



# 23<sup>rd</sup> Task Force Meeting

1 – 3 February, 2010 Tervuren, Belgium

# Programme & Abstracts



### Organizers:



ICP Vegetation Programme Coordination Centre Centre for Ecology and Hydrology Bangor, UK.

> Harry Harmens Gina Mills Felicity Hayes

Local organizers



Veterinary and Agrochemical Research Centre (CODA-CERVA) Tervuren, Belgium

> Ludwig De Temmerman Karine Vandermeiren

### **Programme**

### Monday 1<sup>st</sup> February, 2010

#### 15:00 – 18:00 Continuation of Working Group discussions from ozone workshop in Ispra.

- 18:00 19:00 Registration at CODA-CERVA
- **19:00** Welcome reception at CODA-CERVA

### Tuesday 2<sup>nd</sup> February, 2010

- 8:15 **Registration for late arrivals**
- Session 1: 8:45 10:15 Plenary session Chair: Ludwig de Temmerman
- 8:45 *Pierre Kerkhofs*, director general Veterinary and Agrochemical Research Centre (CODA-CERVA) Welcome.
- 9:00 *Harry Harmens* et al. LRTAP Convention and achievements of the ICP Vegetation in 2009.
- 9:30 *Gina Mills* et al. ICP Vegetation: contributions on ozone for the revision of the Gothenburg Protocol.
- 9:45 *Pierre Kerkhofs* Scientific activities of CODA-CERVA.
- 10:05 General discussion.
- 10:15 11:00 Coffee/tea and poster viewing

#### Session 2: 11:00 – 12:45 Two parallel sessions: Ozone and Heavy Metals/N

Session 2a:	Ozone Cha	ir: Gina Mills
	Flux modelling and flux-based critical lev Workshop on "Flux-based assessment of – 12 November, 2009, Ispra, Italy.	1 0
11:00	Gina Mills – Overview of workshop and d	ecisions to be made.
11:10	<i>Håkan Pleijel</i> et al. – New response fun options exist for crops? (15 mins + 10 min	
11:35	Sabine Braun et al. – Overview on ozone suggested critical levels for forests. (15 mi	1 1
12:00	<i>Felicity Hayes</i> et al. – Progress with find (others to be discussed). (15 mins + 10 ministration of the second se	e
10.05	Comparel discussion	

12:25 General discussion

#### Session 2b: Heavy metals/N Chair: Harald Zechmeister

- 11:00 *Ilia Ilyin* Modelled EMEP heavy metal depositions versus moss measurements: progress in the analysis of the results.
- 11:20 *Winfried Schröder* et al. European wide analysis of factors influencing the spatial variation of metal and nitrogen concentrations in mosses.
- 11:40 *Ilia Ilyin and Ludwig De Temmerman* Are there any opportunities for moss biomonitoring to study the global distribution and the deposition of mercury?
- 12:00 General discussion on country-specific correlations between heavy metal concentrations in mosses and EMEP modelled deposition, including the application of mosses as biomonitors of mercury.

#### 12:45 – 14:00 Lunch

- Session 3: 14:00 15:30 Two parallel sessions: Ozone and Heavy Metals/N
- Session 3a: Ozone Chair: Håkan Pleijel
- 14:00 *Zhaozhong Feng* et al. Apoplastic ascorbate rather than stomatal flux contributes to the different response to ozone between two varieties of winter wheat under fully open-air field conditions.
- 14:20 *Ignacio Gonzalez Fernandez* et al. On the application of the ozone dose-response model for wheat in the Southern Europe.
- 14:40 *Maarten De Bock, Maarten Op de Beeck* et al. Which ozone dose response works best for oilseed rape and broccoli?
- 15:00 *Victoria Bermejo* et al. Ozone dose-response functions for two important horticultural crops: tomato and bean.
- 15:20 General discussion.

Session 3b: Heavy metals/N Chair: Harry Harmens

- 14:00 Harry Harmens Update 2010/11 moss survey.
- 14:15 Discussion: European moss survey in the future (2 discussion groups).
- 15:00 Reporting back from discussion groups and general discussion.
- 15:30 16:00 Coffee/tea and poster viewing

Session 4:	16:00-18:00 Two parallel sessions: Ozone and Heavy Metals/N		
Session 4a:	Ozone Chair first part: Patrick Büker		
16:00	Per Erik Karlsson et al. – Local variations of ozone concentrations in the landscape.		
16:20	mitri Vellisariou, Jürgen Bender et al. – Visible ozone injury on leafy crops.		
16:40	<i>Jesús Ramírez</i> et al. – Tropospheric ozone and its effects on the main agricultural species of Central America and the Caribbean.		
	Chair discussion: Gina Mills		
17:00	Further discussion of flux-based methodology and revision of critical levels.		
Session 4b:	Heavy metals/N Chair first part: Marina Frontasyeva		
16:00	<i>Roland Pesch</i> et al. – Using the moss data to calculate European wide maps on atmospheric depositions of Cd, Pb and N.		
16:20	<i>Sébastien Leblond</i> et al. – Element concentrations in mosses in relation to atmospheric deposition and soil chemistry.		
16:40	<i>Ivan Suchara</i> et al. – Changes in concentrations of 14 elements in moss caused by time and site-specific effects in the Czech Republic between 1995 and 2005.		
17:00	<i>Harald Zechmeister</i> et al Monitoring of indoor pollution by using mosses in t Girona area, Spain.		
	Chair discussion: Harry Harmens		
17:20	General discussion: workplan 2010 and beyond.		
Evoning	Ozonov Completion of report of Ispre and TEM including recommendations for		

**Evening** Ozone: Completion of report of Ispra and TFM, including recommendations for changes to the Modelling and Mapping Manual and for use of flux-based methodology within the LRTAP Convention. Drafting group: Gina Mills, Harry Harmens, Håkan Pleijel, Helena Danielsson, Sabine Braun, Patrick Büker, Felicity Hayes and Ignacio Gonzalez.

Free for other participants to make their own arrangements.

### Wednesday 3<sup>rd</sup> February, 2010

Session 5:	8:30 – 9:30 Plenary Session	Chair: Gina Mills	
	Recommendations from Ispra Working Group discussions, adoption of new flux- based critical levels for ozone and of report from Ispra and TFM. With contributions from Håkan Pleijel, Sabine Braun and Felicity Hayes.		
Session 6:	9:30-10:30 Two parallel sessions: Ozone and Heavy Metals/N		
Session 6 a:	Ozone - Biomonitoring with bean and 2010 survey of leafy crops for ozone injury Chair: Felicity Hayes		
9:30	Felicity Hayes et al. – Overview	Felicity Hayes et al. – Overview of the results of the 2009 bean study.	
9:50	Discussion of plans for bean experiment and injury surveys in 2010 and beyond.		
Session 6b:	Heavy metals	Chair: Ivan Suchara	
9:30	<i>Marina Frontasyeva</i> et al. – Atmospheric heavy metal deposition in Northern Vietnam: Hanoi and Thainguyen case study using the moss biomonitoring technique, INAA and AAS.		
9:50	Zdravko Spiric et al. – Multi-element atmospheric deposition study in Croatia.		
10:10	Lotti Thöni - Sulfur monitoring with mosses – what is the experience?		
10:30 - 11:0	0 Coffee/tea and poster viewing		
Session 7:	11:00 – 12:30 Two parallel sessions: Ozone and Heavy Metals/N		
Session 7a:	Ozone	Chair: Karine Vandermeiren	
11:00	<i>Matthias Volk</i> et al. – Subalpine grassland NEE CO <sub>2</sub> fluxes indicate reduced GPP and Reco at elevated ozone, but no reduction of productivity.		
11:20	Verena Blanke et al. – N, P and $O_3$ -responses of subalpine plants and their mycorrhiza.		
11:40	<i>Sylvia Toet</i> et al. – Ozone effects on methane and carbon dioxide fluxes from peatland mesocosms.		
12:00	General discussion.		

#### Session 7b: Heavy metals Chair: Winfried Schröder

- 11:00 *Ludwig de Temmerman* et al. Is there any measurable direct impact of atmospheric deposition on the trace element contents of the root vegetables, carrots and celeriac?
- 11:20 *Ivan Suchara* et al. Comparison of element contents distribution in moss, grass and spruce needles in coniferous forests in the Czech Republic in 2005–2006.
- 11:40 General discussion.

#### 12:30 - 13:30 Lunch

- 13:30 15:30 Excursion to the Royal Museum for Central Africa
- 15:30 16:00 Coffee/tea and poster viewing
- Session 8: 16:00 18:00 Plenary session

#### **Chair: Harry Harmens**

- Reporting back from ozone and heavy metals sessions.
- ICP Vegetation work programme 2010 2013, including items common to all ICPs/Task Force on Health.
- Collaboration with other LRTAP Convention bodies such as EMEP, Task Force on Reactive Nitrogen and Task Force on Integrated Assessment Modelling.
- Outreach activities to other regions, Global Air Pollution Forum.
- Conclusions and review of the 23<sup>rd</sup> Task Force Meeting.
- Next Task Force Meeting.

#### **19:30** Conference dinner in hotel La Vignette

# **Abstracts**

# **Presentations**

#### N, P AND O3-RESPONSES OF SUBALPINE PLANTS AND THEIR MYCORRHIZA

#### Blanke V., Volk M., Bassin S., Fuhrer J.

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Nutrient-poor grasslands in the Alps are threatened by eutrophication and high tropospheric  $O_3$  levels. To assess the impact of elevated N and  $O_3$  concentrations and their interaction on a subalpine pasture at Alp Flix (Sur, Grisons, Switzerland; 2000 m above sea level) a free-air  $O_3$  fumigation system combined with N fertilization treatments was established in 2004, using grassland monoliths. N enrichment increased total aboveground biomass, due to a strong increment of sedge growth, but so far, there was no significant  $O_3$  effect (Bassin *et al.* 2007).

