS OF MOSS SAMPLES (2010-2011)

Pranvera Lazo<sup>1</sup> and Albert Mazhuni<sup>2</sup>

<sup>1</sup> *University of Tirana, Faculty of Natural Sciences, Tirana, Albania.*  
*pranveralazo@gmail.com*

<sup>2</sup> *University of Pristina, Faculty of Natural and Agriculture Sciences, Pristina, Kosovo*

For the first time the moss biomonitoring technique and AAS analytical technique were applied to study multi-element atmospheric deposition in Albania. 14 trace and biogenic metals were analysed in 25 mosses (*Hypnum cupressiforme*) and soil samples collected during the summer of 2010 and 2011 from 25 sites evenly distributed over the country. Sampling was performed in accordance with the LRTAP Convention – ICP Vegetation protocol and sampling strategy of the European Programme on Biomonitoring of Heavy Metal Atmospheric Deposition. AAS and flame AES analysis made it possible to determine concentrations of 14 elements including key toxic metals such as Pb, Cd, As, and Cu. Cluster and Factor analysis (Principal component analysis with varimax rotation) was applied to distinguish elements mainly of anthropogenic origin from those predominantly originating from natural sources. The range of concentration of heavy metals in moss samples is: Pb (3.6 - 47 mg / kg, DW), Cd (0.028 - 3,053 mg / kg, DW), Zn (14.3 - 76 mg / kg, DW), Co(0.5 - 1.38 mg / kg, DW), Hg (0.04 to 3.47 mg / kg, DW), Cu (2.46 - 3.93 mg / kg, DW) Mn (22,30 - 326 mg / kg, DW), Ni (1.22 - 34.2 mg / kg, DW), Cr (1.63 - 3.47 mg / kg, DW), and Fe (124 - 3081 mg / kg, DW). Levels of metals in moss samples throughout Kosovo region are comparable with Albania, Macedonia, Serbia and Croatia.

The concentration of heavy metals in soil samples varies as follows: Pb (11 - 416 mg / kg, DW), Cd (0.124 to 3.082 mg / kg, DW), Hg (0.33 - 1.46 mg / kg, DW), Zn (35.8 - 277 mg / kg, DW), Cu (10 - 202 mg / kg, DW), Co (20 - 140 mg / kg, DW), Ni (4.32 - 419 mg / kg, DW), Cr (9.96 - 777 mg / kg, DW), Mn (725 - 2983 mg / kg, DW), Fe (2050-265685 mg / kg DW). If we compare our results we see that Cd, Pb, Cu and Ni exceeding the maximum permitted level for Europe and Kosovo. The contaminated state of soils in Kosovo is mainly attributed to anthropogenic pollution, and in some cases to the geological composition of the soil.

This is the first study in Kosovo conducted in order to provide a some preliminary data of air quality throughout the territory of Kosovo and to produce information needed for better identification of pollution sources.

**Keywords:** moss biomonitoring; atmospheric deposition; trace elements; AAS and flame AES analysis; multivariate analysis

## BRYOMONITORING IN SLOVAKIA: PAST, PRESENT AND FUTURE.

Maňková, B.<sup>1</sup>, Oszlányi, J.<sup>1</sup>, Tučeková, A.<sup>2</sup>, Frontasyeva, M.V.<sup>3</sup>, Andráš, P.<sup>4</sup>, Dubieľ, J.<sup>4</sup>

<sup>1</sup>*Institute of landscape ecology, SAS, Štefánikova 3, P.O.Box 254, 814 99 Bratislava, Slovak Republic*

<sup>2</sup>*NFC, Forest Research Institute, Zvolen, Slovak Republic*

<sup>3</sup>*Frank Laboratory of Neutron Physics, JINR, Dubna, Russia*

<sup>4</sup>*Matej Bel University, Tajovského 40, 974 01 Banská Bystrica, Slovak Republic*

The use of mosses as biomonitors 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. In the 1990s, within the framework of UNECE ICP Vegetation programme, systematic studies using moss were carried out 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 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 bryomonitoring, was applied to the whole territory in 1990, 1995, 1996, 1997, 2000, and 2005 (Maňková et al., 2008, Schröder, et al., 2008).

