







21st Task Force Meeting of the ICP Vegetation 26th - 29th February, 2008 Oulu, Finland

# **Programme Abstracts**



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Working Group on Effects

of the UNECE Convention on Long-range Transboundary Air Pollution

#### Organizers:

## Finnish Forest Research Institute Muhos Research Unit

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

#### **Organizing Committee:**



Harry Harmens Gina Mills Jackie Cooper

#### **Local Organizing Committee:**



Eero Kubin Juha Piispanen Jarmo Poikolainen Sirpa Kotikangas-Venäläinen Samuli Kemppainen





#### Convention on Long-range Transboundary Air Pollution

**Working Group on Effects** 

International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops

## **Programme**

21<sup>st</sup> Task Force Meeting of the ICP Vegetation

26<sup>th</sup> – 29<sup>th</sup> February, 2008 Oulu, Finland



Metsäntutkimuslaitos Skogsforskningsinstitutet Finnish Forest Research Institute

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Working Group on Effects of the

Convention on Long-range Transhoundary Air Pollution

#### Tuesday 26th February, 2008

19:30	Welcome	reception	in	Hotel	Restaurant	Lasaretti,	hosted	by	Tytti
	Tuppurai	nen, Chair	wor	nan of	the Council.				

20:00 Welcome to Oulu: Tytti Tuppurainen.

#### Wednesday 27th February, 2008

Session 1:	09:00 - 10:30 Plenary session (Hall 3)
	Chair: Eero Kubin
9:00	Welcome by <i>Heikki Aronpää</i> , Director of North Ostrobothnia Regional Environment Centre.
9:15	Tor Johannessen - News from the Working Group on Effects.
9:25	Matti Johansson - News from the Convention Secretariat.
9:35	Gudrun Schütze – Update on ICP Modelling and Mapping.
9:40	Harry Harmens et al. – An overview of the achievements of the ICP Vegetation in 2007.
10:10	Eero Kubin – Heavy metal surveys in Finland since 1985.

#### 10:30 – 11:30 Coffee/tea and poster session (Hall 1)

Press Conference: Heavy metal deposition in Finland in 2005 (Hall 2)

#### Session 2: 11:30 – 12:20 Plenary session - 'Nitrogen' (Hall 3)

Chair: Per Erik Karlsson

11:30	Ben Gimeno - The ESF programme 'Nitrogen in Europe' (NinE).
11:35	Ben Gimeno et al. – Nitrogen deposition in Mediterranean ecosystems – definition of empirical loads and identifying conceptual problems for the calculation of N critical loads.

- 1.1:50 *Jarmo Poikolainen* et al. Nitrogen deposition in Finland 1990 2006 by using mosses as bioindicators.
- 12:10 *Harry Harmens* Nitrogen work under the ICP Vegetation: potential new developments.

#### Lunch: 12:20 – 13:30 Lunch Restaurant Lasaretti (First floor)

Session 3:	13:30 – 15:15 Two parallel sessions: Ozone (Hall 3) and Heavy Metals (Hall 2)
Session 3a:	Ozone - 'Progress and new developments'
	Chair: Håkan Pleijel
13:30	Felicity Hayes et al. – Evidence of widespread ozone damage to vegetation in Europe (1990-2006).
14:00	Patrick Büker et al. – Update on flux modelling for forest trees and mapping using localised parameterization.
14:20	Gina Mills et al. – Critical levels for (semi-)natural vegetation: potential new developments.
14:40	Håkan Pleijel et al. – Critical levels for agricultural crops: potential new developments.
15:00	Gina Mills, Felicity Hayes et al. – Summary of the results of the 2007 ICP Vegetation ozone experimental programme and introduction to discussion groups for the next session.
Session 3b:	Heavy metals - 'Critical loads and quality assurance 2005/6 survey'
	Chair: Eiliv Steinnes
13:30	Harry Harmens - Introduction to the heavy metal sessions.
13:35	Gudrun Schütze – Status of the CLRTAP Heavy Metals Protocol review and outcome of a workshop on critical loads for heavy metals.
13:55	Harry Harmens – Overview of data received and further data processing of the 2005/6 moss survey.
14:05	Eiliv Steinnes et al. – Experience from the use of reference samples in the 2005/6 European moss survey.
14:25	Sebastien Leblond et al. – Quality control of the 2006 French moss survey.
14:45	General discussion
Coffee/tea:	15:15 – 15:45
Session 4:	15:45 – 17:30 Two parallel sessions: Ozone (Hall 3) and Heavy Metals (Hall 2)
Session 4a:	Ozone - 'Next stages with ICP Vegetation ozone-effects activities'
	Chair: Gina Mills
15:45	Discussion groups. Targeted discussions based on next stages for development of Mapping Manual and data needs for validating risk maps.
17:00	Discussion groups report back.

Session 4b:	Heavy metals - 'Results 2005/6 moss survey'				
	Chair: Harry Harmens				
15:45	Roland Pesch et al Moss survey 2005 in Germany: final results and perspectives.				
16:05	Harry Harmens et al. – Preliminary results of the European moss survey 2005/6.				
16:30	Discussion outcome 2005/6 moss survey, final report and perspectives.				
	Thursday 28 <sup>th</sup> February, 2008				
	Thursday 28 February, 2008				
Session 5:	9:00 – 10:30 Two parallel sessions: Ozone (Hall 3) and Heavy Metals (Hall 2)				
Session 5a:	Ozone - 'Effects on vegetation'				
	Chair: Boris Turk				
9:00	Per Erik Karlsson et al. – Increasing risk for negative ozone impacts on vegetation in northern Sweden.				
9:20	Matthias Volk et al. – Substantial carbon allocation changes suggested by CO <sub>2</sub> fluxes of sub-alpine grassland under high ozone and nitrogen deposition.				
9:40	Gina Mills et al. – Impacts of increasing background ozone on competition, stomatal control and carbon turnover in grassland mesocosms.				
10:00	Helena Danielsson et al. – Visible ozone injury, ozone uptake and effects on growth of four <i>Phleum pratense</i> genotypes.				
10:20	General discussion.				
Session 5b:	Heavy metals - 'Biomonitoring around local sources'				
	Chair: Sebastian Leblond				
9:00	Eiliv Steinnes et al. – Use of indigenous moss sampling in metal deposition surveys around point sources: examples from 15 Norwegian industries.				
9:20	Marina Frontasyeva et al. – Trace element atmospheric pollution in the Balkans studied by the moss technique, ENAA and AAS.				
9:40	Laura Gonzalez et al. — Heavy metals contamination survey in an industrialized area by the use of Hypnum cupressiforme.				
10:00	Matti Niemelä et al. – The use of mosses for biomonitoring traffic-related Pt and Rh deposition near traffic lanes.				
10:20	General discussion				

Coffee/tea: 10:30 - 11:00 (Hall 1) Session 6: 11:00 – 12:30 Two parallel sessions: Ozone (Hall 3) and Heavy Metals (Hall 2) Session 6a: Ozone - 'Biomonitoring experiments and field surveys' Chair: Ben Gimeno 11.00 Ignacio González-Fernández et al. - Leaf stomatal conductance variability in central Spain Mediterranean grasslands and clover flux modeling 11:20 Gina Mills - Conclusion of discussion of next stages in ICP Vegetation ozone programme (experimental, modelling, mapping). Session 6b: Heavy metals - 'Concentrations in food and mosses' Chair: Zvonka Jeran 11:00 John Derome et al. – Heavy metal concentrations in forest berries and edible wild mushrooms in eastern Finnish Lapland and western parts of the Kola Peninsula (NW Russia) 11:20 Hanna Hokana – Metal concentrations in food plants adjacent to a stainless steel works in Finland – additional intake for humans. 11:40 Raluca Mocanu et al. - Studies on atmospheric heavy metal transboundary pollution in Romania-Republic of Moldova based on biomonitoring using the moss Hypnum cupressiforme. 12:00 General discussion on the future of the moss survey. 12:30 – 15:00 Excursion Oulu University 12:30 Bus to Oulu University. f Biology.

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12:50	Welcome - Pr	rofessor Satu	Huttunen, D	epartment d	of

#### 13:00 Lunch in Restaurant Kastari, hosted by Oulu University and Metla

14:00 Presentations (Hall IT 115):

- Dean Jouni Pursiainen Oulu University and Faculty of Science.
- Deputy director Kari Strand, Oulu University, Thule Institute and Professor Satu Huttunen – Northern and Environmental Issues.

14:50 Bus back to Restaurant Lasaretti

Coffee/tea: 15:00 - 15:30

#### **Session 8:** 15:30 – 18:00 Plenary session (Hall 3)

#### Chair: Harry Harmens

- Reporting back from ozone and heavy metals sessions.
- ICP Vegetation work programme 2008 2011.
- Ozone flux-based risk assessment for tree species using localised parameterization.
- Discussion note: 'Guidelines for the monitoring of effects of air pollution under the LRTAP Convention'.
- Collaboration with other relevant bodies/organizations such as new Task Force on Reactive Nitrogen, Convention on Biological Diversity, Malé declaration.
- Conclusions and review of the 21<sup>st</sup> Task Force Meeting.

## 19:30 Conference dinner in Upseerikerho, hosted by the Finnish Ministry of the Environment and METLA.

#### Friday 29th February, 2008

# 8:15 – 15:00 Excursion to Outokumpu Stainless Steel Plant, Tornio 8:15 Bus from Oulu to Tornio. 10:15 Outokumpu Stainless Steel Plant, including a lunch. Dr Juha Kekäläinen, Manager of Environmental Affairs. 12:45 Bus from Tornio to Oulu Airport.

End of the excursion.