As the outcome of fertilization experiments depends on which element is actually limiting plant growth, a similar trial with cross-factorial N and P addition was established and unveiled the vegetation to be co-limited by N and by P.

Arbuscular mycorrhizal fungi (AMF) play an important role in ecosystems, since they colonize roots of the majority of vascular plants, and provide them with nutrients in exchange for photosynthetically fixed carbon (C), on which the fungi are completely dependent. The main function of the arbuscular mycorrhiza (AM) is improving the plants' phosphorus (P) nutrition, but the fungi also have been found to play a role in nitrogen (N) nutrition. Eutrophication of ecosystems often reduces the amount of AMF in roots, because plants get themselves sufficient access to nutrients and stop allocating C to the symbionts. Information about the effect of ozone (O<sub>3</sub>) enrichment on AM is scarce; however, elevated O<sub>3</sub> levels have been shown to reduce root colonization by AMF, because damaged plants reduce their C allocation below-ground.

To examine treatment effects on belowground biomass, AMF and their role in mediating effects on plants, resident plant species in in-growth cores (Johnson *et al.* 2001) were introduced in monoliths of the NxP and the NxO<sub>3</sub>-experiment. These cores allow fungal hyphae to pass and colonize roots, whereas it prevents roots from growing into or out of the cores. Half of the cores were rotated regularly to hamper root colonization and nutrient provision via AMF by destroying the fungal mycelium.

Results from cores in the NxP-experiment show that the percentage of root length colonized (% RLC) by AMF was only reduced by P input but not by N. N addition, however, increased % RLC of the most abundant grass, indicating that N fertilization may amplify P limitation in this species, increasing the need for AM. As grasses contribute most to total plant biomass, an increased N input might even have a positive influence on overall AMF abundance at Alp Flix. Although rotating the cores successfully decreased % RLC, it did not affect growth of respective plants. These data will be discussed with respect to their importance for the plant community and more preliminary results from cores in the NxO<sub>3</sub>-experiment will be shown.

#### References

Bassin S., Volk M., Suter M., Buchmann N., Fuhrer J. 2007: Nitrogen deposition but not ozone affects productivity and community composition of subalpine grassland after 3 yr of treatment. New Phytologist 175: 523-534

Johnson D., Leake J.R., Read D.J., 2001: Novel in-growth core system enables functional studies of grassland mycorrhizal mycelial networks. New Phytologist 152: 555-562

#### IS THERE ANY MEASURABLE DIRECT IMPACT OF ATMOSPHERIC DEPOSITION ON THE TRACE ELEMENT CONTENTS OF THE ROOT VEGETABLES CARROTS AND CELERIAC?

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

#### Veterinary and Agrochemical Research Centre, Leuvensesteensweg 17, 3080 Tervuren ludet@var.fgov.be

During the last decades, only a few studies have shown some impact of airborne trace elements such as Cd and Pb on their concentration in the taproot of carrots (Hovmand et al. 1983; Harrison and Chirgawi, 1989; Dalenberg and Van Driel, 1990). However, the results were not always convincing and the experiments were carried out by using growth chambers (filtered and unfiltered) and/or by using labeled trace elements. Biomonitoring experiments have already resulted in the derivation of transfer functions between atmospheric deposition and the accumulation of trace elements in leafy vegetables (De Temmerman and Hoenig, 2004) but this approach has not yet been used to study any accumulation in storage organs such as taproots of carrots and hypocotyls of celeriac.

In the present study, carrots (*Daucus carota*) and celeriac (*Apium graveolens rapaceum*) were grown in containers filled with a peat based substrate containing low levels of the trace elements studied and provided with filter candles for their water supply. The plants were first raised in a reference area with low atmospheric deposition and thereafter exposed for 2 months (carrots) or 4 months (celeriac) in a polluted area around a lead smelter. In most cases the containers were placed near private gardens were vegetables are cultivated.

At each experimental plot, the containers were exposed in triplicate in order to facilitate statistical treatment of the results. After exposure, the leaves and the storage organs were separated. The storage organs were cleaned, washed thoroughly and peeled. The leaves, the peels and the inner part (pulp) were analyzed separately.

At each site, bulk deposition was measured in order to be able to link the results to atmospheric deposition. Despite the very low accumulation of As, Cd and Pb in the inner part of the storage organs, a clear correlation was observed between the trace element concentration of the pulp and the atmospheric deposition during exposure. This allowed us to derive transfer functions useful for modeling of the atmospheric impact of trace elements on the edible parts of root crops. It remains a matter of discussion whether there is a transfer of the elements from the leaves to the storage organs or a direct uptake of nano particulates by the above ground parts of the storage organs.

#### References

Dalenberg, J.W., Van Driel, W. (1990). Contribution of atmospheric deposition to heavy metal concentrations in field crops. Neth. J. Agricultureal Science, 38, 369-379.

De Temmerman, L., Hoenig, M. (2004). Vegetable crops for biomonitoring lead and cadmium deposition. J. Atmospheric Chemistry, 49, 121-135.

Harrison, R.M., Chirgawi, M.B. (1989). The assessment of air and soil as contributors of some trace metals to vegetable plants. I. Use of a filtered air growth cabinet. The Science of the Total Environment, 83, 13-34.

Hovmand, M.F., Tjell, J.C., Mosbaek, H. (1983). Plant uptake of airborne cadmium. Environmental Pollution (Series A), 30, 27-38.

#### APOPLASTIC ASCORBATE RATHER THAN STOMATAL FLUX CONTRIBUTES TO THE IFFERENT RESPONSE TO OZONE BETWEEN TWO VARIETIES OF WINTER WHEAT UNDER FULLY OPEN-AIR FIELD CONDITIONS

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Two modern cultivars (Yangmai16 (Y16) and Yangfumai 2 (Y2)) of winter wheat (Triticum aestivum L.) with almost identical phenology were investigated to determine the impacts of elevated ozone concentration (E-O<sub>3</sub>) on physiological characters related to photosynthesis under fully open-air field conditions in China. The plants were exposed from the initiation of tillering to final harvest, with E-O<sub>3</sub> of 127% of the ambient ozone concentration (A-O<sub>3</sub>). Measurements of pigments, gas exchange rates, chlorophyll a fluorescence lipid oxidation, and apolastic and leaf tissue ascorbate (ASC) were made in three replicated plots throughout flag leaf development. In cultivar Y2, E-O<sub>3</sub> significantly accelerated leaf senescence, as indicated by increased lipid oxidation as well as faster declines in pigment amounts and photosynthetic rates. The lower photosynthetic rates were mainly due to non-stomatal factors, e.g. lower maximum carboxylation capacity, electron transport rates and light energy distribution. In cultivar Y16, by contrast, the effects of E-O<sub>3</sub> were observed only at the very last stage of flag leaf ageing. The ASC contents in the apoplast (ASC<sub>apo</sub>) and leaf tissue (ASC<sub>leaf</sub>) were significantly decreased when [O<sub>3</sub>] was accumulated to a level, and these decreases increased with foliar senescence. However, oxidized ascorbate (DHA) and redox state in the apoplast and leaf tissue did not differ from those in ambient plants. The ascorbate pool in the apoplast was strongly affected by accumulative  $O_3$ effects as well as O<sub>3</sub> concentrations.

Since the two cultivars had almost identical phenology and very similar leaf stomatal conductance before senescence, the greater impacts of  $E-O_3$  on cultivars Y2 than Y16 cannot be explained by differential ozone flux into the leaf. However, the higher contents of  $ASC_{apo}$  and  $ASC_{leaf}$  in Y16 than those in Y2 was observed, which should have contributed to the differences in the  $O_3$  sensitivity between the varieties.

#### ATMOSPHERIC HEAVY METAL DEPOSITION IN NORTHERN VIETNAM: HANOI AND THAINGUYEN CASE STUDY USING THE MOSS BIOMONITORING TECHNIQUE, INAA AND AAS

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The moss technique is widely used to monitor atmospheric deposition of heavy metals in many countries in Europe, whereas this technique is scarcely used in Asia. To implement this international reliable and cheap methodology in the Asian countries, it is necessary to find proper moss types typical for the Asian environment and suitable for the biomonitoring purposes. Such a case study was undertaken in Vietnam for assessing the environmental situation in strongly contaminated urban areas using local species of moss Barbula indica. The study is focused on two areas characterized by different pollution sources: the Hanoi urban area and the Thainguyen metallurgical zone. Fifty four moss samples were collected there according to standard sampling procedure adopted in Europe. Two complementary analytical techniques, atomic absorption spectrometry and instrumental neutron activation analysis, were used for determination of elemental concentrations in moss samples. To characterize the pollution sources Multivariate statistical analysis was applied. A total of 38 metal elements were determined in the moss by the two analytical techniques. The results of descriptive statistics of metal concentration in moss from the city center and periphery of Hanoi determined by AAS are presented. The similar results for moss from Thainguyen province determined by INAA and AAS are given also. A comparison of mean elemental concentrations in moss of this work with those in different environmental conditions of other authors provides reasonable information on heavy metal atmospheric deposition levels. Factor loadings and factor scores were used to identify and apportion contamination sources at the sampling sites. The values of % total of factors show two highly different types of pollution in the two examined areas -the Hanoi pollution composition with high portion of urban-traffic activity and soil dust (62%), and the one of Thainguyen with factors related to industrial activities (75%). Besides, the scatter of factors in factor planes represents the greater diversity of activities in Hanoi than in Thainguyen. Good relationship between the result of factor analysis and the pollution sources evidences that the moss technique is a potential method to assess the air quality in Vietnam. Moss B. indica widely distributed in Vietnam and Indo-China is shown to be a reliable bryophyte for biomonitoring purposes in sub-tropic and tropic climate. However, the necessity of moss interspecies calibration is obvious for further studies in the area to provide results compatible with those for other Asian countries and Europe.

