Centre for Ecology & Hydrology
NATURAL ENVIRONMENT RESEARCH COUNCIL

Air Pollution and Vegetation

ICP Vegetation* Annual Report 2004/2005

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July 2005

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

Acknowledgements

We wish to thank the UK Department for Environment, Food and Rural Affairs (Defra) for the continued financial support of the ICP Vegetation (Contract EPG 1/3/205). Contributions from Lisa Emberson, Patrick Büker and Steve Cinderby (SEI-York, UK), Mike Ashmore and Andrew Terry (University of York, UK), Mike Holland (EMRC, Reading UK) and Sally Power and Emma Green (Imperial College, UK) as sub-contractors of Contract EPG 1/3/205 are gratefully acknowledged, as are contributions in kind from Ludwig De Temmerman (VAR, Belgium) and Jürg Fuhrer (FAL, Switzerland). In addition, we wish to thank the ICP Vegetation Steering Committee (Jürg Fuhrer, Ludwig De Temmerman, Mike Ashmore and Ben Gimeno) for their advice and all of the ICP Vegetation participants for their continued contributions to the programme.

Executive summary

Background

The ICP Vegetation[1] has studied the impacts of air pollutants on crops and (semi-)natural vegetation in the UNECE[2] region for almost two decades. In recent years, the ICP Vegetation has focussed 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. Two further pollution problems are recently being considered by the programme: plant responses to pollutant mixtures 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 results of studies conducted by ICP Vegetation are reported to the Working Group on Effects (WGE) of the Convention on Long-Range Transboundary Air Pollution (LRTAP), where they are used in assessments of the current, and predictions of the future, state of the environment. Currently, the work of the ICP Vegetation is providing information for the 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. Thirty five parties to the LRTAP Convention participate in the programme. The 18th Task Force meeting of the Programme was held in Almería, Spain, February 2005, and was attended by 62 participants from 17 countries.

Biomonitoring of ozone impacts on vegetation

The summer of 2004 was generally cooler and wetter across Europe and ozone concentrations at the ICP Vegetation biomonitoring sites were lower than in the previous summer. The AOT40[3] for a three-month period ranged from 0.4 ppm h in Bangor (UK) to 13.7 ppm h in Cadenazzo (Switzerland). However, as in 2003, the long-term critical level for (semi-)natural vegetation and agricultural crops for yield reduction, i.e. a three-month AOT40 of 3 ppm h, was exceeded at 80% of the sites.

Ozone-sensitive biotypes of white clover (*Trifolium repens* cv Regal) were used at 20 sites in 12 countries to monitor the frequency of occurrence of leaf injury caused by ozone episodes. The cold, wet summer with low ozone coincided with low injury scores. In 2004, generally no more than 50% of the leaves showed symptoms at any of the sites. Nevertheless, visible leaf injury was widespread across Europe and was also recorded at sites where the critical level of ozone for yield reduction was not exceeded. In 2004, it wasn't possible to validate the new short-term critical level for visible injury as the vast majority of the sites providing adequate quality ozone and vapour pressure deficit data had less than 10% ozone injury at any individual assessment. In addition to leaf injury assessments, mainly 'high-ozone sites' determined the relationship between the biomass ratio of sensitive (NC-S) to resistant (NC-R) biotypes of white clover. The decrease in biomass ratio with increasing ozone exposure from the 2004 data fits the same trend as data from 1996 to 2003.

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[1] The International Cooperative programme on Effects of Air Pollution on Natural Vegetation and Crops.
[2] The United Nations Economic Commission for Europe.
[3] The sum of the differences between the hourly mean ozone concentration (in ppb) and 40 ppb for each hour when the concentration exceeds 40 ppb, accumulated during daylight hours.