The moss samples of *Hylocomium splendens*, *Pleurozium schreberi* and *Dicranum* sp. were collected in Slovakia. Samples were evaluated in National parks, in Landscape protection areas and industrial areas. In comparison to the median northern Norway values of heavy metal contents in moss the Slovak atmospheric deposition loads of the elements were found to be the survey has been repeated and in this paper we report on the temporal trends in the concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn between 1990 and 2005. Metal- and sites -specific temporal trends were observed. In general, the concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn in mosses decreased between 1990 and 2005; the decline was higher for Pb than Cd. The observed temporal trends for the concentrations in mosses were similar to the trends reported for the modelled total deposition of cadmium, lead and mercury in Europe. The level of elements determined in bryophytes reflects the relative atmospheric deposition loads of the elements at the investigated sites. Factor analysis was applied to determine possible sources of trace element deposition in the Slovakian moss. In the industrial area of Central Spiš we found in comparison with Norwegian limit values (Central Norway - as relatively the cleanest region) exceeded levels for Al, As, Ca, Cd, Cl, Co, Fe, K, Mn, Sb, Sm, Sr, W and Zn.

**Keywords:** air pollution, bryomonitoring, heavy metals.

## GROUND LEVEL OZONE BIOINDICATION ON SNAP BEAN IN LATVIA

Melece I.<sup>1</sup>, Indriksone I.<sup>2</sup>, Frolova M.<sup>2</sup>

<sup>1</sup>*Faculty of Geography and Earth Sciences, University of Latvia, Raina bulv. 19, Riga LV-1586 LATVIA; inaramelece@inbox.lv*

<sup>2</sup>*Latvian Environment, Geology and Meteorology Agency, Maskavas Str. 165 Riga, LV-1019*

Ozone –sensitive (S156) and ozone –tolerant (R123) genotypes of snap bean (*Phaseolus vulgaris* L.) was firstly used as a bioindicator plant in Latvia during summer in 2012 at two rural sites Rucava (at the territory of the meteorological station) and Taurene (nearest meteorological station Zosēni) located in different climatic regions of the country. The seeds were sown on June 11, 2012, plants were transplanted into the large pots on June 26 ( day 0 of the experiment). The experiment lasted until September 27. There were 8 to 15 pots for each genotype of bean plants at both sites. Bioindicator plants were exposed to ambient air for approximately 90 days, according to the ICP Vegetation experimental protocol. Ozone concentrations and climatic parameters were monitored at both experimental sites. Assessments of ozone injury were performed every two weeks.

The AOT40 value over the growing season (from day 0 to harvest) was 2.22 ppm h at Rucava site and 2.44 ppm h at Taurene site. Visible injury occurred on the ozone sensitive genotype at both experimental sites, while ozone resistant type didn't show any signs of injuries. At the end of August at Rucava site (coastal site with marine climate) ozone injuries on plants was over 25%, at Taurene (inland site with more continental climate) ozone injuries was 5-25%. At the end of the growing season significant differences were observed between ozone-sensitive and ozone resistant genotype plants. All R genotype plants were green, the signs of aging was just at some lower plant leaves, while all sensitive plants were senesced and dried. Therefore despite of relatively low ozone levels, it caused significant damage and rapid aging of leaves.

The yield biomass ratio evaluation shows that ozone-sensitive genotypes of snap beans have higher number of seeds and matured pods than resistant genotypes, while mean weight of seeds is almost the same. It could be explained by adaptive reaction to environmental stress for plant species with R- strategy.



## METAL CONTENT IN MOSSES CONTINUES TO DECLINE IN SWEDEN

Gunilla Pihl Karlsson & Helena Danielsson

*Swedish Environmental Research Institute, P.O. Box 5302, SE-40014 Göteborg, Sweden  
Corresponding author: gunilla@ivl.se; tel +46 31 7256208; fax +46 31 7256290*

During the past 35 years, between 1975 and 2010, the heavy metal content in mosses in Sweden declined significantly with between 47% and almost 100%. The largest decrease of the metal concentrations was found for lead, followed by chromium, nickel, cadmium, vanadium, arsenic, copper and zinc. Since 1990, the corresponding statistical analysis was not as pronounced and only the concentration of lead and cadmium show a statistically significant decrease. However, for iron, copper, chromium, vanadium a statistically significant decrease in concentrations was found in some parts of Sweden between 1990 and 2010.

For the majority of the heavy metals included in the study 2010, concentrations in mosses have decreased since 2005.