### ON THE APPLICATION OF THE OZONE DOSE-RESPONSE MODEL FOR WHEAT IN SOUTHERN EUROPE

<u>González Fernández I.</u><sup>1</sup>, Bermejo V. <sup>1</sup>, González A.<sup>2</sup>, de la Torre D.<sup>3</sup>, López A. <sup>4</sup>, Serra J.<sup>5</sup>, Elvira S. <sup>1</sup>, Sanz J. <sup>1</sup>, Gimeno BS. <sup>1</sup>, Alonso R. <sup>1</sup>

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Modelling the risk of ozone (O<sub>3</sub>) impacts on vegetation following the DO<sub>3</sub>SE methodology (UNECE 2009), incorporated in the EMEP model, involves the derivation of multiplicative models to estimate stomatal conductance ( $g_s$ ), in order to determine the cumulative flux of ozone absorbed through the stomata. Several species-specific models for  $g_s$  have been developed and applied at a site-specific scale, but wider geographic applications present significant challenges because of the range of climatic conditions that must be considered (Ashmore et al., 2007).

Because of the importance of wheat production to the European economy much attention has focused on assessing the risk posed to this crop by ozone pollution. Ozone exposure experiments developed in northern and central Europe using spring wheat cultivars currently provide the cornerstone data to assess the impacts of ozone pollution on cereal yield across Europe (Pleijel et al., 2007). However, experimental data highlight the need to consider differences between spring and winter wheat and the genetic variability in terms of  $g_{max}$ , phenological development and O<sub>3</sub> sensitivity. This variability should be considered for estimating the impacts of ozone on wheat at a pan-European level using the latest flux-based approaches (González-Fernández et al., 2009).

The aim of this work is to examine and quantify the suitability of current  $DO_3SE$  wheat parameterization for risk assessment on cereal yield in the Mediterranean area, using several datasets of field grown winter wheat from Spain.

#### **References:**

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González-Fernández I., Kaminska A., Dodmani M., Goumenaki E., Quarrie S., Barnes J.D. 2009. Establishing ozone flux-response relationships for winter wheat: Analysis of uncertainties based on data for UK and Polish genotypes. Atmospheric Environment, doi: 10.1016/j.atmosenv.2009.11.021.

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

UNECE, 2009. Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends, Convention on Long-Range Transboundary Air Pollution. Available on line at: http://www.icpmapping.org.

#### AN OVERVIEW OF THE ACHIEVEMENTS OF THE ICP VEGETATION IN 2009

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

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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 and nitrogen to vegetation. In addition, the ICP Vegetation is taking into consideration impacts of nitrogen on vegetation (including interactions with ozone), consequences for biodiversity and the interactions between air pollutants and climate change.

At the 23<sup>rd</sup> Task Force Meeting we will report on the achievements of the ICP Vegetation in 2009, in particular regarding progress made with items to be reported to the WGE in 2010 [2]:

- Ozone biomonitoring experiment with bean in 2009;
- Ozone impacts in Mediterranean areas;
- Ozone flux modelling methods and their application to different climatic regions;
- Outcome of workshop on 'Flux-based assessment of ozone effects for air pollution policy';
- Progress with European heavy metals and nitrogen in mosses survey 2010/11;
- Relationship between heavy metal concentration in mosses and EMEP modelled deposition.

In addition, we will discuss the contribution of ICP Vegetation to the common workplan items of the WGE for 2010 [2].

Apart from looking back to our achievements in 2009, throughout the Task Force Meeting we will be discussing our future plans, in particular the medium-term workplan of the ICP Vegetation (2011 - 2012).

#### Acknowledgement

We thank the UK Department for Environment, Food and Rural Affairs (Defra) for funding the ICP Vegetation Programme Coordination Centre (Defra contract AQ0810).

#### References

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- [2] Working Group on Effects. Draft 2010 workplan. ECE/EB.AIR/WG.1/2009/4. http://www.unece.org/env/documents/2009/EB/wge/ece.eb.air.wg.1.2009.4.e.pdf

#### USING THE MOSS DATA TO CALCULATE EUROPEAN WIDE MAPS ON ATMOSPHERIC DEPOSITIONS OF CD, PB AND N

Holy, M.<sup>1</sup>.; Schröder, W.<sup>1</sup>.; Pesch, R.<sup>1</sup>; Harmens, H.; Ilyin, I.; Fagerli, H.; Alber, R., Ashmore, M., Bakhmet, O., Carballeira Ocaňa, A., Coskun, M., Dam, M., Ermakova, E., Fedorets, N., Fernández Escribano, J.A., Frolova, M., Frontasyeva, M., Galsomies, L., Godzik, B., Goltsova, N., Grodzińska, K., Jeran, Z., Johannessen, T., Krmar, M., Kubin, E., Kvietkus, K., Leblond, S., Liiv, S., Lucaciu, A., Magnússon, S., Maňkovská, B., Matavuly, M., Mocanu, R., Mutschlechner, A., Nikodemus, O., Pihlström, M., Piispanen, J., Rakic, S., Rausch de Traubenberg, C., Riss, A., Rühling, Å., Stafilov, T., Steinnes, E., Suchara, I., Sucharová, J., Szarek-Łukaszewska, G., Thöni, L., de Timmermann, L., Urumov, V., Yurukova, L., Zechmeister, H., Zhuk, I.

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In a European wide investigation data from the Heavy Metals in Mosses surveys were combined with data coming from the European Monitoring and Evaluation programme (EMEP) in order to produce high resolution maps for atmospheric deposition of Cd, Pb and N. In a first step the punctual measurement data on Cd, Pb and N in mosses were investigated with regard to spatial autocorrelation using variogram analysis. Since such could be verified in all three cases spherical variogram models were fitted to the experimental variograms to calculate European wide kriging maps in a resolution of  $5 * 5 \text{ km}^2$ . The according raster cell values then were averaged for each of the 50 \* 50 km<sup>2</sup> EMEP grid cells followed by a statistical investigation of the association between moss concentration and modelled deposition with help of linear regression analysis. Medium to strong association were found for each of the elements (Cd:  $r^2 = 0.44$ ; Pb:  $r^2 = 0.58$ ; N:  $r^2 = 0.63$ ). The resulting regression functions were therefore applied on the estimated raster data on the Cd, Pb and N concentration in mosses. Since the residuals of the linear regression model stand for the unexplained variance of the target variable they were investigated with regard to spatial autocorrelation. In all three cases the experimental variograms showed clear autocorrelation indicating that spatially dependent factors were not included in the analyses. Accordingly, the residuals were mapped with help of kriging and added to the regression maps to produce high resolution maps for atmospheric depositions of Cd, Pb and N.

In this investigation it was shown that data from the Heavy Metals in Mosses surveys can be used for even more than crossborder analysis of the concentration of metals and N in mosses. The deposition maps that derived from the association between moss concentrations and modelled depositions could be applied to improve the quality of exceedance maps for critical loads.

#### EUROPEAN WIDE ANALYSIS OF FACTORS INFLUENCING THE SPATIAL VARIATION OF METAL AND NITROGEN CONCENTRATIONS IN MOSSES

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This study aimed to investigate the correlations between heavy metal and nitrogen concentrations in mosses and depositions modelled within the European Environmental Monitoring and Evaluation Programme (EMEP) as well as other site-specific and regional characteristics to determine which factors primarily affect nitrogen, cadmium, lead and mercury concentrations in mosses. Hence, modelled deposition data and data on the concentration of metals and nitrogen in naturally-growing mosses were integrated into a geographic information system and analysed by means of bivariate rank correlation analysis and multivariate decision trees. The modelled deposition data are validated annually with deposition measurements at up to 63 EMEP measurement stations and mosses were collected at up to 7,000 sites at five-yearly intervals between 1990 and 2005.

As a result, moderate to high correlations were found between cadmium and lead concentrations in mosses and modelled atmospheric depositions: Regarding the metals, spearman rank correlation coefficients were between 0.62 and 0.67 and 0.67 and 0.73 for cadmium and lead respectively (p < 0.001). Multivariate decision tree analyses showed that cadmium and lead concentrations in mosses were primarily determined by the atmospheric deposition of these metals, followed by emissions of the metals. Low to very low correlations were observed between mercury concentrations in mosses and modelled atmospheric deposition of mercury, which does not show much spatial variation. According to the multivariate analyses, the mercury concentration in mosses was primarily determined by potentially varying receptor phenomena like e.g. different moss species, and not by the deposition.

For nitrogen, the Spearman rank correlation analysis showed that the total N concentration in mosses and modelled N depositions and air concentrations are significantly correlated (0.55 < rs < 0.68; p < 0.001). The decision tree analysis indicated that the variation in the total nitrogen concentration in mosses could be mainly explained by the variation in reduced and oxidized nitrogen air concentrations, dry nitrogen deposition as well as the sampled moss species. As for cadmium and lead the nitrogen concentration in mosses appears to mirror land use-related atmospheric concentrations and depositions across Europe. The moss method therefore is a valuable tool in identifying areas with high atmospheric depositions at a high spatial resolution across Europe.

#### ARE THERE ANY OPPORTUNITIES FOR MOSS BIOMONITORING TO STUDY THE GLOBAL DISTRIBUTION AND THE DEPOSITION OF MERCURY?

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Three forms of mercury are emitted by anthropogenic sources: gaseous elemental (GEM), oxidized reactive gaseous (RGM) and particulate mercury (TPM). RGM and TMP are deposited at local and regional scales, while GEM is dispersed globally and oxidized to RGM/TPM, which deposit in regions remote from pollution sources. Main anthropogenic sources of mercury are located in Eastern and South-Eastern Asia (e.g., China, India), Europe and east of the USA. Combustion of fossil fuels is responsible for almost one half (47%) of global anthropogenic emissions. Other main emission sectors are artisan and small-scale gold production (18%), metallurgy (10%) and cement production (10%).