A biomonitoring programme with *Centaurea jacea* (brown knapweed) has been developed by the ICP Vegetation to evaluate the relationship between ozone exposure and effects on the performance and injury symptoms of native plant species. Across Europe ozone-specific leaf injury was observed on the *Centaurea jacea* plants at eight out of the ten participating sites. At four of the sites, the modifying effects of nitrogen pollution on the impacts of ozone pollution on *Centaurea jacea* were also investigated. There were no interactions between nitrogen supply and visible leaf injury at any site. Analysis of rosette leaves showed that the nitrogen concentration and C:N ratio of the leaves were not affected by nitrogen supply. It seems that *Centaurea jacea* is unresponsive to nitrogen as the plants grew well at all sites without added nitrogen. Hence, this aspect of the biomonitoring work will not be continued.

Critical levels of ozone for vegetation

In the recent revision of the LRTAP Convention Mapping Manual stomatal flux-based critical levels of ozone were included for the crops wheat and potato. Review of data available within the scientific literature has provided sufficient information for the development of robust flux models for three additional crop species: grapevine, sunflower and tomato. The flux-effect relationships included in the Mapping Manual relate the ozone flux to a single sun-lit leaf to the effect measured. For white clover, the single leaf flux model has been up-scaled to a whole canopy flux model based on an estimation of average canopy stomatal conductance, using stomatal conductance measurements made by participants in previous years. The canopy flux model will be applied to establish a canopy flux-effect relationship for white clover. The next 'Ozone critical levels Workshop' will be held in Obergurgl (Austria) in November 2005, where further application and development of the flux-based approach will be reviewed and discussed.

Heavy metal deposition to vegetation

The European heavy metals in mosses survey is conducted a five-yearly intervals and provides data on concentrations of ten heavy metals (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn) in naturally growing mosses. The next survey will be conducted in 2005/2006 and the Manual for collecting and analysing moss samples was revised recently.

As a contribution in kind to the ICP Vegetation, Mr Ludwig De Temmerman (VAR, Belgium) determined the heavy metal concentration in clover used in the ozone biomonitoring experiment. Twelve participants grew the NC-R (ozone-resistant) biotype of white clover at their site using a standard soil mixture. Significant linear correlations were found between the heavy metal bulk deposition rates and the heavy metal concentrations in white clover for cadmium, copper and lead. The 'normal' background concentrations and pollution thresholds could be determined for these metals, although the pollution threshould for cadmium is preliminary. At about half of the participating sites in Europe the pollution thresholds for copper and lead were exceeded at some time during the growth period.

Mr Ludwig De Temmerman also reviewed the heavy metal deposition to and potential contamination of crops. Atmospheric deposition of metals has a direct effect on the contamination of crops used for human and animal consumption. Leafy vegetables are particularly vulnerable to the atmospheric impact of arsenic, lead and mercury. Away from pollution sources the deposition of arsenic is rather low but atmospheric deposition remains important as a main source of contamination of leafy vegetables. Vegetables, fruits and cereals are the main source of the more toxic inorganic forms of arsenic in human food. The transfer through terrestrial animals is low and consequently there is less arsenic in animal products. The contribution of atmospheric cadmium to the accumulated level in crops is often less important than that of soilborne cadmium. There is limited transfer of cadmium to humans via consumption of animal products, except for offal. Lead is a widespread pollutant having a direct impact on above-ground plant parts. Even at remote sites there is still a clear impact of lead deposition on its concentration in leaves and wheat grain. Being a toxic element, lead is also important for animal health, but fortunately transfer to foodstuffs from animal origin is rather low. Contrary to arsenic, the inorganic forms of mercury, predominantly present in crops, are much less toxic than the organic forms. In crops, atmospheric deposition is the main source of inorganic mercury. However, most crops have a rather low accumulation rate although some crops (curly kale, some herbs) are able to accumulate considerably more. The food chain through animals and animal products appears to be less important when aquatic organisms are excluded.