The occurrence of most metals in moss samples follows a general gradient with the lowest levels in the mountains and inland parts of northern Sweden. The highest concentrations are generally found in the southern parts of Sweden. There are, however, for some metals effects of local sources can be found on the metal concentrations in mosses, e.g. in the ore fields and along the coastline in northern Sweden.

In addition also a comparison with European and Swedish metal emissions, since 1990, are shown in the poster.

## THE MINING INDUSTRY GROWS RAPIDLY IN FINLAND - MONITORING OF HEAVY METAL DEPOSITION?

Poikolainen J., Piispanen J. & Kubin E.

*Finnish Forest Research Institute, Oulu Unit, B.O.Box 413, FI-90014 University of Oulu, Finland. jarmo.poikolainen@metla.fi*

The mining industry expanded in Finland into important branch of industry, when there were discovered rich ore deposits during the first half of the nineteen hundreds. A large deposit of copper ore was found in Outokumpu in 1908. Outokumpu mines (1913 – 1985), in Northern Karelia formed the main basis for modern mining and metallurgical industries in Finland. There are nowadays twelve metal mines in operation in Finland. Majority of exploration and mining companies are owned by foreign companies. Finland is one of Europe's larger producers of nickel, copper, zinc, gold and chromite. The largest mines are Talvivaara (Ni, Zn, Cu, Co, U), Kevitsa Ni, Cu, Pt, Pd), Suurkuusikko (Au), Kemi (Cr) and Pyhäsalmi (Cu, Zn). Mining started in Talvivaara and in Suurkuusikko 2008 and in Kevitsa 2012. There are founded in Finland also deposits of rare earth metals, which are used in high-tech industry. The mines provide the material for metal industry, with significant processing and refining of copper and nickel concentrates at Harjavalta, zinc at Kokkola, iron at Raahe and chromium at Tornio. The mining industry in Finland grows strongly in the near future, because there are founded many promising ore deposits first of all in Lapland.

The emissions of mining industry (mines, smelteries etc.) have the greatest effect on the heavy metal deposition in Finland. Heavy metal emissions from the Pechenga smelters in the Kola Peninsula, in Russia have an remarkable effect on the nickel and copper deposition in the northeastern Finland. Elevated nickel and copper concentrations in mosses are found in national heavy metal surveys about 100 km westwards from the smelters. Heavy metal survey in 2010 showed only some remarkable heavy metal sources of mining industry within Finnish territory. Copper and nickel concentrations in mosses were elevated in the Harjavalta area (SW Finland), at a distance of 15 kilometers from smelter. Another notable emission source of nickel was Talvivaara mine, in Kainuu, where elevated nickel concentrations in mosses showed at a distance of 10 kilometers. Elevated chromium concentrations were found in the Kemi-Tornio area (SW Lapland), which has a refined steel plant and a chromium mine.

The sample plots in Finnish heavy metal surveys are at a relatively long distance from each other (16 – 36 km). Thus the heavy metal deposition of all emission sources are not found in mosses, if the emission source is located badly between the plots. For example the elevated nickel concentrations in the vicinity of Talvivaara mine came into view only by means of the extra sample plots. The heavy metal emissions in Finland are at present relatively small and therefore the additional decrease of emissions is very expensive. Also the decrease of heavy metal concentrations in mosses have also been small since 2000. It is difficult in this situation to get public funding for moss surveys. One possibility to continue surveys could be, that the moss surveys are the official duty. In that case it should be new points of view for surveys. For example, when the mining industry in Finland grows rapidly in the near future, the extensive monitoring of heavy metal deposition in the vicinity of the major emission sources could be connected with the national surveys.

## AIR SURVEY IN VLORA AREA BY USING HONEY AS BIO-INDICATOR.

Qarri F.<sup>1</sup>, Lazo P.<sup>2</sup>, Kasemi D.<sup>1</sup>

<sup>1</sup> University "I. Qemali", Vlora, <sup>2</sup> University of Tirana. [flora.qarri@gmail.com](mailto:flora.qarri@gmail.com)

This research is about heavy metal contamination of honey. The honey used in this study was collected from beehives situated in the Vlora region, known for the high level of mercury pollution within a former PVC (polyvinyl chloride) plant area situated 3 km west of Vlora center. The sampling network included 7 sites, in the Vlora area. The locations of the sampling sites were determined by GPS and represented by maps.