Annual mean global GEM concentrations calculated by GLEMOS (<u>Gl</u>obal <u>EMEP</u> Multi-media <u>Modelling</u> <u>System</u>) model range between 1.4 - 2.2 ng/m<sup>3</sup> in the Northern Hemisphere and are about 1.2 mg/m<sup>3</sup> – in the Southern Hemisphere. Concentration levels and the gradient between two hemispheres agree well with measurement data.

Contribution of remote (located outside the EMEP domain) anthropogenic and natural sources to pollution of EMEP countries, simulated by regional-scale MSCE-HM model, ranges within 30% - 95%. The contribution of EMEP countries varies from 1% to 70%, and the contribution of natural sources within EMEP is below 5%.

The main sources of uncertainties of mercury modeling results are related to emission data, atmospheric chemistry of mercury, and deposition processes. The bias between modelled and observed concentrations in precipitation and wet deposition fluxes is within  $\pm 50\%$  for most of stations.

Deposition of mercury is rather complex as there occur different forms in ambient air. For wet deposition, it is rather simple but elementary mercury, the most important form in ambient air is not very soluble in rainwater. The importance of dry deposition of particulate matter is depending local conditions but in general, it is less important. For terrestrial ecosystems, dry deposition of elementary mercury is very important. Vegetation is an important sink for mercury. However, the sink strength is not the same for every plant species. Intensive managed grassland is an important sink and based on biomonitoring experiments the deposition velocity for mercury can be calculated to be used in deposition modelling.

In principle also mosses can be used in order to determine the deposition velocity in natural ecosystems but there is a lot of research needed to determine the sink strength of the different moss species, the percentage soil covering and the exposure time. It is also not easy to measure ambient mercury concentrations in a forest environment. In the open field mercury can be measured and/or modelled at any height above the ground. In a forest ecosystem the reference height should be above the forest canopy and the deposition into the forest, even at open spaces in the forest environment is very complex. As deposition, profiles are already made for a number of gases in forest ecosystems (ammonia, ozone) and there are lots of measuring towers available in forest that can be used also for mercury.

It can be concluded that the data form the European heavy metals network can be made useful to study mercury deposition from long-range transport, but some preliminary studies need to be carried out in order to clarify a number of essential parameters for the modellers.

#### LOCAL VARIATIONS OF OZONE CONCENTRATIONS IN THE LANDSCAPE

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Hourly ozone concentrations and meteorology parameters have been measured at monthly intervals at different sites in the rural landscape in south-west Sweden and compared with measurements at the permanent monitoring sites Råö (coastal) and Östads Säteri (inland). Ozone concentrations can differ greatly within relative short geographical distances (kilometers). This can result in large differences in the annual values of AOT40 and maximum 8-h mean concentrations for the different sites. The differences are to a large extent explained by the vertical mixing of the air layers, especially during nighttime. Efforts have been made to characterize the geographical settings that determine high and low ozone occurence. Distance to the coast and the local topography are the main explanatory variables. A methodology to estimate AOT40 from monthly mean ozone concentrations will also be described making use of the diurnal air temperature range as a marker for diurnal ozone concentration range.

### ELEMENT CONCENTRATIONS IN MOSSES IN RELATION TO ATMOSPHERIC DEPOSITION AND SOIL CHEMISTRY

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**Aims.** This study was conducted in the framework of a thesis about the "Dynamic and budget of Trace Metal (TM) in some French forest ecosystems. Modelisation, speciation and critical loads" (L. Gandois, 2009). The relationships between TM concentrations in mosses (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Sb, V, Zn) and metal levels among different ecosystem compartments (atmospheric deposition, soil and soil solution) were monitored in various French forests.

**Methods.** This study was carried out in 5 forested sites (sites managed by the National Forest Office (ONF) and integrated to the ICP Forests of UNECE-LRTAP), with various environments (altitude, air quality, soil constituents). Three moss samples were collected on each sites in october 2007 and 2008. On the same period, soluble (0.22  $\mu$ m) atmospheric total deposit below or outside canopy, TM concentrations in soil and soil solutions were monthly monitored.

**Results.** The preliminary results of the Spearman correlation test showed that there were only few significant relationships between soluble deposition below-canopy or in open-area and concentrations in mosses collected below canopy. There were much more significant relationships between concentrations in mosses and  $H^+$  deposition or  $H^+$  in soil solutions.

This study was supported by the French Agency for the Environment and Energy Management.

### WHICH OZONE DOSE RESPONSE WORKS BEST FOR OILSEED RAPE AND BROCCOLI?

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Broccoli and oilseed rape are important crops. Broccoli has been attributed anti-carcinogenic properties and is considered important for human health. Oilseed rape can be used for both oil production and as feed, it is therefore of economic importance. For both species open top chamber (OTC) experiments were conducted over three consecutive years and different ozone treatments were applied: for oilseed rape three levels and for broccoli two levels were tested. Ozone caused a reduction in seed yield, 1000-seed weight and oil percentage in oilseed rape. For broccoli, ozone effects on yield were not significant, probably because the exposure period is limited and vegetables are harvested before the plants start to senescence.

Stomatal conductance measurements from the entire growing season were used to test and compare two stomatal models: a multiplicative, Jarvis-type model and a semi-empirical, Ball-Berry-Leuning type model coupled with the biochemical photosynthesis model of Farquhar. The multiplicative model was then used to calculate the cumulative ozone flux (CUO) in the different treatments and years as compared to the accumulated ozone concentration over a threshold of 40 ppb (AOT40). The response of the yield parameters were examined versus AOT40 and CUO. Although clear ozone effects were seen in different years, also differences between years were observed. This is explained by other climatic variations between different growing seasons, surely ozone is not the only parameter affecting these results.

### TROPOSPHERIC OZONE AND ITS EFFECTS ON THE MAIN AGRICULTURAL SPECIES OF CENTRAL AMERICA AND THE CARIBBEAN

<u>Jesús Ramírez<sup>1</sup></u>, Lourdes Valdés<sup>1</sup>, Don Mckenzie<sup>2</sup>, Cesar García<sup>3</sup>, Víctor Gutiérrez<sup>4</sup>, Rafael Ramos<sup>5</sup>, Adam Fenech<sup>6</sup> and Luz.G.Calzadilla<sup>7</sup>

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**INTRODUCTION:** Tropospheric ozone is the air pollutant that causes the most damage to forests, agricultural crops and vegetation in general. It is a major factor in the appearance of disease and illnesses in agricultural cultivations and forests. While initially attributed to highly industrialized countries, damage from tropospheric ozone now extends to less developed nations as in the case of Cuba and other smaller countries in the Americas. In addition to being an air pollutant, tropospheric ozone is also a major greenhouse gas - the third largest, in fact - having a direct influence on climate change.

**RESULTS:** This paper reports on research conducted in agricultural areas of Mexico, Panama and Cuba showing the link between the long-range transport of air pollutants and the high levels of atmospheric ozone concentrations and their impact on forests and agricultural crops. In the places studied in Mexico, the variation of daily ozone values during the whole period of measurement. More than 50% of the values break the threshold established for agricultural crop protection in Cuba of 40 ppb (Ramirez, 1998). We also observe that 37% of the days have ozone levels higher than 110 ppb, a level set in Mexico as harmful to human health (Ramos, 2002). In Panama more than 50% of the values break the threshold established for agricultural crop protection in Cuba of 40 ppb, in July, 48% in August and 57% in September, in the meteorological station of Tocumen (Ramírez, 2009).

The paper demonstrates the importance of an early warning system of projected high levels of atmospheric ozone so that farmers and government agencies can take appropriate response measures to protect vegetation.

**CONCLUSION:** A next step to the investigation could be to extend monitoring ozone concentrations to non-urban areas of other countries inside and outside America, that present similar problems as Cuba, Mexico and Panama.

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#### ASSESSMENT OF METAL ACCUMULATION IN Rhodobryum roseum IN RELATION TO ATMOSPHERIC EMISSION SOURCES IN UTTARAKHAND, INDIA.

#### Dinesh K. Saxena, Shivom Singh and Kajal Srivastava

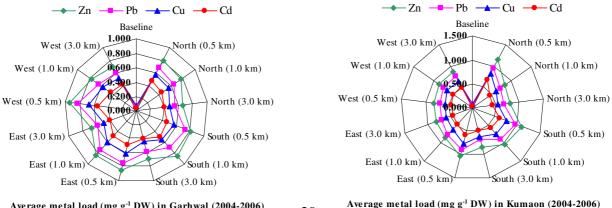
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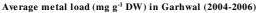
Mankind has become the most important factor in altering global biogeochemistry of metals. Global anthropogenic metal inputs to ecosystems through air, water and soils have increased substantially worldwide over the last century. Automated, continuous active biomonitoring is a useful tool for determining levels of atmospheric contamination, but it suffers from certain limitations amongst which is the high cost resulting from the need for a large number of sampling sites. Many recent studies of atmospheric pollution have used bryophytes (mosses) as biomonitors. The use of these organisms allows several sites to be monitored simultaneously at low cost. The use of mosses as biomonitors, whereby analysis is made of the total contents of metals in these organisms, is an often-used method for determining levels of atmospheric deposition of contaminants. Mosses obtain most of their nutrients via atmospheric deposition; therefore the elements contained in their tissues may reflect the gaseous, dissolved or particulate elements in the atmosphere (Couto, et al, 2004).