15:00

# Abstracts Oral presentations

### List of oral presentations

- Danielsson H., Karlsson, P. E. & Pleijel, H. Visible ozone injury, Ozone uptake and effects on growth of four *Phleum pratense* genotypes.
- Derome John. & Isaeva L. Heavy metal concentrations in forest berries and edible wild mushrooms in eastern Finnish Lapland and western parts of the Kola Peninsula (NW Russia).
- Frontasyeva M. Trace element atmospheric pollution in the Balkans studied by the moss technique, ENAA and AAS.
- Gimeno, B. S., Mark Fenn, Josep Peñuelas, and Jesús M. Santamaría. Nitrogen deposition in Mediterranean ecosystems definition of empirical loads and identifying conceptual problems for the calculation of N critical loads
- González L.; Elustondo D.; Lasheras E.; Bermejo R. and Santamaría J.M. Heavy metals contamination survey in an industrialized area by the use of "Hypnum Cupressiforme".
- Harmens H., Mills, G., Hayes, Jones, M.L.M., Norris D.A. and the participants of the ICP Vegetation. An overview of the achievements of the ICP Vegetation in 2007.
- Harmens H., Norris D.A., and the participants of the European moss survey 2005/2006 Preliminary results of the European moss survey 2005/6.
- Hayes, F., Mills, G., Harmens, H. & Norris, D.. Evidence of widespread ozone damage to vegetation in Europe (1990 2006).
- Hookana H. Metal concentrations in food plants adjacent to a stainless steel works in Finland additional intake for humans.
- Karlsson, P.E., Tang, L., Sundberg, J., Chen, D., Lindskog, A. and Pleijel, H. Increasing risk for negative ozone impacts on vegetation in northern Sweden.
- Leblond S., Rausch de Traubenberg C. Quality control of the 2006 French moss survey.
- Mills, G., Hayes, F., Harmens, H., Wyness, K., Jones, L., Hill, P., Jones, D., Wilkinson, S., Sharpe, R., Davies, B., Peacock, S. & Barnes, J. Impacts of increasing background ozone on competition, stomatal control and carbon turnover in grassland mesocosms.
- Niemelä, M., Piispanen, J., Poikolainen, J. & Perämäki, P.. The use of mosses for biomonitoring traffic-related Pt and Rh deposition near traffic lanes.
- Pesch R., Schröder W. & Holy M. Moss survey 2005 in Germany: Final Results and Perspectives.
- Poikolainen, J., Piispanen, J., Karhu, J. & Kubin, E. Nitrogen deposition in Finland 1990 2006 by using mosses as bioindicators.
- Schuetze, G. Status of the CLRTAP Heavy Metals Protocol review and outcome of a workshop on critical loads for heavy metals.
- Steinnes E., Berg, T &, Uggerud, H.T. Use of indigenous moss sampling in metal deposition surveys around point sources: examples from 15 Norwegian industries.
- Volk M., Novak K., Obrist D., Giger R., Bassin S &, Fuhrer J. Substantial carbon allocation changes suggested by CO<sub>2</sub> fluxes of sub-alpine grassland under high ozone and nitrogen deposition.

#### VISIBLE OZONE INJURY, OZONE UPTAKE AND EFFECTS ON GROWTH OF FOUR PHLEUM PRATENSE GENOTYPES

Danielsson, H.a, Karlsson, P.E.a and Håkan Pleijelb

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Timothy (*Phleum pratense*) plants were exposed to different ozone concentrations in open-top chambers in experiments in 1996 and 2001. Stomatal conductance data from 2001 were used for calibration of a Jarvis type multiplicative stomatal conductance model for timothy. The parameterisation of the stomatal flux algorithm follows the principles used for wheat and potato included in the UNECE in Mapping manual (2004). The highest conductance value for each genotype was considered as  $g_{max}$ . The values used are shown in Table 1.

Table 1. Parameterisation for the stomatal flux algorithm for *Phleum pratense*.

Parameter		Units	Value	Parameter	Units	Value
g <sub>max</sub>	Gotland	mmol O <sub>3</sub> m <sup>-2</sup> s <sup>-1*</sup>	538	light <sub>a</sub>	(constant)	0.01
of each	Barents sea.	mmol $O_3 \text{ m}^{-2} \text{ s}^{-1*}$	488	$T_{min}$	°C	12
genotype	S. Norway	mmol $O_3$ m <sup>-2</sup> s <sup>-1*</sup>	480	$T_{opt}$	°C	27
	Comm. cv	mmol $O_3$ m <sup>-2</sup> s <sup>-i*</sup>	436	$T_{max}$	°C	42
$\mathbf{f}_{\min}$		(fraction)	0.1	$\mathrm{VPD}_{\mathrm{min}}$	kPa	1.8
fphen_a		(fraction)	1	$\mathrm{VPD}_{\mathrm{max}}$	kPa	5.4
fphen_b		(fraction)	0.01	$\Sigma VPD_{cri}t$	kPa	4.5
fphen_c		°C days	620	$Af_{st}0_{min}$	mmol m <sup>-2</sup>	15
fphen_d		°C days	680	$Af_{st}0_{max}$	mmol m <sup>-2</sup>	25

<sup>\*</sup> Projected leaf area (PLA)

The highest dose-response correlation was found when accumulating ozone uptake over a threshold of 3 nmol m<sup>-2</sup> s<sup>-1</sup> (PLA) starting 75 °C days after emergence. The relationship between AF<sub>st</sub>3 and relative growth resulted in an  $r^2$ -value of 83%, higher than the AF<sub>st</sub> with any other uptake rate threshold or any other accumulation period (Figure 1). It was also higher than any relationship based on the accumulated ozone exposure over 40 nmol mol<sup>-1</sup> (AOT40,  $r^2$ =68%).

The results also indicated a positive correlation between the maximum stomatal conductance and the development of visible ozone injury (Table 2).

Table 2. Extent of developed visible leaf ozone injury scored at harvest (average  $\pm$  SE).

	Genotype	g <sub>max</sub>	NF	NF+
-	Gotland	538	$0.60 \pm 0.245$	$2.90 \pm 0.100$
	Barents sea	488	$0.80 \pm 0.200$	$2.80 \pm 0.100$
		100	$0.80 \pm 0.200$ $0.80 \pm 0.200$	
	South Norway	480	****	$2.63 \pm 0.125$
	Commercial cv.	436	$0.60 \pm 0.245$	$0.80 \pm 0.122$

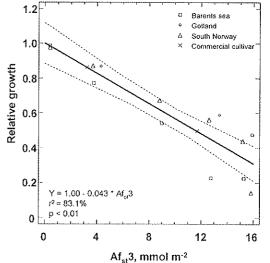


Figure 1. Relative growth in relation to the calculated ozone uptake using an ozone uptake threshold of 3 nmol m<sup>-2</sup> s<sup>-1</sup> (Af<sub>st</sub>3).

# HEAVY METAL CONCENTRATIONS IN FOREST BERRIES AND EDIBLE WILD MUSHROOMS IN EASTERN FINNISH LAPLAND AND WESTERN PARTS OF THE KOLA PENINSULA (NW RUSSIA)

#### Derome J. 1 & Isaeva L. 2

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The collection and consumption of forest berries and edible wild mushrooms have a long tradition in Fennoscandia and Northern Russia. Nowadays these products are extensively collected for home consumption and, e.g. in Finland, for sale to the foodstuff industry for both the domestic and export markets. According to the official statistics, the amount of berries collected in Finnish Lapland and sold to the foodstuff industry in 2006 were: bilberry (Vaccinium myrtillus) 0.9 mill. kg ( $2.2 \in \text{kg}$ ), cowberry (V. vitis-idaea) 0.4 mill. kg ( $1 \in \text{kg}$ ), cloudberry (Rubus chamaemorus) 0.18 mill. kg ( $5.9 \in \text{kg}$ ) and crowberry (Empetrum hermaphroditum) 300 kg ( $1.4 \in \text{kg}$ ). These figures do not include the amount collected for home consumption or for sale at local markets. The collection and consumption of edible wild mushrooms (primarily *Boletus*, *Leccinium*, *Suillus*, *Cantharellus*, *Russula*, *Lactarius* spp.) is extremely important for the inhabitants of the Kola Peninsula, as well as to a lesser extent in Finnish Lapland. It is clear that these natural products are important for the local population as both a source of tax-free income and a dietary supplement, and it is essential to ensure that their intake does not represent a health hazard as a result of e.g. elevated heavy metal concentrations.

The main sources of heavy metal emissions in the region are the Ni-Cu smelters at Monchegorsk and Nikel on the Kola Peninsula., and a range of heavy metals are deposited over an extensive area around the smelters, and even reach parts of Eastern Lapland. The deposition of heavy metals in the region has been well documented in a number of projects, and especially in the ICP Vegetation surveys of heavy metal accumulation in mosses.

During 2006-2007 samples were taken of forest berries (V. myrtillus, V. vitis-idaea, R. chamaemorus, E. hermaphroditum) and edible wild mushrooms (*Boletus*, *Leccinium*, *Suillus*, *Russula*, *Lactarius*) on 47 of the permanent plots of the Finnish 8<sup>th</sup> National Forest Inventory (same network used by ICP Vegetation for moss sampling) in eastern Lapland, and at 25 points in the western part of the Kola Peninsula. The concentrations of a range of metals (Cu, Ni, Cd, Cr, Fe, Mn, Mo, Pb, Zn) were determined on the samples.

The berries and mushrooms collected at most of the Russian sites contained heavy metal concentrations exceeding the maximum allowable levels set by the Russian food safety authorities. The concentrations in berries and mushrooms on the Finnish side were much lower. Maximum allowable levels for wild berries and mushrooms have so far not been published by the food safety authorities in Finland. There was considerable variation in the heavy metal concentrations of different species of berry collected at the same site, indicating a certain degree of specificity in their metal uptake via the roots. The variation in metal concentrations between different mushroom species was even greater, and there was also clear variation in the concentrations in the separate parts (stem, cap and gills/pores) of the fruiting bodies.

## TRACE ELEMENT ATMOSPHERIC POLLUTION IN THE BALKANS STUDIED BY THE MOSS TECHNIQUE, ENAA AND AAS

#### Frontasyeva M.

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In 1995, 2000, and 2005/2006 JINR contributed to the international programme «Atmospheric Heavy Metal Deposition in Europe – Estimations Based on Moss Analysis» with the results obtained in collaborative studies with a number of countries including several Balkan countries: Bulgaria, Romania, Northern Serbia and Bosnia, Macedonia, Croatia, and the European part of Turkey (Thrace Region).

A combination of instrumental ENAA at the IBR-2 reactor in JINR, Dubna, and AAS in relevant counterpart laboratories provides data for concentrations of about 40 chemical elements (AI, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Hf, Hg, I, In, La, Lu, Mg, Mn, Na, Nd, Ni, Pb, Rb, Sb, Sc, Se, Sm, Ta, Tb, Ti, Th, V, W, Yb, Zn) that substantially exceeds the requested number of elements (marked as bold) by the European Atlas of Heavy Metal Atmospheric Deposition edited under the auspices of the United Nations Economic Commission for Europe (UNECE).

The above trace elements are not all strictly relevant as air pollutants, but most of them can be used as air-mass tracers. Multivariate statistical analysis applied to the data sets obtained has revealed the origin of pollutants and the character of pollution sources within the sampled area, as well as those sources affecting this area through long-range atmospheric transport. Maps of elemental distributions created by modern **GIS** technology (geographical information system) are presented.

# NITROGEN DEPOSITION IN MEDITERRANEAN ECOSYSTEMS – DEFINITION OF EMPIRICAL LOADS AND IDENTIFYING CONCEPTUAL PROBLEMS FOR THE CALCULATION OF N CRITICAL LOADS

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Increased N deposition has induced the alteration of the N cycle in forested areas of North America and Europe. However, although the Critical Load of N as a nutrient  $CL_{nut}(N)$  is exceeded in more than 70% of the territory of most European Mediterranean countries, scarce information on N deposition effects on their ecosystems has been published. This is not the case for Californian ecosystems as a great deal of information is available for mixed conifer forests (MCF) across an N deposition gradient.