The amount of Pb, Cd, Zn and other heavy metal contained in the samples harvested in the area specified above have been determined by AAS method using flame/and or electro-thermal system. CVAAS method was used for mercury determination.

Mosses samples from the same sites as the honey natural were analyzed for the same parameters and a good linear correlation between elements was found between mosses and honey samples. Principal component factor analysis and cluster analysis was used to identify the most polluted areas and characterize different pollution sources. The results suggested that honey could be used to detect contaminating agents from the environment.

**Key words:** air pollution, moss survey, bio-indicator, honey samples, heavy metals, AAS method, PCA, Cluster analysis

ELEMENTAL SURVEY OF METALS FROM 2000 TO 2010 BY USING THE  
MOSS *HYPNUM CUPRESSIFORME* L. EX HEDW. FROM EASTERN  
AND NORTH-WESTERN PART OF INDIA

Dinesh Kumar Saxena

*Department of Botany, Bareilly College, Bareilly, UP, India. Dinesh.botany@gmail.com*

Moss transplant of the species *Hypnum cupressiforme* L. ex Hedw. was used as active biomonitoring organism and used to compare the metals load (for **Pb, Zn, Fe and Cu**) in two extreme regions of the country. These samples were exposed for 4 months seasonally in eastern part of the country (Assam and Bengal) and as well as in the north-western part of the country (Punjab, Himanchal, and Grahwal) from 1990 to 2010.

Fe and Cu in the nine sectors of eastern region that were the largest in 1990 and 2010. Fe contribution in analyzed moss transplants *Hypnum* species was about 72% in 1990 and 67% in 2008 in the collected moss from eastern region of the India. On the contrary the Cu values were quite low and were 12 % and 17 %. In 1990, the maximum contribution to the total for Pb and Zn values in mosses from eastern part of the country was 75% and 21 %. Values did not show any big changes in 2010 in moss samples analysed and were 71 % and 26 %.

The values in the north-western part of the country were quite low except for Pb, where average Pb values had an increasing trend from 59 % of 1990 values to 89% in 2010. Rest of the values did not show much different.

Anthropogenic sources generally outweigh natural emissions and, even with the current trend towards reductions in the former, releases into the environment continue to lead to slow increases because of the persistence of the metals. There are minor differences in the accumulation of the individual metals in moss and their concentrations in moss are also affected by factors other than atmospheric pollution, however, trend can predict about the atmospheric load.

## FLUX-BASED OZONE RISK ASSESSMENT FOR ADULT BEECH AND SPRUCE FORESTS

Schröder M.<sup>1</sup>, Grünhage L.<sup>1</sup>, Matyssek R.<sup>2</sup>, Häberle K.-H.<sup>2</sup>, Pretzsch, H.<sup>3</sup>

<sup>1</sup> Department of Plant Ecology, Heinrich-Buff-Ring 26, D-35392 Giessen

Matthias.Schroeder@bio.uni-giessen.de Ludger.Gruenhage@bio.uni-giessen.de

<sup>2</sup> Ecophysiology of Plants, <sup>3</sup> Forest Growth and Yield Science, TUM, Wissenschaftszentrum Weihenstephan, Hans-Carl-von-Carlowitz Platz 2, D-85354 Freising-Weihenstephan

matyssek@wzw.tum.de haeberle@wzw.tum.de Hans.Pretzsch@lrz.tum.de

Rising tropospheric ozone (O<sub>3</sub>) concentrations pose a critical threat to forest ecosystems. The 8-year canopy level free-air O<sub>3</sub> enrichment experiment at Kranzberg Forest near Freising/Germany, performed during 2000 through 2007, is worldwide the only O<sub>3</sub> fumigation experiment with adult Norway spruce (*Picea abies*) and European beech trees (*Fagus sylvatica*). The study focused on 10 representative Norway spruce and 10 European beech trees, which were about 60 years old and up to 28 m high. Five of the 10 study trees of each tree species were exposed to a twice-ambient O<sub>3</sub> regime (2xO<sub>3</sub>). A respective number of trees were investigated under the unchanged ambient O<sub>3</sub> regime (1xO<sub>3</sub>) as control. In each regime, the individual tree was considered as the replication unit. The results presented here demonstrate improvement and validation of the LRTAP Convention's leaf-level stomatal flux-effect approach for European beech and Norway spruce.