In present study, levels of 4 trace elements were measured in samples of the *Rhodobryum roseum* Hedw. collected cross section wise at nearly equi-distance from all the four directions of Kumaon and Garhwal hills of Uttarakhand, using transplant technique. Metal bioaccumulation in moss was estimated seasonally (summer, monsoon and winter) from 2004 to 2006 in order to obtain deposition patterns and individuate potentially toxic metals emitted from the catchments sites. All four metals showed highest bioaccumulation values in west direction at the distance of 0.5 km in Garhwal and at north 0.5 km in Kumaon region during all the three consecutive years. Highest values of metals were during summer followed by winter and lowest in monsoon. Rapid economic development and many fold increase in tourist activity, could be responsible for the same (Saxena, et al, 2008). Bioaccumulative ability in moss was evaluated statistically using Dunkun's Multiple Range test showed an overall change in plant elemental concentrations throughout the different seasons in four undertaken metals during the period 2004-2006. Study also reflects the potential of the moss R. roseum for biomonitoring of atmospheric metals in arid climatic conditions, which gave a complete map of the undertaken metal deposition throughout the study sites of Uttarakhand, India. Likely important consequences for ecosystem structure and functioning and even for human health may be expected from these changes in mineral concentration.

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#### MULTIELEMENT ATMOSPHERIC DEPOSITION STUDY IN CROATIA

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For the first time the moss biomonitoring technique and two complementary analytical techniques – neutron activation analyses (NAA) and atomic absorption spectrometry (AAS) – were applied to study multielement atmospheric deposition in the Republic of Croatia. Moss samples were collected during the summer 2006 from 98 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 Heavy Metal Atmospheric Deposition. Conventional and epithermal neutron activation analyses made it possible to determine concentrations of 41 elements including key heavy metals such as Pb, Cd, Hg, and Cu determined by AAS. Principal component analysis (factor analysis 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 for Croatia are consistent with the corresponding values for all Europe for most elements. It was shown that the Adriatic coastline of Croatia may be considered as an environmentally pristine area. This study was conducted in order to provide reliable assessment of air quality throughout Croatia including areas used as military polygons ("Eugen Kvaternik" in Slunj), and producing information needed for better identification of pollution sources and improving the potential for assessing environmental and health risks in Croatia associated with toxic metals.

#### CHANGES IN CONCENTRATIONS OF 14 ELEMENTS IN MOSS CAUSED BY TIME AND SITE-SPECIFIC EFFECTS IN THE CZECH REPUBLIC BETWEEN 1995 AND 2005

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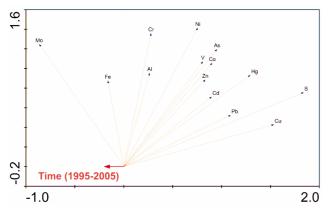
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Emissions of atmospheric pollutants from industrial sources peaked in the mid to late 1980s in the Czech Republic (the western half of former Czechoslovakia). After the political and economic changes, the emissions swiftly decreased between 1990 and 2005 to less than one tenth of the peak values. The element concentrations in moss, which mainly reflect the atmospheric deposition rates of these elements, were determined in the Czech Republic in the autumns of 1991–1992, 1995, 2000 and 2005. Significant decreases in average element concentrations in moss were determined in successive campaigns, with a few exceptions for individual elements. Multivariate statistics was applied (SW Canoco for Windows 4.5) to evaluate the temporal effects on element concentrations in moss.

Real long-time changes in the element concentrations in moss, regardless of site-specific factors, were studied using redundancy analysis (RDA – a multivariate linear direct gradient analysis). The raw concentrations of the 14 elements determined exclusively in *Pleurozium schreberi* moss samples collected at 151 (identical) sites in 1995, 2000 and 2005 were evaluated. The use of locality identities as the covariable enabled the influence of constant site-specific factors to be eliminated (e.g., altitude, land-cover, etc.) The precipitation sum over a period of 2.75 years before each moss sampling campaign was used as the second covariable. We standardized the deposition of each element separately to ensure comparable scales between elements.

The temporal pattern was highly significant (p < 0.01, F = 54.821) and attributed to ca 15.5% of the element concentration variability. A temporal decrease in the concentrations of S, Cu, Hg, Pb, Cd, Zn, Co, As, V, Ni, Al and Cr was detected (Figure 1). Mo and Fe were exceptions, and did not follow this pattern.

As the concentrations of most elements decreased in time, the relative velocity of the change seemed to be worth investigating. This question was addressed using the very same method (partial RDA with localities and precipitations as covariables), but with the data standardized both for the concentration of each element and for the samples, ranking the concentration for



each element separately within each sample. This operation enhanced the compositional variability of the samples.

This analysis revealed that the velocity of the decrease was high for As, Pb and S, while the proportion of Cr, Zn, Cd, Ni remained more or less constant and the proportion of Mo, Fe, Al increased in time.

Figure 1 RDA ordination biplot for the element contents in moss and the time variable.

#### COMPARISON OF ELEMENT CONTENT DISTRIBUTION IN MOSS, GRASS AND SPRUCE NEEDLES IN CONIFEROUS FORESTS OF THE CZECH REPUBLIC IN 2005–2006

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In the framework of project CZ0074 (www.norwaygrantCZ0074.eu), supported by the Norwegian Financial Mechanism, biogeochemical explorations of forests in the Czech Republic have been initiated at the permanent monitoring plots used for the UNECE ICP-Vegetation moss campaigns. Leaves of Wavy hairgrass (*Deschampsia flexuosa*) and annual and biennial needles of Norway spruce (*Picea abies*) were collected at circa 250 monitoring plots. Contents of Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hg, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Rb, S, Sb, Se, Sn, Sr, Th, Tl, U, V, Y, and Zn were determined in unwashed samples, using ICP-MS methods. The analytical results were compared with the moss (reference) analytical data for the given sampling plots obtained in the moss monitoring survey 2005 (Sucharová et al. 2008). Basic statistics of the analytical data have been collected, and maps of the element distribution in the grass and needles specimens have been constructed.

The moss samples showed the highest content of the investigated elements, except for Ba, Cs, Mn and Sr, which were more accumulated in spruce needles, while Cs, Mo and Rb were more concentrated in grass. The contents of Co and Ni in spruce needles and Ni and S in grass leaves reached similar concentrations as in moss. The contents of Cs, Cu, K, Mo, Ni and Rb were higher in annual spruce needles than in biennial needles. No significant differences in Ag, Cd, Co, Cr, Cu, Fe, Pb, S and Zn contents were determined in annual and biennial needles, while the remaining elements tended to be more accumulated in biennial needles.

All species showed a most similar pattern of distribution of Bi, Co, Cs, Fe, Mo, Pb, Rb, Sb, Se and U. The greatest differences were found in Cr, Cu, Mn, S and Zn distributions. The element variability is caused by differences in the proportion of element origin from surface contamination and from element uptake from the soil. However, the potential uptake of elements from soil covers will be evaluated after completing our work on determining the element contents in samples of forest floor humus and eluvial and illuvial soil horizons collected from the permanent moss monitoring plots.

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#### SULPHUR MONITORING WITH MOSSES: WHAT IS THE EXPERIENCE?

#### Lotti Thöni

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The aim of this study is to give some basis for discussion, whether the determination of sulphur in moss can help to estimate the sulphur input to the ground.

At three rural locations in Switzerland, one in the northern Pre-alps (ZG), a second on the Plateau (HM) and a third in the Southern Alps (TI) the S-loads (through precipitation and deposition dust) were determined with the Bergerhoff method between September 1993 and August 1994. Five replicates were taken monthly at each site. Five samples of the moss species *Hylocomiums splendens* (Hs), *Pleurozium schreberi* (Ps), and *Hypnum cupressiforme* (Hc) were collected at the end of the deposition measurements at each site. The results of recovery experiments and comparison with reference material were good for both methods.

<u>Results:</u> Higher burdens of sulphur deposition were found in the Southern Alps, partly because of higher amount of precipitation (Fig. 1). The moss species Ps and Hc did not show a significant difference (p < 0.05) (Fig. 2). Hs showed a significant higher value at the site HM, however, it was collected near trees (unlike Ps and Hc). Figure 3 shows the regression between Sulphur in deposition and in mosses. Higher deposition showed also higher concentration in moss, however, as sulphur is a macronutrient, the background level of S is very high and therefore the slope of the regression line was small.

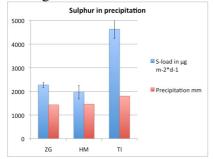
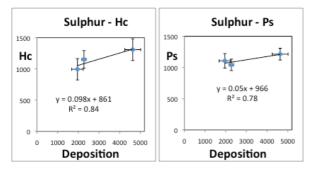


Fig. 1: Sulphur in precipitation (Bergerhoff)



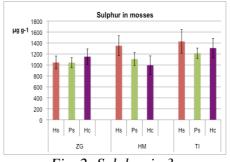


Fig. 2: Sulphur in 3 moss species

*Fig. 3: Comparing the sulphur deposition* ( $\mu g m^{-2} d^{-1}$ ) with the moss concentration ( $\mu g g^{-1}$ ) of Hc and Ps

<u>Discussion</u>: Taking into account the standard deviation, it is not sure if the S-concentration in moss is (among other things) dependent on the S-deposition, especially as the contents in mosses where not very different at the three sites.

<u>Outlook:</u> We are going to repeat this study at 18 sites within the 2010 survey, but with bulk-sampler. Are there other countries that have done such comparisons and/or would do this in 2010?

#### OZONE EFFECTS ON METHANE AND CARBON DIOXIDE FLUXES FROM PEATLAND MESOCOSMS

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Tropospheric ozone poses a significant threat to crop yield and forest productivity of sensitive species at current levels in Europe, while background levels are expected to increase further. The impact of ozone on peatlands, and ecosystem functioning in general are limited by current knowledge. This study shows clear effects of ozone on methane emission, gross photosynthesis and *Sphagnum* growth.