Critical loads for N as a nutrient for terrestrial ecosystems have been estimated under the framework of the Convention on Long Range Transboundary Air Pollution (CLRTAP). Recently, empirical critical loads for Californian mixed conifer forests (MCF) have been derived. However, the calculation of CL<sub>nut</sub>(N) for Mediterranean ecosystems pose several conceptual problems, regarding the poor characterization of N deposition and its discontinuous nature, the seasonality of vegetation and microbial activity, the temporal asynchrony of N deposition and maximum biological activity, and the conservative use of N by Mediterranean ecosystems. In addition, recurrent fire events are also a characteristic feature of most Mediterranean ecosystems but they are neglected in current critical load calculations.

A data compilation indicating potential impacts of atmospheric N deposition in N cycling of different Spanish ecosystems will be carried out. A discussion will follow on the most suitable approaches to cover the gap in knowledge regarding Mediterranean ecosystem responses to increased loads of atmospheric N. Thus, recent results related with the definition of empirical critical loads for mixed conifer forests in southern California will be presented. Also, the estimation of air pollution emissions from a wildfire on a MCF under different pre-fire N deposition loads and under different fire severities will be presented in order to discuss its implications for the calculations of CL<sub>nut</sub>(N).

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## HEAVY METALS CONTAMINATION SURVEY IN AN INDUSTRIALIZED AREA BY THE USE OF "HYPNUM CUPRESSIFORME"

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Bryophytes and lichens have been used over the past 30 years in the assessment of the deposition of airborne pollutants -particularly trace metals- all over the world (Gerdol *et al.*, 2002; Purvis *et al.*, 2007). Recently, they have been widely employed as active and passive biomonitors, in small scale surveys, to estimate the deposition of atmospheric pollutants in the areas surrounding industrial facilities such as geothermal power plants, metal smelters, chloralkali plants and steel industries (Calasans and Malm, 1997; Rusu *et al.*, 2006; Fernández *et al.*, 2007).

The objectives of this study were to evaluate the heavy metal deposition in the surroundings of two steel industries, and to estimate the range and impact of a number of trace metals in the studied area. For this purpose, *Hypnum cupressiforme* Hedw. samples were collected in several transects distributed around two steel industries located in the North of Spain. These transects were established according to the topography of the area, starting as close as possible to the industrial facility and climbing up to the basin's watershed.

All samples were subjected to total mineralisation, and subsequently analysed for their content in Ti, V, Cr, Mn, Co Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Zr, Nb, Mo, Cd, Ag, Sn, Sb, Cs, Ba, Nd, Sm, W, Tl, Pb, Th and U by means of ICP-MS. In this work we show the preliminary results on the metal content of mosses along these transects, as well as the observed trends of the pollutants and their spatial distribution in the area of study.

#### References:

- Calasans, C.F & Malm O. (1997). Elemental mercury contamination survey in a chlor-alkali plant by the use of transplanted Spanish moss, *Tillandsia usneoides* (L.) The Science of the Total Environment 208, 165-177.
- Fernández, J.A.; Aboal, J.R.; Real, C. & Carballeira, A. (2007). A new moss biomonitoring method for detecting sources of small scale pollution. Atmospheric Environment.
- Gerdol, R., Bragazza, L. & Marchesini, R. (2002). Element concentrations in the forest moss *Hylocomium splendens*: variation associated with altitude, net primary production and soil chemistry. *Environmental Pollution* 116, 129-135.
- Purvis, O.W.; Dubbin, W.; Chimonides, P.D.J.; Jones & Read, H. (2007). The multi-element content of lichen Parmelia sulcata, soil and oak bark in relation to acidification and climate. Science of the Total Environment.
- Rusu, A.M.; Chimonides P.D.J.; Jones, G.C.; García-Sánchez, R. & Purvis, O.W. (2006). Multielement including rare earth content of lichens, bark, soils and waste following industrial closure. Environmental Science Technology 40, 4599-4604.

#### AN OVERVIEW OF THE ACHIEVEMENTS OF THE ICP VEGETATION IN 2007

Harmens H., Mills, G., Hayes, Jones, M.L.M., Norris D.A. and the participants of the ICP Vegetation

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The ICP Vegetation is an international programme that reports to the Working Group on Effects (WGE) of the Convention on Long-range Transboundary Air Pollution (LRTAP) on the effects of air pollutants on natural vegetation and crops (Harmens et al., 2007). The ICP Vegetation focuses on two air pollution problems of particular importance: quantifying the risks to vegetation posed by ozone pollution and the atmospheric deposition of heavy metals to vegetation. Recently, two further pollution problems were considered by the programme: plant responses to pollutant mixtures (i.e. ozone and nitrogen interactions) and the impacts of nitrogen pollutants on vegetation. In addition, the ICP Vegetation is taking into consideration consequences for biodiversity and the modifying influence of climate change on the impacts of air pollutants. The work of the ICP Vegetation currently aims to provide information for the review and possible revision of the Gothenburg Protocol (1999) designed to address the problems of acidification, nutrient nitrogen and ground-level ozone, and the Aarhus Protocol (1998) designed to reduce emissions of heavy metals. Over 180 scientists from 35 countries of Europe and North-America contribute to the programme.

We will report on the achievements of the ICP Vegetation in 2007, in particular regarding:

- Evidence of widespread ozone damage to vegetation in Europe (1990 2006);
- Ozone biomonitoring experiments and field surveys;
- Further development of ozone critical levels and their application;
- (Semi-)natural vegetation at risk from ozone pollution, including the modifying influence of pollution;
- Biomonitoring of heavy metal and nitrogen pollution using mosses: preliminary results of the European moss survey 2005/2006;
- Input of the ICP Vegetation to the revision of the Protocols of the Convention.

Apart from looking back to our achievements in 2007, throughout the Task Force Meeting we will be discussing our future plans, in particular the medium-term work plan (2008-20010) of the ICP Vegetation and the required deliverables to the Working Group on Effects.

#### Reference:

Harmens, H., Mills, G., Hayes, F., Jones, L., Norris, D, Führer, J. and the participants of ICP Vegetation. (2007). Air pollution and vegetation. ICP Vegetation annual report 2006/2007. ISBN: 978 1 85531 233 3. http://icpvegetation.ceh.ac.uk

#### PRELIMINARY RESULTS OF THE EUROPEAN MOSS SURVEY 2005/6

Harmens H., Norris D.A., and the participants of the European moss survey 2005/2006

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The European heavy metals in mosses biomonitoring network provides data on the concentration of ten heavy metals in naturally growing mosses and is currently coordinated by the UNECE ICP Vegetation (United Nations Economic Commission for Europe International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops). The technique of moss analysis provides a surrogate, time-integrated measure of metal deposition from the atmosphere to terrestrial systems. It is easier and cheaper, less prone to contamination and allows a much higher sampling density than conventional precipitation analysis. The European moss survey has been repeated at five-yearly intervals since 1990.

Here we report on the preliminary results of the concentration of arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, vanadium and zinc in mosses in 2005/6. For the first time also the total nitrogen concentrations in mosses was determined to assess whether mosses can be used to monitor atmospheric nitrogen pollution at the European scale. Data were received from 28 countries for heavy metals and 16 countries for nitrogen. For quality assurance purposes the participating laboratories also determined the metal and nitrogen concentration in the standard moss reference material M2 and/or M3 that were developed for the 1995/6 European moss survey (Steinnes et al., 1997).

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 previous surveys shows that for some metals the concentration in mosses has declined further between 2000/1 and 2005/6, whereas for other metals the concentration in mosses has not changed. However, as reported before, the temporal trends are country- and metal-specific (Harmens et al., 2007; 2008) and in several countries increases have been observed for some metals.

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## EVIDENCE OF WIDESPREAD OZONE DAMAGE TO VEGETATION IN EUROPE (1990 – 2006)

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During the last two years, the ICP Vegetation Programme Coordination Centre has collated evidence of damage to crops and (semi-)natural vegetation in Europe caused by ambient ozone pollution over the time-scale 1990 – 2006, to quantify the link between field observations and critical level exceedance (Hayes *et al.*, 2007). The overall aim of this study was to answer the policy maker's question "is there any evidence of actual ozone damage in areas predicted to have high ozone flux or concentration (AOT40)?"

Visible ozone injury symptoms have been recorded on over 30 crop and 80 (semi-)natural vegetation species. In all, there are over 500 records of injury from 16 countries, representing all regions of Europe, i.e. from northern as well as southern Europe. Crops that have shown visible injury symptoms attributed to ozone include maize, bean, potato, lettuce, and watermelon. ICP Vegetation experiments have shown that ozone injury symptoms on well-watered clover plants occur throughout the period May to October in most regions of Europe, with symptoms being most severe in July and August. The largest impacts of ozone on the biomass of clover plants were consistently found in southern Europe, particularly in Italy and Greece where biomass reductions of over 30% have been demonstrated in some years.

By comparing the locations of effects of ozone in ambient air with EMEP generic flux maps for crops (AF<sub>st</sub>3<sub>gen</sub>), increasing stomatal flux was found to be associated with increasing incidences of ozone injury, greater severity of ozone symptoms and increasing biomass reductions. There was either no or minimal impact of ozone in EMEP grid squares with ozone fluxes close to zero. This study has also shown that the AOT40 –based critical level for agricultural crops appears to be underestimating the potential for ozone damage in Europe. AOT40 worked best as a regional-scale indicator of damage, with both ozone injury score and biomass reduction linearly related to the mean EMEP modelled AOT40 for the 50 x 50 km grid squares that the ICP Vegetation sites represent. At this scale, a mean biomass reduction of greater than 10% occurred in Continental Central Europe and Eastern Mediterranean, where EMEP risk maps indicated that mean AOT40s were at or below the critical level. Furthermore, at the local scale, approximately one third of the ozone injury data points were in grid squares where the maps indicated that the critical level for yield reduction was not exceeded.

In conclusion, stomatal flux (AF<sub>st</sub>3<sub>gen</sub>) maps were better at predicting the widespread occurrence of ozone damage on vegetation than ozone concentration (AOT40) maps. The AOT40-based risk maps underestimated the impact of ozone across Europe and especially in northern Europe. These results have been used in the recent review of the Gothenburg Protocol.

#### Reference:

Hayes, F., Mills, G., Harmens, H, Norris, D. (2007). Evidence of widespread ozone damage to vegetation in Europe (1990 – 2006). NERC publication. ISBN: 978-0-9557672-1-0. 58 pages.

## METAL CONCENTRATIONS IN FOOD PLANTS ADJACENT TO A STAINLESS STEEL WORKS IN FINLAND – ADDITIONAL INTAKE FOR HUMANS

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Near a Stainless Steel Works in the western part of Finnish Lapland, organisms are exposed to metal emissions. A significant metal in the particle emissions is chromium, because it is needed as an alloy in the production: chromium makes steel stainless. These works are the largest production plant in Europe that relies on recyclable steel material. In addition chromium is relevant because of its dualistic nature: in trivalent form it is an essential element but in hexavalent state it is toxic and inhaled carcinogen.