Based on measurements of diameter increment at breast height, a statistically not significant mean annual loss by 11.4 % for Norway spruce and 11.5 % for beech were observed under 2xO<sub>3</sub> relative to 1xO<sub>3</sub>. The exposure of the tree cohorts during 8 years to 2xO<sub>3</sub> induced some shift in resource allocation into height growth but reduction of diameter growth in both tree species. In the case of Norway spruce, this change in allometry leads to cone-shaped stem forms, perhaps lowering stem stability on the long term. In the case of beech, the allometric changes led to neiloidal stem forms. Taking into account the effect of O<sub>3</sub> on stem shape, the 8-year exposure to 2xO<sub>3</sub> caused, on average, a statistically non-significant increase by 2.4 % in annual volume growth in Norway spruce and a statistically significant decrease by 43.5 % in beech in relation to the annual growth rate occurring under 1xO<sub>3</sub>.

### First conclusion:

Derivation of dose-effect relationships by epidemiological studies under ambient air restricted to increment measurements at breast height appears to be questionable.

Potential losses in biomass formation under the 2xO<sub>3</sub> regime – estimated according to the LRTAP Convention's stomatal flux approach – relative to the modelled potential losses under 1xO<sub>3</sub> are compared with the actually observed losses under 2xO<sub>3</sub> at Kranzberg Forest.

### Second conclusion:

Comparison of observed and modelled loss in annual volume growth under 2xO<sub>3</sub> relative to whole-stem productivity under 1xO<sub>3</sub> seems to confirm the LRTAP Convention's leaf-level stomatal flux approach and the associated response function for Norway spruce up to twice-ambient O<sub>3</sub> exposure.

For European beech it must be emphasized, that the LRTAP Convention's methodology may underestimate the O<sub>3</sub>-related risk for loss in whole-stem productivity. When accounting for the observed increase in below-ground productivity the apparent offset between the observed and modelled losses becomes smaller due to a conversion of whole-stem into whole-tree productivity.

## SOUTH EUROPEAN MEDITERRANEAN BASIN: DECREASE IN OZONE MEAN CONCENTRATIONS AT REMOTE SITES AND INCREASE IN THE CITIES

Sicard P., De Marco A., Renou C., Paoletti E.

*ACRI-ST, 260 route du Pin Montard, BP 234, 06904 Sophia-Antipolis Cedex, France  
pierre.sicard@acri-st.fr*

The Mediterranean Region has many morphologic, geographical, historical and societal characteristics, which make its climate scientifically interesting. The Mediterranean Basin is expected to be more strongly affected by ongoing global climate change, including ozone pollution, than most of the other regions. Ozone is an important air quality issue and the negative effect on human health, crops and forests has been widely discussed since the 1950s. Surprisingly, however, a comprehensive analysis of ozone and ozone precursor's trends in the Mediterranean Europe has not been carried out. A main limitation has been the short duration of monitoring. An important objective of many environmental monitoring programs is to detect changes or trends in pollution levels over time. Using ozone hourly data from 321 European background sites and ozone precursor's emissions over the time period 2000-2010, the annual averages were calculated with associated trends obtained with the Mann-Kendall test. A decreasing trend was observed at rural stations (average:  $-0.19\%.\text{year}^{-1}$ ) and in urban and suburban stations, an increase was recorded ( $+0.49\%.\text{year}^{-1}$  and  $+0.23\%.\text{year}^{-1}$ , respectively). At cities where NO<sub>x</sub> road traffic emissions decreased, ozone levels increased (less ozone destruction by NO), but peaks decreased. In urban stations, the paradox which shows an increase in O<sub>3</sub> concentrations associated with a reduction of precursor emissions over Europe is highlighted. For all station types, a significant reduction in the peaks was found at more than 70% of stations (98<sup>th</sup> percentiles,  $-0.63\%.\text{year}^{-1}$ ; hourly maxima,  $-1.08\%.\text{year}^{-1}$  and daily maxima,  $-0.57\%.\text{year}^{-1}$ ). The peaks reduction may largely be attributed to the reduction in NO<sub>x</sub> and VOC emissions within the European Union since 1990. In parallel, to compare the annual trends in urban and rural stations, with similar geographical location and characteristics, we selected stations for which both typologies are available within a radius of 50 km around the station. From the results, a negative annual trend of  $-1.5\%.\text{year}^{-1}$  in rural stations contrary to a positive annual trend of  $+0.3\%.\text{year}^{-1}$  in urban are obtained. For 98<sup>th</sup> percentiles and hourly maxima, negative annual trends around  $-1.3\%.\text{year}^{-1}$  and  $-1.7\%.\text{year}^{-1}$ , respectively, are obtained in both stations. The ozone levels show different trends, with peaks reduction and average increments in urban stations and peaks and average decrease in rural stations. These trends can be interpreted as a result of several factors such as changes in anthropogenic precursor's emissions, geographical emission patterns, effects of intercontinental transport and climate changes. The results suggest a convergence of ozone pollution at remote and urban sites all around the Mediterranean Europe. As pointed out by some authors increasing tropospheric background ozone concentrations have considerable significance for future assessments of the risks of ozone impacts on vegetation in Europe. This work was made possible with the contribution of the LIFE financial instrument of the European Union (LIFE10 ENV/FR/208) for the FO<sub>3</sub>REST project.