### SUBALPINE GRASSLAND NEE CO<sub>2</sub> FLUXES INDICATE REDUCED GPP AND RECO AT ELEVATED OZONE, BUT NO REDUCTION OF PRODUCTIVITY

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Ozone (O<sub>3</sub>) and nitrogen (N) deposition affect plant carbon (C) dynamics and may thus change ecosystem C-sink/-source properties. We studied effects of increased background O<sub>3</sub> concentrations (up to ambient x 2) and increased N deposition (up to +50 kg ha<sup>-1</sup> a<sup>-1</sup>) on mature, subalpine grassland during the third treatment year. Here, only responses to ozone are reported.

During the 2006 vegetation period, we measured ecosystem-level  $CO_2$  fluxes with a steady state cuvette. Light dependency of gross primary production (GPP) and temperature dependency of ecosystem respiration rates ( $R_{eco}$ ) were established. Using  $R_{eco}$  and GPP values, we calculated seasonal net ecosystem production (NEP), based on hourly averages of global radiation and soil temperature.

Under high  $O_3$  and with unchanged aboveground biomass,  $R_{eco}$  and GPP decreased similarly throughout the season. Accordingly, NEP indicated an unaltered CO<sub>2</sub>-C balance. Independent of treatment, we also observed a negative NEP of 146.4 g C m<sup>-2</sup> (±15.3). This C loss was likely due to a transient management effect, equivalent to a shift from pasture to hay meadow and a drought effect, specific to the 2006 summer climate. There was no interaction between  $O_3$  and N treatments.

Detrimental effects of  $O_3$  on grassland plant species — ranging from visible injury to substantially decreased productivity — are well documented. In our study, the highly significant - 8%  $O_3$  effect on mean GPP<sub>pot</sub> was indicative of damage to the photosynthetic system. The similar reduction in R<sub>eco</sub> is likely a direct consequence of smaller C gains in GPP, because R<sub>eco</sub> is mostly associated with plant-growth processes and soil respiration that feed on plant C with an age of hours to days (fine roots and exudates). As a result, the O<sub>3</sub> treatment did not significantly affect either seasonal NEP or dry matter production (<-1%).

This observation is consistent with negative  $O_3$  effects on productivity in previous studies. Those were found where photosynthetic capacity is more likely a limiting factor (very productive or newly established systems, *e.g.* in agriculture), where low genetic diversity prevented gapfilling through resistant genotypes and/or where experimental situations tended to amplify the effects of  $O_3$  via altered microclimatic conditions. In contrast, this study refers to a low productivity subalpine grassland community (~120 g m<sup>-2</sup> a<sup>-1</sup>), consisting of >90 vascular plant species. Most of the biomass of such systems is allocated belowground. These protected resources allow repeated establishment of a new photosynthetic canopy, even after years of O<sub>3</sub>related low GPP and they are lending the system a large resilience toward declining biomass production. Also, treatments in earlier experiments usually simulated O<sub>3</sub> "smog" events with very high peak concentrations and a strong diurnal fluctuation that may affect plants differently than the increased background concentration applied in our study. Our study has shown that coupled effects of O<sub>3</sub> on GPP and R<sub>eco</sub> did not significantly alter seasonal C balance.

### MONITORING OF INDOOR POLLUTION BY USING MOSSES IN THE GIRONA AREA, SPAIN.

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In the Girona area, Spain mosses were used to obtain indoor pollution. This study was performed in cooperation with eight institutions from Spain and Austria. It was aimed to assess indoor pollution data for correlation with human health data.

Moss (*Hylocomium splendens*) was sampled in a background area of Austria, reduced to its green parts and washed three times in double distilled water. Five gram of moss was exposed in mesh covered frames for two months at each of 20 residential homes. There was no treatment of moss (e.g. wetting etc.) during this period. Before displacement moss was sprayed slightly to prevent a loss of adhering particles. Another set of moss was exposed at the outside of the windows at rooms having indoor collectors to get indoor / outdoor ratios. Parallel to the moss, NO<sub>2</sub> samplers (tubes) were exposed to get comparisons to conventional methods for estimating traffic pollution. At three outdoor bulk collectors moss was exposed too.

Moss was analysed for metals (<sup>195</sup>Pt at low resolution (LR), <sup>27</sup>Al, <sup>52</sup>Cr, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>95</sup>Mo, <sup>111</sup>Cd, <sup>118</sup>Sn, <sup>121</sup>Sb, Pb) on an Element 2 ICP-SFMS (ThermoFisher, Bremen, Germany) at the University of Applied Sciences, Vienna and for the 16 EPA-PAH plus coronene at the Umweltbundesamt, Vienna.

In the due course of the study these moss data will be compared to various other data on air pollution, noise and other effects mainly deriving from road traffic sources. Finally all these data will be connected to human health data from the REGICOR cohort study, one of Europe's biggest health studies.

# **Abstracts**

### **Posters**

#### COMPARISON OF NITROGEN CONTENT AND $\delta^{15}$ N-SIGNATURES IN MOSSES (*HYPNUM CUPRESSIFORME*) AND LICHENS (*PARMELIA SULCATA*) WITH NITROGEN DEPOSITION RATES OF GERMANY

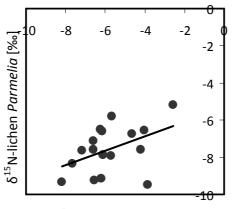
#### <u>Stefanie H. Boltersdorf</u>, Johannes Schultze, Willy Werner University Trier, Department of Geobotany, Behringstraße 21, 54286 Trier, Germany

Mosses and lichens are passive biomonitors of our changing environment: the sensitivity of particular moss and lichen species and assemblages to a very broad spectrum of environmental conditions, both natural and unnatural, is widely appreciated. Mosses and lichens are therefore used increasingly in evaluating threatened habitats, in environmental impact assessments, and in monitoring environmental perturbations, particularly those resulting from a disturbingly large and growing number of chemical pollutants. In the present study we tested whether the nitrogen concentrations and  $\delta^{15}N$  signatures of selected epiphytic species can be used to estimate deposition rates and sources of these compounds.

In autumn 2008 epiphytic moss *Hypnum cupressiforme* and epiphytic lichen *Parmelia sulcata* were sampled from 18 sites located in Germany. Samples were collected within a radius of 2 km around field stations for deposition measurement (Federal Environment Agency).

*Hypnum cupressiforme* and *Parmelia sulcata* showed high nitrogen concentrations on sites in northern and eastern parts in Germany. In areas of pure air we found less N-concentrations.

On closer inspection of  $\delta^{15}N$  ratios of investigated mosses and lichens, we found moderate correlations between  $\delta^{15}N$  ratio and  $N_{min}$ -deposition respectively  $NH_4^+$ -N-deposition. As expected, the  $\delta^{15}N$  ratio is more negative in *Parmelia* grown under high ammonia deposition, where the N-deposition is from agricultural origin. There exist significant correlations between  $NH_4^+$ -N-proportion of  $N_{min}$ -deposition and  $\delta^{15}N$  ratio of *Parmelia*. The weak correlation between  $\delta^{15}N$  ratios of *Parmelia* and *Hypnum* (r=0.45) suggests, that the two species make use of different nitrogen sources on the same place (Fig.1). The better correlation of N-deposition and  $\delta^{15}N$  ratio in lichens indicates that they are better monitors for atmospheric N-deposition than mosses. The study demonstrates the possibility to estimate the deposition of total nitrogen and of ammonium on the basis of the nitrogen concentration and  $\delta^{15}N$  ratio of epiphytic lichens.



 $\delta^{15}$ N-moss *Hypnum* [‰]

**Fig.1:** Correlation between  $\delta^{15}$ N ratios of *Parmelia sulcata* and *Hypnum cupressiforme* (r=0,45+, n=17; 0,05>p<0,1)

### PRELIMINARY OZONE DOSE-RESPONSE FUNCTION FOR TOMATO IN THE MEDITERRANEAN AREA

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Ozone  $(O_3)$  levels continue increasing in the Mediterranean region due to the fact that in southern Europe, ozone formation is particularly favored by the intense solar radiation, high temperatures and re-circulation processes of the polluted air masses. The Mediterranean countries, and particularly Italy and Spain, lead the annual production of tomato in Europe; their production ranks in the sixth and ninetieth worldwide position respectively (FAOSTAT, 2007). Flux-based O<sub>3</sub> critical levels have been established for wheat and potato but only a concentration-based critical level has been derived so far for horticultural crops (UNECE CLRTAP, 2004). In this study, five independent experiments carried out in Italy and Spain have been used to derive a dose-response function. Tomato was cultivated in late spring and summer seasons, according to the typical agronomic cycle of this horticultural crop in the Mediterranean area. Different cultivars of tomato were grown in well irrigated pots under Open Top Chamber conditions, and exposed to different  $O_3$  concentrations from emergence to the end of crop cultivation. Experiments were carried out in Benifaió (Valencia, Spain), Delta del Ebro (Tarragona, Spain), and Curno (Bergamo, Italy) sites. Field stomatal conductance (gs) measurements were used to reparameterize the g<sub>s</sub> module included in the Deposition of Ozone and Stomatal Exchange model (DO<sub>3</sub>SE). Using this new proposed parameterization for tomato, a dose-response function is derived from reductions in tomato yield (ripe fruits fresh-weight) in relation to ozone stomatal flux. A preliminary stomatal flux-based O<sub>3</sub> critical level is proposed for this crop.