The objective of the study was to evaluate the additional dietary intake of chromium of people consuming collected and cultivated food plants near the works. The metal concentrations of blueberry (*Vaccinium myrtillus*), lingonberry (*Vaccinium vitis-idaea*) and common lettuce samples were analyzed from 1 to 8 kilometers distance of the works. The metal concentrations of berries were compared to two reference areas, which had different natural chromium concentrations in the fine fraction of moraine. In reference area 1 (Kantojärvi), the chromium concentration in moraine was ca. 50mg/kg, as in the factory area. In reference area 2 (Sodankylä), the chromium concentration was 500 to 1500mg/kg.

Altogether 42 blueberry, 45 lingonberry and 40 lettuce samples were analyzed. One to three replicates were analyzed per sampling site. Microwave assisted acid digestion for organically based matrices—method (EPA 3052, 1996) was used for digestion of food plants. NIST1573a tomato leaves, was used as a reference material in the digestion procedures. The quantization of berry samples was made with ICP-AES(-MS) and lettuce samples with ICP-OES.

The chromium concentrations of food plants decreased exponentially (for berries p < 0.001, for lettuce p = 0.0053) with increasing distance from the works. A statistically significant decrease was observed as well with Mo, Ni, Fe, Si, Co and Pb. The opposite behaviour was seen with Mn, Bo and Ba concentrations which increased with increasing distance. Near the works, the chromium concentrations of lingonberries (1.5mg/kg f.w.) were approximately three times higher than in blueberries (0.4-0.6mg/kg f.w.). The difference was not observed in the reference areas. Near the works, the chromium concentration in lettuce was 2-2.5mg/kg f.w. The average chromium concentrations in food plants were 20 to 80 times higher one-kilometre away from the works than in the reference areas. There were no differences in the chromium concentrations of the berries between the reference areas with different background concentrations.

A large-scale consumer of blueberry, lingonberry and lettuce one-kilometre from the works is exposed to 2.5-4.3 times higher amounts of dietary chromium than a large-scale consumer at the reference areas. The large-scale consumer consumes twice as much as a normal person. The estimates include the normal daily dietary intake of chromium, calculated from the FINDIET study. The daily chromium dietary intake (101-172µg) of the large-scale consumer of food plants near the works did not exceed the estimated safe and adequate daily dietary intake range (50-200µg) of USA-FNB.

## INCREASING RISK FOR NEGATIVE OZONE IMPACTS ON VEGETATION IN NORTHERN SWEDEN

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Trends were found for increasing surface ozone concentrations during April – September in northern Sweden over the period 1990-2006 as well as for an earlier onset of vegetation growing season. The highest ozone concentrations in northern Sweden occurred in April and the ozone concentrations in April showed a strong increasing trend. A model simulation of ozone flux for Norway spruce indicated that the provisional ozone flux based critical level for forests in Europe is exceeded in northern Sweden.

Future climate change would have counteracting effects on the stomatal conductance and needle ozone uptake, mediated on the one hand by direct effect of increasing air temperatures and on the other through increasing water vapor pressure difference between the needles and air. Thus, there is a substantial and increasing risk for negative impacts of ozone on vegetation in northern Sweden, related mainly to increasing ozone concentrations and an earlier onset of the growing season.

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#### QUALITY CONTROL OF THE 2006 FRENCH MOSS SURVEY

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Since the launching of the European heavy metals in mosses biomonitoring network, the metal concentration in mosses decreased with time for most of elements analysed. Generally, analytical errors increase as the concentration of the analyte decreases. That's the reason why, a quality assurance system has to be developed in the framework of the moss survey.

The aims of this study are, to list the main sources of possible errors and to estimate quantitatively the errors linked to each step of the whole analytical procedure used for the 2006 French moss survey. The whole procedure can be divided into the following steps: sampling, handling (cleaning, grinding,...) and element analysis; each step contains an error.

Handling and element analysis are two steps, which can easily be characterized. Quality control of the analytical process was carried out using European standards, Moss M2 and Moss M3. These two standards were respectively analyzed 10 and 30 times to check the reproducibility of the process. In order to check the reproducibility of the whole analytical procedure, including sampling, 10 moss samples were collected at the same time, in the same area, and analyzed independently.

The most difficult step is the sampling. The main problem is how to guarantee the representativeness of the samples. Several parameters can affect the interpretation of analytical data. We could distinguish the ecological parameters, as moss species (concentration of trace elements can vary between species), canopy influence (conifer or deciduous tree), substratum (on ground or on decaying stumps) or geographical parameters, as altitude, precipitation, distance to the sea (some elements present, in relatively large amounts, as sea salts, can interfere with the uptake of others).

The forward objective is to define a value of global uncertainty associated with every value of concentration, this value would help us to validate or not the differences observed between sites.

A growing number of studies (concerning critical loads for metals, metal contents in agricultural soils,..) needs to quantify the atmospheric metallic inputs. In France, only one monitoring station continuously measures the atmospheric metal deposition (Peyrusse-Vieille, EMEP network), which is insufficient to characterize the whole country. At national level, two types of data are thus available: 1- the modelled depositions of Cd, Hg and Pb provided by the EMEP network (EMEP:MSC-East), 2- the metal concentrations of naturally growing mosses provided by the French moss survey, but which need to be converted into deposition fluxes.

The general conversion formula of moss concentration value into total deposition flux is  $\mathbf{D} = (\mathbf{C}.\mathbf{B}) / \mathbf{k}$  where D is the atmospheric deposition of the element ( $\mu g.m^{-2}.year^{-1}$ ), C the metal concentration in moss ( $\mu g.g^{-1}$ ), B the biomass of moss per unit of surface and time ( $g.m^{-2}.year^{-1}$ ) and k the efficiency of metal uptake and retention by moss.

The 2000 French moss survey provides values of metal concentration in moss. While five moss species were collected, only the samples of *Scleropodium purum* (which is the most frequent species, n = 294 samples), is taking into account. The mean total biomass per surface unit of *Scleropodium* is  $327\pm128$  g.m<sup>-2</sup> (calculated from 32 stations, n=157 samples) and the age of the moss is estimated at 3.5 years old. Considering only non-essential elements and neglecting any influence of the ground, to simplify the conversation, the efficiency parameter (k) is estimated to be equal to 100% (that is to say that the moss uptakes and retains all the contaminants). Then, the conversion formula proposed is: D (deposition flux) =  $92.1 \times C$  (metal concentration in moss)-

To validate these estimated deposition values from mosses (French survey, year 2000, n=294), a comparison was attempted with the modelled ones (EMEP, year 2000). Each moss sample is compared with the EMEP grid in which it is located. The relationship between both is found to be very low for Cd, Hg and Pb, even if the correlation is significant for the three trace metals (Pearson test, r<0.25, p<0.001). The spatial pattern of contaminants varies according to estimated or modelled deposition data. In addition, values of estimated and modelled deposition rates are significantly different (Sign Test, p<0.001): for Cd, moss values are higher than EMEP values and conversely for Hg and Pb.

As a conclusion, it is difficult to determine which values, the estimated ones (moss values) or the modelled ones (EMEP values), characterize the best the actual atmospheric deposition. Each of them present a number of drawbacks (variation of the efficiency parameter (k) and influence of sea salts for mosses, evolution of the EMEP model according to new parameters, few deposition monitoring stations necessary to validate the EMEP model,...). However, mosses have advantages: the number of available elements is more important, a value of uncertainty can be calculated and associated to every value of deposition flux and mosses are more prone to represent the local reality of the ground.

## IMPACTS OF INCREASING BACKGROUND OZONE ON COMPETITION, STOMATAL CONTROL AND CARBON TURNOVER IN GRASSLAND MESOCOSMS

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Species from UK grasslands were exposed to ozone in the solardomes at CEH Bangor for 20 weeks to investigate the effects of increasing background ozone concentration in the absence of 'peaks' of ozone. Ozone exposure was based on an upland profile from Snowdonia (North Wales) and the treatments used were: ambient air (AA), AA-20 ppb ozone, AA+12, AA+24, AA+36, AA+48, AA+60 and AA+72. Two-species mixtures of *Leontodon hispidus* grown with *Dactylis glomerata, Anthoxanthum odoratum* or *Poa pratensis* were used. Communities were cut back to 6cm mid-way through the exposure to simulate a hay meadow cut and were left to die back naturally outdoors after the end of exposure.

Earlier and increased senescence occurred with increasing background ozone treatment for all species, with increases evident as the mean ozone concentration exceeded the current Snowdonia ambient concentration of 40 ppb. The magnitude of response of *Leontodon hispidus* was influenced by the competing species, with largest effects occurring when grown in competition with less vigorous *P. pratensis*, intermediate effects with the intermediate competitior A. *odoratum* and least effects when grown with the vigorous competitor *Dactylis glomerata*.

During the last few weeks of the 20 week exposure, clear evidence emerged that increasing background ozone increasingly impairs stomatal functioning. Under comparable climatic conditions, stomatal conductance increased with increasing ozone concentration for non-senesced inner canopy leaves of *Dactylis glomerata* and *Leontodon hispidus*, with the current ambient treatment being an approximate threshold for this effect. Leaves exposed to rising background ozone were also less able to close their stomata when severe water stress was imposed. This may possibly be due to a lack of response to the plant hormone, abscisic acid (ABA). Unlike in the ambient – 20 ppb treatment and the ambient + 24ppb treatment, *Leontodon hispidus* leaves from the ambient + 60 ppb treatment failed to close their stomata in response to feeding with ABA.

The effects of premature senescence of older foliage due to ozone damage during the summer on the root-soil interface during the winter are currently being studied. Some preliminary results will be presented at the ICP Vegetation Task Force Meeting.

<sup>\*</sup> We are grateful to Defra and NERC for supporting this study

## THE USE OF MOSSES FOR BIOMONITORING TRAFFIC-RELATED Pt AND Rh DEPOSITION NEAR TRAFFIC LANES

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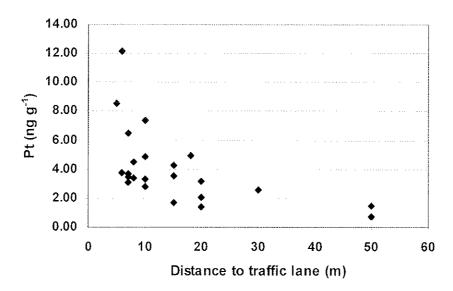
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The mean lead concentration in moss samples in Finland has decreased dramatically in past few decades. This is mainly due to the replacement of leaded by unleaded gasoline. At the same time the amount of pollutants (e.g. nitrogen oxides, carbon monoxide and hydrocarbons) emitted in exhaust gases from motor vehicles have been successfully reduced using catalytic converters. These catalytic converters typically contain platinum group elements (PGEs), mainly Pt, Pd and Rh, as active components, which has led to an increase of PGE emission. Thus it is possible that, in the long run, the accumulation of PGEs in the environment and enrichment in the food chain may have severe consequences. Because of this, during the past decade more attention has been paid on the monitoring of the anthropogenic emission of PGEs.