Nitrogen deposition to mosses

The European moss survey provides an excellent opportunity to test whether carpet forming mosses can be used as biomonitors of atmospheric nitrogen deposition at a European scale. In a pilot study the total nitrogen concentration in mosses in Norway was well correlated with the atmopheric nitrogen deposition rate, independent of nitrogen speciation in deposition. Both nitrogen deposition rates and nitrogen concentrations in mosses showed no temporal trend in recent decades. The Task Force meeting recommended to include the determination of the total nitrogen concentration in mosses in the 2005/2006 European moss survey.

Future work

The ICP Vegetation will continue the ozone biomonitoring programme with white clover. The formulation and parameterisation of the canopy stomatal conductance model for white clover will be further improved with the ultimate aim to produce a canopy flux-effect model for clover for both ozone injury and biomass reduction. In addition, work will focus on the validation of flux-based critical levels for additional agricultural crop and tree species by reviewing the literature on effects of ozone together with data on stomatal conductance-environmental parameter relationships for these species. Biomonitoring of the impact of ozone on (semi-)natural vegetation, using *Centaurea jacea* as a model species, will continue with the ultimate aim of completing a flux-effect model for this species. The revised critical levels for ozone will be used to further develop critical level exceedance maps. The ICP Vegetation is constructing a conceptual spatial framework that can be applied across Europe for mapping impacts of ozone on communities of (semi-)natural vegetation using the European Nature Information System (EUNIS) classification. In addition, the interactive impacts of ozone and nitrogen pollution on vegetation and the impacts of ozone on vegetation in a changing climate will be reviewed.

For heavy metals, the European moss survey 2005/2006 has started in several European countries. The concentration of heavy metals in mosses in the 2000/2001 survey is being compared with EMEP heavy metal deposition data for cadmium, mercury and lead for validation purposes. In addition, temporal trends in the existing European data set between 1990 and 2000/2001 are being conducted and these trends will be compared with trends in EMEP heavy metal deposition data.

For nitrogen, the ICP Vegetation will review the modifying influence of nitrogen deposition on the impacts of ozone on vegetation. In addition, long-term trends in the nitrogen concentration in mosses using herbarium samples will be determined for selected countries. The Task Force recommended to participants to include the determination of the total nitrogen concentration in mosses in the 2005/2006 survey.

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1. Introduction

The ICP Vegetation

The ICP Vegetation[1] 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. The WGE considers the effects of air pollutants on waters, materials, forests, vegetation, ecosystems, and health in Europe and North America. In recent years, the ICP Vegetation has focussed on two air pollution problems of particular importance in the UNECE region: quantifying the risks to vegetation posed by ozone pollution and the atmospheric deposition of heavy metals to vegetation. Two further pollution problems are recently being considered by the programme: plant responses to pollutant mixtures and the impacts of nitrogen pollutants on vegetation. Thus, the work of the ICP Vegetation currently aims to provide information for the 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. 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. Over 180 scientists from 35 countries of Europe and North America contribute to the programme by conducting experiments, sampling vegetation or modelling pollutant deposition and effects. The ICP Vegetation is chaired by Mr Harry Harmens at the Coordination Centre at the Centre for Ecology and Hydrology, Bangor, UK, and the coordination is supported by the UK Department for Environment, Food and Rural Affairs (contract EPG 1/3/205).

The ICP Vegetation:

- Conducts coordinated experiments to determine the effects of ozone pollution on crops and (semi-)natural vegetation in Europe and North America.

- Develops computer models to quantify and interpret the influence of climatic conditions and environmental stresses on the responses of plants to ozone, and uses the models to establish critical levels for effects of ozone.

- Develops maps showing where vegetation is at risk from ozone pollution within the UNECE region, including areas where critical levels are exceeded.

- Assesses the economic losses caused by the effects of ozone on crops.

- Collates and reviews information on the effects of ozone on plant biodiversity.

- Collates and reviews information on the effects of ozone in a changing climate.

- Collates and reviews monitoring data on the atmospheric deposition of heavy metals, and subsequent accumulation by mosses and higher plants.

[1] The International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops.