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### TEMPORAL TRENDS IN THE CONCENTRATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN MOSSES IN BERTIZ NATURAL PARK (NORTHERN SPAIN)

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Herbarium mosses (*Dicranum scoparium* Hedw., *Hypnum cupressiforme* Hedw., *Thamnobryum alopecurum* Hedw. Gangulee and *Thuidium tamariscinum* Hedw. Schimp.) from 1879-1881, 1973-1975 and 2006-2007 periods were used to investigate the historical changes of atmospheric deposition of polycyclic aromatic hydrocarbons (PAHs) at a remote site located in Northern Spain. The mosses had been conserved in the Herbarium PAMP of the University of Navarra, which contains specimens of bryophytes collected in the Natural Park of Bertiz since 1879. Natural abundance of nitrogen and carbon isotopes was also measured in order to assess the evolution of emissions from anthropogenic sources. Nitrogen concentrations, <sup>13</sup>C, <sup>15</sup>N and PAH levels were significantly higher in 19<sup>th</sup> century samples with respect to the present century samples. Moreover, PAH distribution varied over the centuries, following a tendency of light PAH enrichment. The carbon, nitrogen and PAH levels measured in the mosses tissue were related to the historic evolution of anthropogenic emissions in the area, mainly influenced by changes of economic activities, domestic heating and road traffic density. Mosses provided by herbaria seem to offer the possibility to study long-term temporal evolution of atmospheric PAH deposition (Foan *et al.*, 2010).

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L. Foan, C. Sablayrolles, V. Simon, D. Elustondo, E. Lasheras, L. González, A. Ederra, J.M. Santamaría, Reconstructing historical trends of Polycyclic Aromatic Hydrocarbons deposition in a remote area of Spain using moss material from a herbarium, *Atmospheric Environment*, submitted.

### THE EFFECT OF ELEVATED TROPOSPHERIC OZONE ON THE FEEDING VALUE OF RICE STRAW

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Up to 80 percent of rice straw, a by-product of rice grain is used as cattle feed in many developing Asian countries (Devendra and Sevilla, 2002), making it one of the most important animal feed resources in this part of the world. The protein content, composition of the fiber fraction, content of antinutritive factors especially phenolics and silica, and rumen digestibility, are the main factors that determine the straw quality. These factors can be influenced by genotype, managerial practices and environmental effects. One of the major environmental factors affecting rice straw quality in the future could be rising tropospheric ozone concentrations. This is particularly relevant considering that ozone concentrations are projected to rise in Asian rice producing countries to a larger extent than elsewhere in the world (The Royal Society, 2008). Therefore, this study aimed at evaluating the effect of elevated ozone concentration on the chemical composition and feeding quality of rice straw.

In an earlier experiment we exposed young rice plants to elevated ozone concentration (120 nL L<sup>1</sup>, 18 days, 7h/day) in open top chambers, and subsequently compared the feeding value of plant materials to that of non-treated control plants (Frei et al., 2010). Feeding value was assessed by chemical analyses and gas production values in an *in vitro* rumen fermentation system. We observed reduced gas production from the ozone exposed samples, which is a correlate for reduced digestibility and feed intake *in vivo*. This was explained by increased lignin and phenolic concentrations in ozone treated plant materials. Protein content dropped as a consequence of ozone exposure. In our subsequent larger-scale greenhouse experiment, rice plants of six different genotypes were exposed to four different ozone concentrations (charcoal filtered, ambient, 2 x ambient, and 2.5 x ambient) throughout the growth period (~three months) and feeding value of mature straw is being determined.

In conclusion, ozone was shown to affect the chemical composition and the digestibility of rice plants, and further analyses are being carried out to assess a dose-specific ozone effect in mature straw from various genotypes. The results of these experiments will be discussed.

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**Acknowledgement:** This research was partly supported by the Global Environment Research Fund (Ba-086) of the Ministry of the Environment, Japan.

#### ASSESSMENT OF TROPOSPHERIC OZONE IMPACT ON CROPS IN CRETE (GREECE) USING SNAP BEAN AS BIOINDICATOR

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In this study the S156/R123 snap bean (*Phaseolus vulgaris* L.) biotype system was evaluated in Crete (Greece) as a potential bioindicator system. Seeds were supplied by the ICP-Vegetation Co-ordination Centre at Bangor, UK. Plants were grown at a field site (latitude 35°20'N, longitude 25°8'E, 10 m.a.s.l.) situated in the suburbs of Heraklion, using a standardised protocol developed by the UNECE ICP-Vegetation appropriate to the proposed investigations. Plants were transferred at the field on 1 August and pods were collected on 30 September 2009. Pods were separated into mature or small sterile, counted, dried to constant weight at 70°C, and weighed. Stomatal conductance and physical variables were monitored and ozone injury was assessed. The sensitive and tolerant genotypes were compared for differences in leaf total antioxidant activity, total phenolics, lipid peroxidation and proline content to determine whether antioxidants and stress indicators were related to ozone tolerance. Fully expanded leaves were analyzed at four different growth stages. Genotypes R123 and S156 developed the same number mature pods but the biomass per mature pod was greater for R123. Meteorological data, ozone exposure information, pods biomass and visible injury assessment are summarized in Table 1.

**Table 1**. Meteorological data, ozone exposure information, biomass data and visible injury assessment over the course of the field experiment conducted on snap bean (*Phaseolus vulgaris* L.) S156 and R123 biotypes in the suburbs of Heraklion, Crete.

Growth period	1/8 - 30/9/2009
24-h mean temperature (°C)	24
24-h mean VPD (kPa)	1.1
Mean daytime PAR ( $\mu$ mol m <sup>-2</sup> s <sup>-1</sup> )	485
AOT40 (ppb h)	418
S156 mature pod (number per plant)	25.9
S156 sterile pod (number per plant)	10.9
S156 mature pod weight (g dry wt. plant <sup>-1</sup> )	20.1
S156 average mature pod weight (g dry wt. pod <sup>-1</sup> )	0.8
S156 damaged leaves (scored as >25% injury) on 29/9/09 (%)	57.1
R123 mature pod (number per plant)	25.7
R123 sterile pod (number per plant )	5.0
R123 mature pod weight (g dry wt. plant <sup>-1</sup> )	30.1
R123 average mature pod weight (g dry wt. pod <sup>-1</sup> )	1.1
R123 damaged leaves (scored as >25% injury) on 29/9/09 (%)	14.7
Yield ratio (S156:R123)	0.7

Abaxial surface stomatal conductance measurements were recorded on the 25<sup>th</sup>, 33<sup>rd</sup>, 40<sup>th</sup> and 48<sup>th</sup> experimental day on the most recently fully-expanded leaf but no differences were found between the two genotypes. Total antioxidant activity, total phenolics and proline content were found increased, and statistically significant, in the tolerant genotype over the course of the experiment.

#### YIELD RESPONSES OF RICE AND SOYBEAN PLANTS EXPOSED TO OZONE

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Recent rising tropospheric ozone concentration is one of important key issues in developing countries associated with increasing energy and food supply for their sustainable development. Rice and soybean plants as well as wheat are very important crops for food production in the world. There are many ozone exposure experiments in wheat and soybean. Rice plant as Asian major crop plants has wide varieties; however, their sensitivity to ozone was not much studied. Our previous screening studies in rice cultivars suggested that Kirara 397 and Takanari grown in the elevated ozone concentration showed significant grain yield reduction. However, Koshihikari and Nikomaru did not show any significant yield reduction.

Ozone-sensitive Kirara 397 (*japonica*) and Takanari (*indica*) were grown in the box containers under the ambient air conditions in the glasshouse (12h-mean  $O_3$ : 30ppb) or under the  $O_3$  added conditions (12h-mean  $O_3$ : 76ppb). Relative yield responses were compared to those of 20 soybean cultivars grown in pots under the same air conditions for discussing future food supply under the global climate change conditions.

Total ozone dose (12-hours) from transplanted to headed day in Kirara 397 as an early maturing variety was 12/28 ppmh (Ambient/Ambient+O<sub>3</sub>) and that in Takanari as an relatively late maturing was 27/65 ppmh. Kirara 397 significantly reduced panicle weight per plant by 20% in the ambient+O<sub>3</sub> conditions, but Takanari did not even though it received more than 2 times higher ozone dose in this experiment.

Cultivars of soybean showed significant differences in leaf injury occurrence and seed yield responses. Especially Japanese cultivars of Nakasennari and Tamahomare induced severe necrosis in the leaves and these two were most sensitive to elevated ozone stress by injury development. As shown in Fig.1, Tamahomare showed significant reduction in dry seed weight, however, Nakasennari did not. Based

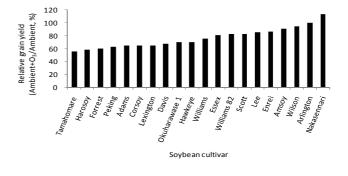


Fig. 1. Relative grain yield of soybean cultivars after ozone exposure

on the yield response rather than leaf injury, Nakasennari could be the most  $O_3$  tolerant among the tested 20 cultivars. These results as well as our previous report in the rice cultivars suggested that mechanism of leaf injury development was not directly correlated with yield reduction mechanism in both rice and soybean plants.

This research was financially supported by the Global Research Fund (Ba-083), Ministry of the Environment, Japan.

Reference: Sawada, H., and Y. Kohno(2009) Plant Biology, 11(suppl.1):70-75.

#### TEMPORAL AND SPATIAL TRENDS (1990- 2005) IN HEAVY METALL ACCUMULATION IN MOSSES IN SLOVAKIA

Blanka Maňkovská, B., Oszlányi, J.