In this study, a method for the determination of PGEs (especially Pt and Rh) in moss samples was developed. The developed method was based on microwave-assisted sample digestion and inductively coupled plasma mass spectrometric (ICP-MS) determination. The results showed that trace and ultra trace concentrations of Pt and Rh can be determined in moss samples by ICP-MS. However, in order to obtain accurate results with a low resolution quadrupole ICP-MS the use of mathematical correction or separation of interfering elements from the analytes (e.g. Te coprecipitation) is necessary. The moss samples collected from Finland in and around areas with heavy traffic had elevated Pt and Rh concentrations (Fig. 1). Furthermore, the results indicated a common traffic-related source of Pt and Rh. However, the preliminary results also showed that Pt and Rh concentrations in mosses are elevated only in areas located very close to traffic lanes.



**Figure 1.** Pt concentrations determined in moss samples as a function of distance to the traffic lane (samples were collected from Greater-Helsinki region, Finland).

#### MOSS SURVEY 2005 IN GERMANY: FINAL RESULTS AND PERSPECTIVES

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Like the previous campaigns in 1990, 1995 and 2000, the objective of the German moss survey 2005 was to quantify the atmospheric bioaccumulation of selected metal elements in background areas of the Federal Republic of Germany with the aid of selected ectohydric moss species. Additionally, the nitrogen (N) bioaccumulation was to be determined for the first time. The sampling was based on a monitoring network optimised with regard to efficiency and sufficiency, whereas the 1028 measuring sites from the campaign in 2000 were reduced by about 1/4 to 726 measuring sites. The results of the quality controlled chemical analyses show nationwide significant increases of Cd, Cr, Cu, Sb and Zn since 2000. Particularly Cr shows considerable increases (160 %) and almost reaches its high level in 1990. Significant decreases can be stated for Hg, Pb and Ti. The respective tendencies for the federal states and for ecological landscape units are yet varying. The metal loads in mosses, except for Cr, show spatial distributions similar to those in 1995 and 2000. Hot spots are mostly found in the urbanised and industrially influenced Ruhr Area, the densely populated Rhein-Main region and in the industrially influenced regions of former East Germany (e.g. Halle-Leipzig region). Cr also shows highest values in real background areas like in Mecklenburg-Vorpommern. The spatial patterns of N bioaccumulation are to most parts hardly traceable, as especially in the regions characterized by high cattle densities, e.g. in Lower Saxony, relatively low nitrogen loads were found. Yet highly significant correlations with agriculture densities derived from Corine Landcover 2000 were found throughout Germany. The bi- and multivariat statistical data evaluation revealed significant dependencies between N and also metal bioaccumulation and the canopy drip effects of trees. This effect, as it mirrors the natural conditions in the open landscape, should be taken into account in future analyses and research on a European-wide standardisation of methods.

## NITROGEN DEPOSITION IN FINLAND 1990 – 2006 BY USING MOSSES AS BIOINDICATORS

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The atmospheric nitrogen deposition in Finland was investigated by using mosses (*Pleurozium schreberi, Hylocomium splendens*) as bioindicators in the surveys carried out in 1990, 1995, 2000, and 2005/06. The moss samples were collected from permanent sample plots of the National Forestry Inventory established in 1985 – 1986. The nitrogen concentrations were measured using the Micro-Kjeldahl method.

Nitrogen concentrations were highest in all surveys in the southern part of the country and decreased gradually on moving northwards. The maximum concentrations varied in the different surveys from 2.32% to 1.76% (dry wt.) and the minimum concentrations from 0.32% to 0.45%. The mean of the one hundred lowest concentrations in 2005/06 was 0.45%. The mean nitrogen concentration in Finland decreased between the years 1990-2000 from 1.00% to 0.78%, but it increased to 0.85% in 2005/06.

According to the surveys, the nitrogen concentrations of mosses are in most of the country low (< 1.00%). The concentrations in mosses reflected nitrogen deposition in Finland in the sense that both decreased on moving northwards. However, the correlation between the nitrogen concentrations in mosses and the nitrogen deposition modelled on the sample plots remained relatively low. On the grounds of the studies mosses are suitable for monitoring of nitrogen deposition in Finland in the extensive repeated surveys. However, the sampling, pretreatment and analysing methods have to be uniform and standardized. Mosses could prove to be useful in determining the nitrogen critical loads for terrestrial ecosystems in low deposition areas.

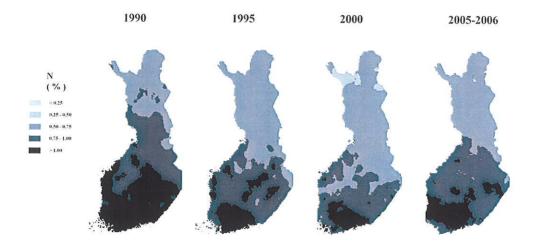


Fig. 1. The nitrogen concentrations (% dry wt.) in mosses (*Hylocomium splendens*, *Pleurozium schreberi*) in Finland in 1990, 1995, 2000 and 2005/06.

#### STATUS OF THE CLRTAP HEAVY METALS PROTOCOL REVIEW AND OUTCOME OF A WORKSHOP ON CRITICAL LOADS FOR HEAVY METALS

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The Working Group on Effects under the Convention on Long-range Transboundary Air Pollution (CLRTAP) was involved in the technical assessment of the sufficiency and effectiveness of the Protocol on Heavy Metals. It contributed to a chapter on the best available information on effects of heavy metals from LRTAP providing results of the monitoring and assessment work of the ICPs. It also delivered a chapter on critical loads of Pb, Cd and Hg and their exceedances in Europe.

While the sufficiency and effectiveness review of the Protocol has been completed by the end of 2006 (ECE/EB.AIR/89), the work of the Task Force on Heavy Metals acting under the Working Group on Strategies and Review is still ongoing. It is now focused on potential options from a technical point of view for further reducing the emissions of the three metals and compiling advantages and disadvantages of their cost-effectiveness. Health and ecosystem benefits of further measures to reduce emissions are being assessed. The Task Force will carry out further work in 2008 and 2009 as required by the Executive Body.

A workshop on critical loads of heavy metals was organised by CEH Lancaster under the auspice of ICP Modelling and Mapping and held from 21 to 22 November 2007, in Windermere, United Kingdom. Its purpose was to discuss and review methodologies for calculation of critical loads of heavy metals including methods of setting toxic thresholds (critical limits), dynamic models and uncertainties of results of these methods.

Conclusions and recommendations related to steady state critical loads methods aimed at the improvement of databases and methods for deposition modelling, refinement of the assessment of partitioning and transfer functions, in particular for Hg. The calculation of current exceedance of critical limits and the application of dynamic models in addition to steady state critical loads exceedance was considered important for a correct interpretation of results.

With respect to the sophistication of critical limits for metals in soils and surface waters proposals were made i. a. to include new available data, more pathways of metal transfer in the system air-soil-water-biota, information on secondary poisoning, to consider the effects of pollutant mixtures and variations in the sensitivity of the natural environment. Items for necessary research were also identified with respect to processes like ageing, transfer functions and lab-field extrapolation.

The influence of a changing environment (e.g. climatic factors, exposure to other atmospheric pollutants, land use) on metal fluxes, biouptake and toxicity should be reviewed by means of dynamic modelling. The systematic evaluation of key processes (kinetics of partitioning, ageing, weathering) as well as biotic turnover rates and retention times of metals was recommended. Simple dynamic models should be used for mapping at national and European scales. Intermediate and complex models can be used for scenario analyses and complex models were recommended for validation of process studies at catchment scale.

The workshop also noted a need for further harmonising methods of measurement of heavy metals in the environment and to establish harmonised international databases for mapping.

## USE OF INDIGENOUS MOSS SAMPLING IN METAL DEPOSITION SURVEYS AROUND POINT SOURCES: EXAMPLES FROM 15 NORWEGIAN INDUSTRIES

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In 2000 the Norwegian State Pollution Control Authority decided to carry out a study of atmospheric deposition of inorganic pollutants around 15 industrial plants in Norway. The industries in question were five aluminium smelters, one zinc smelter, six ferroalloy plants, two cement factories, and one carbide factory. The method used was sampling and analysis of naturally growing moss (*Hylocomium splendens*) at distances of 1-10 km from each plant. Typically 10-15 sampling sites were selected at each site considering factors such as topography and prevailing wind directions. The concentrations of 32 elements in the moss were determined by ICP-MS.

Among the trace elements studied <u>gallium</u> was the most typical "marker" of the Al industries. Another element observed in small but still elevated amounts at all sites was <u>bismuth</u>. Relatively high levels of <u>vanadium</u> and <u>nickel</u> were evident at three of the sites, most likely associated with the use of heavy fuel oil. Other elements observed at elevated levels at several sites were <u>beryllium</u>, <u>chromium</u>, <u>arsenic</u>, <u>molybdenum</u>, <u>antimony</u>, and <u>tungsten</u>. High deposition of <u>zinc</u>, <u>cadmium</u>, and <u>mercury</u> were observed around the Odda zinc smelter. Still the highest general metal deposition levels were observed at the town Mo i Rana where the main industries are a ferroalloy smelter and a factory recovering metals from scrap. Huge deposition of <u>chromium</u> was particularly evident, and metals such as <u>beryllium</u>, <u>vanadium</u>, <u>cobalt</u>, <u>nickel</u>, <u>arsenic</u>, <u>zirconium</u>, <u>tungsten</u>, <u>lead</u>, and <u>bismuth</u> were also present at appreciable levels. A dense sampling network and use of factor analysis facilitated to define the main polluting source in each case. Emissions from the cement industries were relatively modest.

The survey was repeated at reduced scale in 2005 at some of the most polluted sites. In several cases only small or no improvement was evident since 2000. At Mo i Rana the chromium had been replaced by a similar level of <u>manganese</u> deposition, following a change in production from ferrochrome to ferromanganese. Apparently there is still considerable work to be done at some industrial sites in Norway to reduce metal emissions to acceptable levels.

Experience from this work shows that the use of naturally growing moss for studies of atmospheric metal deposition may be useful also on the local scale in areas considerably affected by emission from industries.

# SUBSTANTIAL CARBON ALLOCATION CHANGES SUGGESTED BY CO<sub>2</sub> FLUXES OF SUBALPINE GRASSLAND UNDER HIGH OZONE AND NITROGEN DEPOSITION

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Effects of increasing levels of atmospheric O3 and N deposition on grasslands are largely unknown. This comes from a lack of studies with experimental applications of these pollutants under natural, on site conditions. But environmentally driven changes of the systems C-exchange patterns may affect ecosystem functioning locally and may also affect the greenhouse gas budget globally, as grassland habitats cover 25% of the terrestrial surface.