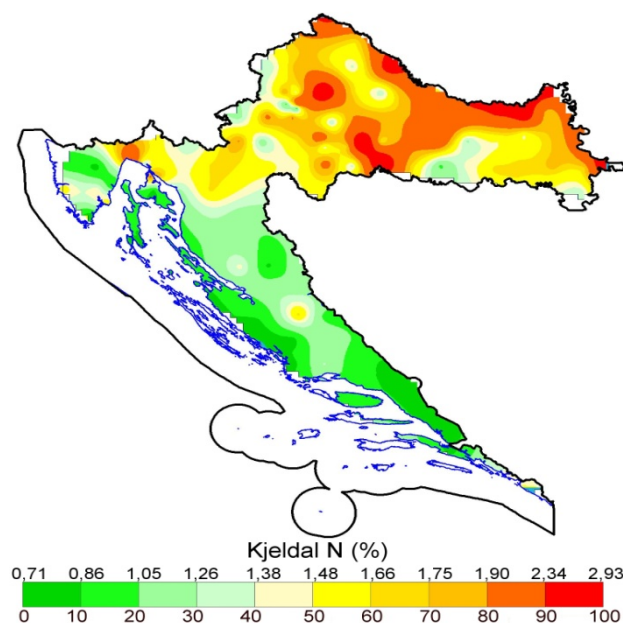
## PRELIMINARY RESULTS ON NITROGEN IN CROATIAN MOSS SURVEY 2010

*Špirić, Z.<sup>1</sup>, Glad M.<sup>2</sup>, Kušan V.<sup>1</sup>*

<sup>1</sup> OIKON Ltd. – Institute for Applied Ecology, Trg senjskih uskoka 1-2, 10020 Zagreb, Croatia. [zspiric@oikon.hr](mailto:zspiric@oikon.hr)

<sup>2</sup> Teaching Institute of Public Health, Primorsko-Goranska County, Rijeka, Croatia.

Since 2006, Croatia has participated in a moss survey within the framework of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops with heavy metals in Europe <http://icpvegetation.ceh.ac.uk>. In accordance with the sampling strategy of the European moss survey program, moss samples were collected in 2010 in Croatia on a nearly regular network of 23 x 23 km. Moss samples were collected during the summer/autumn 2010 from 121 locations evenly distributed across the country with additional samples in/around urban/industrial areas (with a total of 161 locations). The most dominant moss species in this study area were *Hypnum cupressiforme*, *Pleurozium schreberi*, *Brachythecium rutabulum* and *Homalothecium sericeum*.



In addition to the comprehensive qualitative and quantitative chemical analysis of all samples collected (Spiric et al. 2012 and Spiric et al. 2013), laboratory research by using the Kjeldahl analytical method was conducted in order to determine nitrogen concentration in all collected moss samples. The total nitrogen concentration in mosses can potentially be used to estimate total nitrogen deposition and to identify areas with high nitrogen deposition in Croatia. The spatial variation in nitrogen concentration in mosses across Croatia should be analysed in greater detail to identify and understand the main causes of this variation. A Geographical distribution map of the nitrogen over the sampled territory was constructed using GIS technology (see figure).

There is a clear need to continue these studies in order to assure a reliable assessment of air quality throughout Croatia. This will provide information needed for better identification of ecosystems in Croatia which are at risk from nitrogen pollution and will enhance the potential for assessment and control of environmental and health risks associated with nitrogen.

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