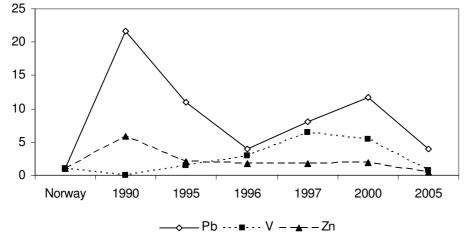
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Biomonitoring of multielement atmospheric deposition using terrestrial moss is a wellestablished technique in Europe. The moss samples of *Hylocomium splendens, Pleurozium schreberi* and *Dicranum* sp. were collected in the Slovakia. Separate we are evaluated National parks (Vysoké Tatry, Nízke Tatry, Západné Tatry –Jelenec, Slovenský raj), in Landscape protection area (Veľká Fatra) and Báb Research Site. 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 Cd, Pb and Hg 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.

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Concentration of Pb, V and Zn (average) in mosses for Slovakia in all survey years

Note: Year (number of PMP): 1990(58);1995(79); 1996(69); 1997 (74); 2000 (86); 2005(82); PMP- permanent monitoring plots

#### BOREAL FOREST MOSSES AS INDICATORS OF NITROGEN DEPOSITION IN FINLAND: THE RESEARCH PLAN

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Potentially, mosses are suitable indicators for monitoring nitrogen deposition because they obtain most of their nutrient supply directly from rainwater and dry deposition. In Finland, nitrogen concentrations have been analysed in national surveys in 1990, 1995, 2000 and 2005/06. In these surveys the nitrogen concentrations have correlated relatively well with the modelled nitrogen deposition. In order that mosses could be used as indicators of nitrogen deposition, more information must be obtained about the factors that affect the nitrogen concentration in mosses.

The suitability of widely distributed, boreal forest mosses as bioindicators of nitrogen deposition in Finland is to be investigated in this project by determining how the growing environment, composition of nitrogen deposition and factors related to the mosses themselves, affect the nitrogen concentration in mosses. In addition, the role of forests mosses and the cyanobacteria present on the surfaces of mosses in nitrogen cycling in forest ecosystems will also be studied.

The research will contribute to the use of mosses as bioindicators of nitrogen deposition, and support the European surveys. The results can be utilized in determining critical loads for nitrogen, and will provide new information about the biological response of plants to nitrogen deposition under natural conditions. Low levels of nitrogen deposition are known, over 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. The results of the project can also be utilised in studies on the effects of nitrogen deposition levels on the development of eutrophication in boreal, nutrient-poor forest ecosystems.

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#### EFFECT OF ELEVATED OZONE ON LEAF SENESCENCE, GROWTH AND YIELD OF RICE CULTIVARS

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Surface ozone concentrations are expected to rise significantly throughout the 21st century. Ozone thereat for food production is increasing in Asian countries. Our previous report suggested that high concentration of ozone significantly reduced grain yield in sensitive rice cultivars (Sawada and Kohno, 2009). To clarify mechanism of ozone affecting rice yield, we conducted ozone exposure experiments in the glass houses. Six rice cultivars showing different sensitivity to ozone were grown under an ambient air (24h mean  $O_3$ , 32 ppb) or ozone-added (77 ppb) conditions throughout the cropping season until grain harvest.

Senescence of flag leaves was accelerated remarkably in Kirara 397 but slightly in Koshihikari in the elevated ozone level. Senescence rate in the leaves of Takanari, Nikomaru, Kasalath, and Jothi showed no significant difference between ambient and ozone-added treatment. Concentration of ethylene precursor, 1-aminocyclopropane-1-carboxylic acid (ACC), in flag leaves was the highest before and after heading date in ozone-added Kirara 397 and ambient plants, respectively. Moreover, ACC level in ozone-added Kirara 397 maintained higher than plants grown in ambient level. ACC concentration in flag leaves of Takanari was the highest and similar level before heading date both ozone-added and ambient plants. It was suggested that acceleration of leaf senescence by elevated ozone is partially involved in increase of ethylene concentration.

Grain weight per panicle in Kirara 397, Koshihikari, and Jothi reduced with elevated ozone exposure due to mainly decreased grain number per panicle. The decrease in 1000-grain weight by elevated ozone was only observed in Kirara 397 which showed significant acceleration of leaf senescence. These results suggested that yield reduction in Kirara 397 is related to not only the decrease in grain number, but also the poor ripening of grains caused by accelerated senescence. In the present experiment, however, the reduction of grain weight per panicle was offset with increased number of panicles under elevated ozone treatment. The interaction between seasonal ozone pattern and plant response depending on growth stage will be discussed.

This research was financially supported by the Global Environment Research Fund Ba-086 by the Ministry of the Environment, Japan.

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#### OAK FORESTS UNDER OZONE STRESS IN EASTERN AUSTRIA? A TREND ANALYSIS 1990-2007

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In the semi-arid north-eastern part of Austria (Weinviertel) sessile and pedunculate oak (*Quercus petraea* and *Qu. robur*) constitute the dominant tree species. These oak forests have experienced serious stress episodes in the previous decades, leading to dieback symptoms of mature trees and difficulties for silviculture. In the frame of this study we have investigated the question to which extent surface-level ozone might have contributed to the stress situation of these oak forests, exemplified for the case study Hochleithenwald in Eastern Austria.

This study tested two hypotheses about the development of stress trends due to ozone:

- Hypothesis 1: Ozone concentrations exhibit a long-term increasing trend, leading to higher exposure doses.
- Hypothesis 2: Climate-change induced variations in meteorological parameters that are important for stomatal conductance reduce the ozone fluxes, leading to constant or reduced uptake doses.

The tests of the hypotheses relied on the local meteorological and ozone data from 1990 to 2007, provided in 30-minutes resolution by the Lower Austrian air quality monitoring network for the stations Mistelbach and Wolkersdorf. The data from April to October of each year were analysed for the whole period or in monthly resolution for the existence of significant time trends by linear regression analyses, Neumann-tests and Cox and Stuart-tests. Ozone data were corrected for atmospheric conductance and measurement height. Ozone exposure was calculated as AOT40 or 7 h-mean value (9 a.m. -4 p.m.). Ozone uptake calculations used the multiplicative Emberson-model (Emberson et al., 2007):

 $g_{sto} = g_{max} * f_{phen} * f_{light} * max \{ f_{min}, (f_{temp} * f_{VPD} * f_{SWP}) \}$ considering a flux threshold of 1,6 nmol.m<sup>-2</sup>.s<sup>-1</sup>, a  $g_{O3max}$  of 160 mmol.m<sup>-2</sup>.s<sup>-1</sup>, and a  $f_{min}$  of 0,13. All parameters were derived from published literature data for *Qu. petraea* or *Qu. robur*.

The calculations confirmed an increasing trend of ozone exposure for both 7 h-mean of ozone (p=0,010; +0,31 ppb per year) and for AOT40 (p=0,06; +360 ppb.h per year) from April to October. The proportion of very high ozone concentrations (>80 ppb), however, remained constant at about 0-2 % of daylight hours. There was also no significant trend for precipitation (neither for the whole year nor for the summer months) and for vapour pressure deficit (April – Oct.). However, temperature increased significantly (p=0,022; +0,06 °C per year) as well as global radiation (p=0,0002; +2,2 W.m<sup>-2</sup> per year) and wind speed (p=0,013; +0,04 m.s<sup>-1</sup> per year). Consequently, also stomatal uptake by the oak leaves increased significantly over the 18 years (sun leaves: p=0,0008; +0,26 mmol.m<sup>-2</sup> per year; shade leaves: p=0,0004; +0,15 mmol.m<sup>-2</sup> per year). The results have confirmed hypothesis 1 but not hypothesis 2.

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#### LARGE-SCALE DISTRIBUTION OF LEAD AND SELECTED LEAD ISOTOPES IN MOSS AND GRASS OF CONIFEROUS FORESTS ACROSS THE CZECH REPUBLIC IN 2005

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Local lead compounds in soil covers and in industrial emissions have specific lead isotope ratios. In order to prove the effects of major natural and anthropogenic pollution sources at the individual moss monitoring plots used in the UNECE ICP-Vegetation campaigns, the concentrations of <sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb isotopes were determined in moss and grass samples collected at the Czech monitoring plots in 2005 and 2006.

Samples of pleurocarpous moss, mainly of Schreber's moss (*Pleurozium schreberi*), and Wavy hairgrass (*Deschampsia flexuosa*), were collected at 280 and 266 sampling plots throughout the Czech Republic. Air-dried samples were milled and triple digested in a mixture of nitric acid and hydrogen peroxide in a microwave digestion system. Besides the subtotal concentrations of 37–40 elements, including Pb, concentrations for the three lead isotopes <sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb were determined separately, using the ICP-MS methods. The analytical results were checked by analysing international reference materials. Trueness of the Pb isotope determinations was checked through the common lead isotopic standard (NIST Standard Reference Material 981). In addition, 10 samples each were analysed in parallel on a high resolution ICP-MS in the laboratory of the Geological Survey of Norway.

The median value for Pb in the Czech Republic in moss is 4.95 mg.kg<sup>-1</sup>, and in grass it is 0.37 mg.kg<sup>-1</sup>. The median value for the <sup>206/207</sup>Pb-isotope ratio in the Czech Republic was found to be 1.151 in moss and 1.162 in grass. Though the Pb concentrations vary by more than an order of magnitude, the regional patterns remain the same.

Maps of the distribution of measured and linearly interpolated total lead concentrations in the bio-indicators showed hot spots at the sites of a secondary lead smelter, a glass works and a non-ferrous metallurgical centre. Different <sup>206/207</sup>Pb-isotope ratios in the analysed samples were found mainly in areas of industrial regions and along the Czech-Polish border, especially near industrialized regions in southern Poland. Anthropogenic emission sources may control the detectable <sup>206/207</sup>Pb-isotope ratios at distances up to 50 km. The Pb isotope ratio indicated only a slight effect of automotive transport, probably because all sampling plots are required to be distant from roads. More complex results are expected after completing the determination of Pb isotope ratios in forest floor humus and soils, and in samples additionally collected close to a major national highway.