In the study presented here, we assessed effects of increased atmospheric ozone concentrations (3 levels: ambient, amb. x 1.2 and amb. x 1.6) and increased nitrogen deposition (3 levels: ambient, ambient + 10 kg ha-1 a-1, amb. + 50 kg ha-1 a-1) in the third year of a long-term experiment. During ten days and 13 nights, covering the vegetation period of the year 2006, daytime and night time ecosystem-level CO2 exchange of an intact, subalpine grassland ecosystem was measured. All gas exchange responses to the fully factorial treatment combination were analysed in a split-plot repeated measures ANOVA.

The daily and seasonal changes of night time net respiration rates are tightly controlled by soil temperature, with a strong secondary control through soil water content (SWC) at levels below 30%, which occurred during two pronounced drought periods. Net assimilation during cloudless days reflected mostly the canopy development with only small effects of SWC.

Neither high ozone nor nitrogen deposition caused significant effects on night time and daytime gas exchange across the season, although whole season respiration was found to be slightly increased under high N (+ 3%) and decreased under high O3 (- 8%) compared to control throughout the season. Similarly, whole-season assimilation was slightly, but not significantly, decreased both under high N (- 5%) and high O3 (- 7%) compared to control. There was no interaction between the two treatments.

The surprising lack of response of respiration and assimilation to the N-treatment was contrasted by a 30% increase of aboveground productivity, equivalent of 12.3 g C m-2, in the high N-treatment. But the balance of assimilation/respiration for the high N-treatment versus the control suggests a carbon loss, rather than a carbon gain.

A possible explanation of this phenomenon is a positive  $\geq$  12 g C-allocation shift towards the shoots under high N. Consequently, reduced belowground C-allocation would decrease belowground system respiration. To match the data presented here, this assumed reduction must be sufficiently large to result in an unaltered total (above- plus belowground-) system respiration, despite the higher aboveground biomass.

# Abstracts Poster presentations

### List of poster presentations

- Akinshina N., Azizov A., Usmanov V., Abdullaev A. To tropospheric ozone level and crop productivity in Uzbekistan.
- Cieslik, S. Stomatal and total ozone flux measurements over Europe: A review.
- Gerosa G., Finco A., Vitale M., Mereu S., Manes F., Ballarin Denti A. Comparison of seasonal variations of ozone exposure and fluxes in a Mediterranean Holm oak forest between the exceptionally dry 2003 and the following year.
- Gerosa G., Finco A., Marzuoli R., Ballarin Denti A. Ozone, water, carbon dioxide and energy fluxes over the Mediterranean macchia at Castelporziano (Italy).
- Gerosa G., Marzuoli R., Rossini M., Panigada C., Faoro F., Iriti M. Leaf damages, photosynthetic efficiency and productivity of bean plants exposed to ozone: A flux-based study.
- Goumenaki E., and Barnes J. Mechanisms underlying diurnal variation in the sensitivity of plants to ozone.
- Kapusta P., Szarek-Łukaszewska G., Godzik B. Element stoichiometry in mosses Pleurozium Schreberi plan of study.
- Kubin, E., Piispanen, J., Poikolainen, J. & Karhu, J. Heavy metal deposition in Finland during 1985 2006 using mosses as bioindicators.
- Maňkovská B., Oszlányi J., Percy. K.E., Karnosky D.F. Influence of greenhouse gases on epicuticular waxex of *Populus Tremuloides* michx.: Results from an open-air exposure and a natural O<sub>3</sub> gradient.
- Mastrorilli M., Fagnano M., Katerji N., Rana G. Impact of ozone on growth and yield of a soybean cultivated in Mediterranean conditions.
- Oszlányi J., Maňkovská B., Frontasyeva M., Ermakova E. Use of mosses as biomonitors of heavy metal deposition in the Carpathian Mountains (Slovak part).
- Rana G., Fagnano M., Katerji N., Mastrorilli M. Impact of ozone on water status of soybean cultivated in Mediterranean conditions.
- Schrader, S., Bender, J., Weigel, H.J. Ozone exposure of field-grown winter wheat affects the diversity of soil mesofauna in the Rhizosphere.
- Spiric Z., Frontasyeva M., Stafilov T., Enimiteva V., Barandovski L., Urumov V. Atmospheric deposition of Cd, Hg, and Pb in Croatia and neighbouring countries: Assessment based on moss analysis.
- Steinnes E., Frontasyeva M.V., Gundorina S.F., Pankratova Yu.S. Identification of metal emissions from adjacent point sources using moss biomonitoring and factor analysis.
- Villányi V., Ürmös, Z., Balogh, J., Horváth, L., Csintalan, Z., Tuba, Z. Ozone biomonitoring at several sites in Hungary: preliminary findings.

## TO TROPOSPHERIC OZONE LEVEL AND CROP PRODUCTIVITY IN UZBEKISTAN

<sup>1</sup>Akinshina N., <sup>1</sup>Azizov A., <sup>2</sup>Usmanov V., <sup>2</sup>Abdullaev A.

Analysis of long-term observations for tropospheric ozone level in air of Tashkent district area in Uzbekistan (Central Asia) has been made.

#### It has been revealed:

- Background concentrations of surface ozone 0,015-0,020 mg/m<sup>3</sup>.
- Average long-term annual concentrations of tropospheric ozone in Tashkent district air are 1,5-3 higher than hygienic maximum-permissible daily concentration actually and correlate with similar characteristics of European countries 0,05-0,09 mg/m<sup>3</sup>.
- Average long-term values of maximal ozone concentrations (June-July-August) run up to 0,2 mg/m<sup>3</sup>. (This is higher than in Europe, but it is not smog situation).

Uzbekistan is an agriculture country; the most of population live in rural areas and are engaged in farm production. Reduction of crop productivity is the most important consequence of ozone effects to vegetation as a practical matter.

Maximum-permissible daily ozone level for vegetation and coefficients of crops productivity reduction under impact of various ozone concentrations in case study of Tashkent district were calculated. The results are presented in table 1.

Table 1.

Coefficients of productivity reduction for main crops in Tashkent district under impact of various ozone concentrations

	Ozone $(O_3)$ Maximum-permissible daily concentration for vegetation $0.029~\mathrm{mg/m}^3$					
	0,03-0,04	0,04-0,05	0,05-0,06	0,06-0,07	0,07-0,08	
Maize	0,028	0,056	0,085	0,119	0,141	
Rice	0,020	0,041	0,063	0,086	0,109	
Wheat (not irrigable)	0,134	0,267	0,401	0,534	0,668	
Wheat (irrigable)	0,081	0,161	0,242	0,323	0,403	
Cotton	0,030	0,045	0,060	0,078	0,091	

Moreover, inverse relation between O<sub>3</sub> and SO<sub>2</sub> levels in air and chlorophyll content in leaves of different plants has been detected. Leaves of cherry, apple, walnut, plum and apricot are more sensitive to ozone impact in compare with cotton and mulberry-tree.

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## STOMATAL AND TOTAL OZONE FLUX MEASUREMENTS OVER EUROPE: A REVIEW

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Ozone flux is an important parameter in the assessment of potential plant damage by ozone. It has been proved that the stomatal contribution to ozone flux is preferable to any index based on ozone concentration records. Its knowledge is not sufficient, however, as its does not take into account the possible in-cell detoxification processes.

This presentation reviews direct measurements of ozone fluxes over the European continent, with emphasis on the Mediterranean area which presents some special characteristics, as ozone concentrations and fluxes behave in very different ways there, with consequences on ozone risl assessment. The calculation algorithm of stomatal ozone fluxes, still inaccessible through direct measurement, from total ozone fluxes and water vapour fluxes, is presented and discussed. New perspectives for alternative methods permitting the determination of stomatal conductances are presented.

# COMPARISON OF SEASONAL VARIATIONS OF OZONE EXPOSURE AND FLUXES IN A MEDITERRANEAN HOLM OAK FOREST BETWEEN THE EXCEPTIONALLY DRY 2003 AND THE FOLLOWING YEAR.

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Ozone and energy fluxes have been measured using the eddy covariance technique, from June to December 2004 in Castelporziano near Rome (Italy), and compared to similar measurements made in the previous year. The studied ecosystem consisted in a typical Mediterranean Holm oak forest. Stomatal fluxes have been calculated using the resistance analogy and by inverting the Penmann-Monteith equation. Results showed that the average stomatal contribution accounts for 42.6% of the total fluxes. Non-stomatal deposition proved to be enhanced by increasing leaf wetness and air humidity during the autumnal months.

From a comparison of the two years, it can be inferred that water supply is the most important limiting factor for ozone uptake and that prolonged droughts alter significantly the stomatal conductance, even two months after the soil water content is replenished. Ozone exposure, expressed as AOT40, behaves similarly to the cumulated stomatal flux in dry conditions whereas a different behaviour for the two indexes appears in wet autumnal conditions. A difference also occurs between the two years.

## OZONE, WATER, CARBON DIOXIDE AND ENERGY FLUXES OVER THE MEDITERRANEAN MACCHIA AT CASTELPORZIANO (ITALY)

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Ozone, carbon dioxide, sensible and latent heat fluxes were measured by means of the eddy covariance technique over a coastal Mediterranean macchia ecosystem, from 5th May 2007 until the end of the month. Additional measurements of air temperature and humidity profiles, net radiation, photosynthetically active photon flux density, soil moisture content, leaf wetness and temperature were also made.

Ozone fluxes were partitioned in a stomatal component and a non-stomatal one by means of a resistive approach, based on the inversion of the Penmann-Monteith equation for evapotranspiration.

The measurement site was characterised by a marked sea-breeze regime. The measuring period was dry, with only 5 mm of rain the last days of the month, and with an average air temperature of 19.1 °C. The sandy soil was very dry: soil water content was slightly above 4% v/v at the beginning of the campaign and slowly declined up to less than 3.5% at the end of May. Similarly the evapotranspirative fluxes decreased following the water shortage.

For all the measuring period, with the only exception of the rainy days, the sensible heat flux H showed a typical behavior with a maximum of 600 W m<sup>-2</sup> around 2.00 pm and a minimum of -20 W m<sup>-2</sup> in the night. The latent heat flux LE was ever lower than H showing a maxima slightly decreasing from 200 W m<sup>-2</sup> of the beginning of the campaign to 70 W m<sup>-2</sup> just before the rain episodes of the end of the month, after that increased again.

## LEAF DAMAGES, PHOTOSYNTHETIC EFFICIENCY AND PRODUCTIVITY OF BEAN PLANTS EXPOSED TO OZONE: A FLUX-BASED STUDY

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Open-Top Chamber (OTC) experiments on *Phaseolus vulgaris* were conducted in summer 2006, to study the ozone effects on visible and invisible leaf injury, photosynthetic efficiency and plant productivity.

A Jarvisian stomatal conductance model was drawn up and parameterized allowing the calculation of stomatal ozone uptake in filtered and non filtered OTCs. A multidisciplinary approach was employed to evaluate the ozone effects on plants including: chlorophyll fluorescence and reflectance measurements, histo-cytochemical analyses and yield analysis.

The results showed that microscopical leaf symptoms preceded by 3-4 days the appearance of visible symptoms and were strictly correlated with ozone stomatal uptake

Stomatal flux critical level for visible leaf injury onset was found around 1.33 mmol  $O_3$  m<sup>-2</sup>. Significant linear dose-response relationships were obtained between cumulative ozone stomatal flux and optical indices (i.e. PRI, NDI and  $\Delta F/Fm$ ). The negative ozone effects on photosynthesis inevitably reduced plant productivity, affecting the number of pods and seeds, but not seed weight.

These results, besides contributing to the development of a flux-based ozone risk assessment for crops in Europe point out the great potentiality of spectral reflectance in evaluating photosynthetic activity reduction in crops.

## MECHANISMS UNDERLYING DIURNAL VARIATION IN THE SENSITIVITY OF PLANTS TO OZONE

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The diurnal shifts in the sensitivity of *Lactuca sativa* cv Paris Island and its closest wild relative *Lactuca serriola* to ozone-induced oxidative stress was investigated in this study. Equivalent ozone fluxes during the day-time *versus* night-time were administered by carefully managing the ozone exposure in conjunction with measurements of stomatal conductance. Plants exposed to equivalent ozone fluxes exhibited a significant (P< 0.01) decline in biomass in both conditions. Two-way ANOVA revealed a statistically significant ozone x day/night interaction (P< 0.01); biomass losses attributable to equivalent ozone flux were greater when ozone was administered at night *versus* day.

The linkage between AA(L-ascorbic acid) content, redox status of the leaf apoplast (and symplast) and  $O_3$  injury was probed in both genotypes. To do this, light levels were used to manipulate sub-cellular pools of AA. Plants were exposed to prolonged darkness to reduce AA in the leaf cell walls, and shifts in AA monitored on subsequent transfer of plants to the light. Interestingly, the depletion of the AA pool in the apoplast appeared to be more affected by light-dark transition than the respective whole leaf pool. Analysis of variance revealed no statistically significant genotype x dark-treatment interaction, implying a similar response in both genotypes studied. Stomatal conductance was measured, and this was used to deliver equivalent  $O_3$  fluxes to leaves with contrasting AA levels. Ozone impacts were assessed using gas exchange approaches. The  $O_3$  treatment administered resulted in a significant (P< 0.05) decline in  $A_{sat}$  in both Lactuca sativa cv Paris Island and Lactuca serriola when assayed 2 and 9 h after re-illumination. Following the recovery of apoplast washing fluid to pre-treatment AA levels (after 24 h re-illumination) no significant effects of the same  $O_3$  treatment were observed.

The results of the present investigation showed that plants are more sensitive to ozone at night-time and emphasize the potential importance of diurnal shifts in apoplast AA content and/or redox status in determining the reaction of plant tissues to ozone-induced oxidative stress. Depletion of the AA pool in the apoplast alters 'sensitivity' to ozone in a manner that is predictable based on diffusional limitations and biochemical reactions following the uptake of the gas into the leaf interior.

## ELEMENT STOICHIOMETRY IN MOSSES *PLEUROZIUM SCHREBERI* – PLAN OF STUDY

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Plants may be considered as self-balancing systems in terms of acquisition and use of resources because they try to maintain a specific (and characteristic for a given species) body chemical composition. However, this homeostatic ability confronted with strongly uneven in space and time availability of nutrients is insufficient to retain internal chemical balance. As a result, plant stoichiometry considerably varies according to a current element supply in the environment.

Mosses – due to their limited element uptake from soil (because of lack of typical roots) – are organisms which react to atmospheric input of elements (particularly heavy metals) very distinctly. Their utility in bioindication of air quality was shown in numerous publications. By contrast, there is a little knowledge about relationships between concentrations of heavy metals in mosses and moss requirements for nutrients. Our research project (presented here) focuses on this issue.

We plan to use a common moss species *Pleurozium schreberi*. Its green and brown parts will be collected from approximately 200 study plots evenly distributed throughout Poland. Contents of heavy metals (especially Cd, Cu, Zn, Pb) as well as mineral nutrients will be determined. We hypothesise, that high concentration of heavy metals in mosses (expected in the most contaminated regions of the country) affects directly cell metabolism (e.g. by initiation of protective mechanisms associated with protein synthesis and energy expenditure) and indirectly nutrient uptake and nutrient ratios in tissues (e.g. C:N, C:P, Ca:Mg). There are many other agents potentially affecting plant stoichiometry including habitat properties, climate, genetic variability of plant populations; many of them will be controlled in the study.

## HEAVY METAL DEPOSITION IN FINLAND DURING 1985 - 2006 USING MOSSES AS BIOINDICATORS

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The atmospheric heavy metal deposition was investigated in Finland by using mosses (*Hylocomium splendens, Pleurozium schreberi*) in surveys carried out in 1985, 1990, 1995, 2000 and 2005/06. The concentrations of As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn (As and Hg since 1995) were determined on moss samples collected from permanent National Forest Inventory plots.

The heavy metal concentrations were in all surveys relatively low in the most parts of Finland and they decreased generally on moving northwards. The concentrations of most heavy metals were higher in Southern Finland, which is the region with the most industrial activities and the highest traffic density. There were also locally elevated levels of some heavy metals in Finland. Relatively high Cu and Ni concentrations were found near the Harjavalta smelter in Western Finland and in NW Lapland near the smelters in the Kola Peninsula in NW Russia. Elevated Cr concentrations were found near the steel plant in Kemi-Tornio area.

The concentrations of Pb, Cd and V decreased considerably and of Cr, Cu, Fe, Zn in some degree between the years 1985 – 2000. However, after the year 2000 the concentrations have not decreased more significantly or not at all except arsenic. The decrease in heavy metal concentrations in mosses in Finland is due to decrease in domestic emissions as well as to the decrease in the long-range transport of heavy metals into Finland.

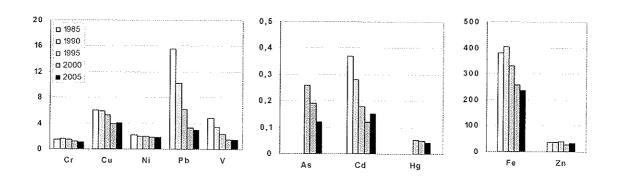


Fig. 1. Heavy metal concentrations (mg/kg) in mosses (*Hylocomium splendens*, *Pleurozium schreberi*) in Finland in 1985, 1990, 1995, 2000 and 2005/06.

# INFLUENCE OF GREENHOUSE GASES ON EPICUTICULAR WAXES OF *POPULUS TREMULOIDES* MICHX.: RESULTS FROM AN OPEN-AIR EXPOSURE AND A NATURAL O3 GRADIENT

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Influence of greenhouse gases on epicuticular waxes of *Populus tremuloides* Michx.: Results from an open-air exposure and a natural O3 Gradient. Epicuticular waxes of three trembling aspen (Populus tremuloides Michx.) clones differing in O3 tolerance were examined over six growing seasons (1998-2003) at three localities (Rhinelander, WI -clean and control site:Kalamazoo, MI -moderate pollution loading and Kenosha, WI -high pollution loading) in the Lake States region of the USA and at FACTS II (Aspen FACE) site in Rhinelander, WI. Differences in epicuticular wax structure were determined by scanning electron microscopy and quantified by a coefficient of occlusion. Statistically significant increases in stomatal occlusion occurred for the three O<sub>3</sub> bioindicator sites as we predicted with the higher O<sub>3</sub> sites having the most affected stomata for all three clones as well as for all treatments including elevated CO2, elevated O3, and elevated CO2 + O3. The results suggest that O3 pollution of the Kenosha and Kalamazoo sites show significant negative impact on epicuticular waxes of aspen and these impacts are the most severe on the most O<sub>3</sub> sensitive clones. We recorded statistically significant differences between aspen clones, between sampling period (spring, summer, fall) and localities between Rhinelander, Kalamazoo and Kenosha. However, we found no statistically significant differences in stomatal occlusion between treatments or aspen clones in stomatal frequency.

Keywords: Populus tremuloides Michx., O3 tolerance, epicuticular wax, stomatal frequency

## IMPACT OF OZONE ON GROWTH AND YIELD OF A SOYBEAN CULTIVATED IN MEDITERRANEAN CONDITIONS

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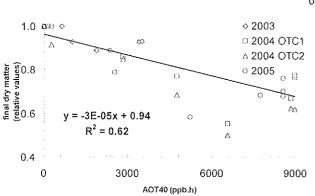
Soybean plants were subjected, during their growing seasons, to well-watered and water-stressed conditions, and three levels of ozone concentration (zero, low and high) in open top chambers (OTCs). At the end of the soybean growing season accumulated AOT40 values were zero, 3400 and 9000 ppb.h for the filtered (control), low and high levels of ozone concentration, respectively.

In well-watered conditions, an increase in ozone concentration led to a reduction in leaf area, dry matter and reproductive organs. Whereas, an increase in ozone had no effect on plants in water-stressed conditions. At a high level of ozone concentration, there was a 47% reduction in yield and a 25% reduction in WUE in comparison with the control treatment. The reduction in yield was due to a lower number of pods per plant and 1000-grain weight. Despite changes in the grain yield, the yield quality was not altered by ozone.

During the three-year study, AOT40 was significantly correlated with the leaf area (Fig. 1) and the final above-ground dry matter (Fig. 2). The latter was less sensitive to ozone than leaf area. These results were reliable and would be useful in soybean yield-prediction models.

Finally, the conclusion highlights the reliability of the approach adopted, which was to make observations on various time scales (hourly, daily and entire crop cycle).

Figure 1. Relationships between AOT40 (in ppb.h) and relative values of maximal leaf area observed for well-watered crop. Measurements were repeated in two OTC in 2004.



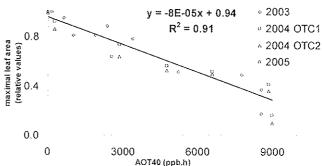


Figure 2. Relationships between AOT40 (in ppb.h) and relative values of final dry matter. Relative values are the ratios of low ozone concentration values (2003) or high ozone concentration values (2004 and 2005) to control treatment values observed at the same times.

## USE OF MOSSES AS BIOMONITORS OF HEAVY METAL DEPOSITION IN THE CARPATHIAN MOUNTAINS (SLOVAK PART)

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The results obtained from biomonitoring of atmospheric deposition of 45 elements in Slovak part of the Carpathian Mountains using the moss biomonitoring technique are presented. Concentrations of Ag, Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Hf, Hg, I, In, K, La, Mg, Mn, Mo, N, Na, Ni, Pb, Rb, S, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn, Zr in segments of Pleurozium schreberi, Hylocomium splendens and Dicranum sp. from 6 sites: Geldek, Štefanová, Poľana, Východná, Stolíky, Morské oko are discussed in the context of their values and in relation to of element concentrations in foliage of *Picea abies L., Fagus* sylvatica L. The comparison with the median Norwegian values of heavy metal contents in moss has shown that, on average, the Slovak atmospheric deposition loads of the elements are higher. We have found maximal concentrations of As (45 times higher), Cd (110 times higher), Cu (64 times higher), Fe (44 times higher), Hg (174 times higher), Pb (105 times higher) and Zn (14 times higher) on the site Stoliky; Cr (218 times higher) and Mn (7 times higher) on the site Morské oko; V (34 times higher) on the site Štefanová as compared to the Norwegian values. A statistically significant decrease of nitrogen concentration on all sites compared to the data from the moss survey in 2000 has been revealed. The concentration of S was lower in 2000 than in 2005 on 4 sites, and higher in 2000 than in 2005 on the sites Geldek and Morské oko. The difference between 2000/2005 in S concentrations was not statistically significant. A statistically significant difference between concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn in humus and mosses was observed. The obtained data can be useful as reference levels for comparison with the future measurements of air pollution in the examined area and also for biodiversity study.

## IMPACT OF OZONE ON WATER STATUS OF SOYBEAN CULTIVATED IN MEDITERRANEAN CONDITIONS

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This study has been carried out during 3 successive years (2003-2004-2005) in the southern Mediterranean region of Europe (south Italy), under conditions favourable to ozone rise, together with soil and atmospheric drought. Soybean plants were subjected to well-watered and water stress conditions, and three levels of ozone (filtered, low and high) in open top chambers during growing seasons. Cumulated AOT40 values were zero, 3400 and 9000 ppb for filtered (control), low and high ozone concentration treatments, respectively.

Under well-watered conditions, the increase of ozone concentration levels leads to a reduction in stomatal conductance and daily actual evapotranspiration (AET), whereas an ozone increase has no effect under water stress conditions. Compared to the control treatment under well-watered conditions, total AET reduction were 14% and 28% at low and high ozone levels, respectively. Hence, water consumption results observed for the entire growing seasons and specific stomatal conductance results were coherent.

During the 3-year study, significant relationships were found between AOT40 and relative (low or high to control ozone treatments) stomatal conductance (Fig. 1) and AOT40 and relative AET (Fig. 2). The liability observed for these relationships suggest that they would be useful in soybean growth and yield-prediction models.

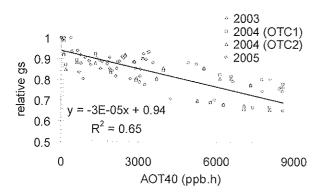
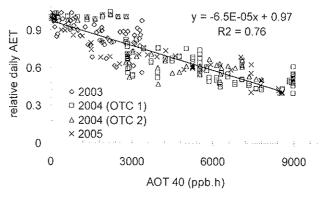


Figure 1. Relationships (observed for well-watered soybean crops) between AOT40 and relative values of stomatal conductance (gs); Relative values are the daily ratios of gs measured under low (in 2003) or high (in 2004 and 2005) levels of ozone concentration, to the corresponding control treatment values. Measurements were repeated twice (OTC1 and OTC2) in 2004.

Figure 2. Relationships (observed for well-watered soybean crops) between AOT40 and relative values of daily actual evapotranspiration (AET). Relative values are the daily ratios of AET measured under low (in 2003) or high (in 2004 and 2005) levels of ozone concentration, to the corresponding control treatment values.



## OZONE EXPOSURE OF FIELD-GROWN WINTER WHEAT AFFECTS THE DIVERSITY OF SOIL MESOFAUNA IN THE RHIZOSPHERE

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It is well known that tropospheric ozone levels reduce growth, biomass and yield in many crop species. This negative effect is often associated with reduced partitioning of photosynthates to sink tissues such as roots which would be expected to affect root vigor and the rhiosphere environment. However, little is known about the impact of ozone on belowground processes. Furthermore, there is no information available on how soil mesofauna in the rhizosphere of ozone-exposed crops is affected. A 2-year open-top field chamber experiment (2006 and 2007) was conducted to examine the effects of ozone on plant growth and on selected groups of soil mesofauna in field-grown winter wheat (cv. Astron). Enchytraeids (potworms), collembolans (springtails) and acari (mites) were analysed because they play an important role for the C-turnover in soil food webs and are known to be sensitive to chemical changes in the soil environment. In each year, two ozone treatments were conducted from May through June in four replicate chambers: non-filtered (NF) ambient air as control or NF with additional 50 ppb ozone (NF+) for 8 h day-1 (10:00-18:00 h). Soil sampling was performed at three dates according to different crop developmental stages. Ozone reduced plant growth and biomass in 2006, but had little effect in 2007. Root biomass decreased during plant development in NF+ with the lowest biomass (-20%) observed at the end of anthesis. Generally, the individual density of all three mesofaunal groups decreased in the rhizosphere of winter wheat, which was cultivated in the NF+ treatment. This result was significant for acari in both years and for collembolans and enchytraeids in the second year. Furthermore, significant results were found at anthesis and at grain maturity, (sampling dates 2 and 3), respectively, but not during stem elongation (sampling date 1). In conclusion, elevated atmospheric ozone concentrations seem to deteriorate the nutritional conditions for the analysed mesofaunal groups in the rhizoshere of cereal crops. It can be assumed that such effects will influence the dynamic of decomposition processes and the turnover of nutrients.

## ATMOSPHERIC DEPOSITION OF Cd, Hg, AND Pb IN CROATIA AND NEIGHBOURING COUNTRIES: ASSESSMENT BASED ON MOSS ANALYSIS

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The results of comparison of median concentrations of most toxic elements Cd, Hg, and Pb in moss samples collected in Croatia in 2006 and in neighboring countries such as Hungary, Serbia, Macedonia, Austria, Italy, Romania, and Bulgaria (moss survey 2000/2001) are reported. As follows from the figure below, Croatia has shown to be among most pristine territories with regard Cd and Pb contamination. The median Hg concentrations do not vary greatly in the compared areas.

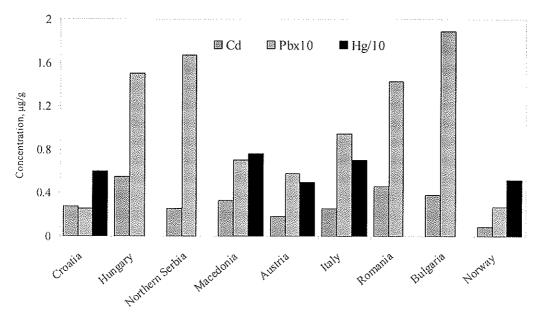


Figure. Median concentrations of Cd, Pb, and Hg in moss samples collected in Croatia (94 sampling sites), Hungary (32), Northern Serbia (198), Macedonia (73), Austria (221), Italy (198), Romania 214), Bulgaria (217), and Norway (464) used as country with base line concentrations of these elements

The GIS maps of elemental distributions of Cd, Hg, and Pb constructed for Croatia evidence that the highest concentrations of Cd (max 1.9  $\mu$ g/g) and Hg (max 0.3  $\mu$ g/g) are observed along the north-east border with Hungary and could be attributed to a long range atmospheric transport from this neighbouring country, whereas Pb (max 82  $\mu$ g/g) is associated with the local pollution sources in the industrial central part of Croatia. So far it is realized now that human health and wellbeing is affected by much lower levels of heavy metals than previously assumed the importance of these studies is ever growing.

## IDENTIFICATION OF METAL EMISSIONS FROM ADJACENT POINT SOURCES USING MOSS BIOMONITORING AND FACTOR ANALYSIS

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Atmospheric deposition of 34 trace metals around an iron smelter complex in a town in northern Norway was studied in 2000 and 2005 using neutron activation analysis of naturally growing moss. Specific contributions from two adjacent but distinct smelters and changes in operation that had occurred between the two sampling years were identified by factor analysis, and relative contributions from the two sources at different sampling sites were demonstrated by means of the factor scores. In 2000 emission from a ferroalloy smelter (Smelter I) caused substantial deposition of Cr and Fe, and this smelter was also the main source of Al, V, Co, Ni, As, Mo, and W. Another nearby plant (Smelter II) recovering metals from used materials caused considerable deposition of Mn and Zn and was also the main source of Sb and W deposition. Following a transition from ferrochrome to ferromanganese production Smelter I in 2005 showed substantial deposition of Mn. This smelter also still was the main source of Cr, Co, Ni, As, and Mo. Smelter II maintained a considerable Zn deposition and showed increased emissions of Sb and W. In most of the urban area the contribution from Smelter I was dominant. An exception was two sites in the northeast direction from the industries where emissions from Smelter II dominated in 2000 as well as 2005.

#### OZONE BIOMONITORING AT SEVERAL SITES IN HUNGARY: PRELIMINARY FINDINGS

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Phytotoxicity of the increasing tropospheric ozone is a global problem. However, there are very few studies concerned with measuring the impact of this serious pollutant on plants in the Central European Hungary so far. Our experiment started in June, 2007. For test-plant we applied the ozone bioindicator clover (Trifolium repens NC-S and NC-R) clones. For cultivation of plants and for assessing the injuries the protocol of the ICP Vegetation was used. The clover pots were located in three experimental sites. Gödöllő is in downs with moderate climate, Bugacpuszta is a lowland site with hot and dry climate while Mátraháza is a mountainous site. Besides injuries and total dry weight, the number of flowers and the leaf area index were also measured. Our results showed that the typical symptoms of ozone injury were appeared on sensitive clones on every site. The degree of injury increased gradually from June to September reaching the maximum in the middle of September. Regarding the dry weight there was no difference between sensitive and resistant clones. However, the number of flowers differed significantly in Gödöllő. The sensitive clones developed slightly more flowers than the resistant ones. On the contrary the number of flowers was markedly higher on the resistant plants in Mátraháza. Leaf area index (LAI) of the sensitive clones was usually higher than that of the resistant clones, but no difference proved to be in the LAI of the different clones at the site of Mátraháza. Dry weight and number of flowers revealed linear relationship which was more expressed in Gödöllő than in Mátraháza. The connection between dry weight and LAI exhibited saturating curve. Comparison between sites showed no difference in dry weight or in LAI. However, there were definite differences between the numbers of flowers: in Gödöllő and Bugac (where the ozone pollution was substantially lower) the plants developed much more flowers than in Mátraháza. Therefore the number of flowers could also be a useful indicator of tropospheric ozone in addition to the extent of ozone injuries. Future experiments are proposed to manage with measurements of physiological parameters such as stomatal conductance, net assimilation and chlorophyll fluorescence.