- Considers the evidence for effects of nitrogen deposition on communities of (semi-) natural vegetation in Europe, including its modifying effect on the impacts of ozone.

The specific objectives of the ICP Vegetation are presented in Annex I.

Impacts of ozone on crops and (semi-)natural vegetation

As part of the work programme for the ICP Vegetation, information is collected on the effects of ambient ozone episodes on crops and example species of (semi-)natural vegetation in Europe and the USA by conducting biomonitoring experiments, and by assessing information in the scientific literature. Ozone episodes can cause short-term responses in plants such as the development of visible injury (fine bronze or pale yellow specks on the upper surface of leaves) or reductions in photosynthesis. If episodes are frequent, longer-term responses such as reductions in growth and yield can occur.

Throughout the years, participants in the ICP Vegetation carried out systematic surveys of commercial crops for characteristic visible symptoms of ozone damage, on days following visible injury in the clover bioindicator system. Ozone injury was detected on the foliage of over 20 agricultural and horticultural crops including on crops such as lettuce, chicory, parsley and spinach for which such foliar damage results in loss in commercial value. The documentation of the extent of visible injury due to ozone, both in field surveys and in the biomonitoring studies, provides important evidence for the significance of ozone as a phytotoxic pollutant across Europe.

The negotiations concerning ozone for the Gothenburg Protocol (1999) were based on exceedance of a then so-called level I long-term critical level of ozone for crops and (semi-) natural vegetation. This value, an AOT40[2] of 3 ppm h accumulated over three months was set at the Kuopio Workshop in 1996 (Kärenlampi and Skärby, 1996) and was considered to be the lowest AOT40 at which significant yield loss due to ozone could be detected, according to current knowledge (Mapping Manual, 1996). However, several important limitations and uncertainties have been recognised for using the concentration-based approach. The real impacts of ozone depend on the amount of ozone reaching the sites of damage within the leaf, whereas AOTX-based critical levels only consider the ozone concentration at the top of the canopy. The Gerzensee Workshop in 1999 (Fuhrer and Achermann, 1999) recognised the importance of developing an alternative critical level approach based on the flux of ozone from the exterior of the leaf through the stomatal pores to the sites of damage (stomatal flux). This so-called level II approach required the development of mathematical models to estimate stomatal flux, primarily from knowledge of stomatal responses to environmental factors. In recent years, the terminology has changed such that ‘level I’ and ‘level II’ are no longer used and have been replaced by ‘concentration-based’ and ‘flux-based’, respectively (Mapping Manual, 2004).

In the first step towards an ozone-flux based critical level, Lisa Emberson and colleagues developed a multiplicative model of stomatal conductance of ozone (Emberson *et al.*, 2000a). This model includes functions for the effects of phenology, light, temperature, vapour pressure deficit (VPD) and soil water potential on the stomatal conductance of several species including wheat and potato, beech and birch. At the Gothenburg Workshop in 2002 (Karlsson

[2] The sum of the differences between the hourly mean ozone concentration (in ppb) and 40 ppb for each hour when the concentration exceeds 40 ppb, accumulated during daylight hours.

et al., 2003), it was concluded that for the time being it was only possible to derive flux-based ozone critical levels for the crops of wheat and potato. Since the Gothenburg Workshop, the parameterisation of the conductance model presented in Pleijel *et al*. (2002, 2003) and Danielsson *et al*. (2003) has been revised to achieve full compatibility with the EMEP model calibration (Emberson *et al*., 2000b). The new flux-based critical levels for crops are included in the revised Mapping Manual (Mapping Manual, 2004). Also included are provisional flux-based critical levels for the tree species, birch and beech. A vapour pressure deficit-modified concentration-based critical level was developed and included in the new Mapping Manual to define the short-term critical level for the development of visible injury on crops. New data collated since the Kuopio Workshop support the concentration-based critical level of 3 ppm h for agricultural crops, based on a growth period of 3 months. In addition, a separate concentration-based critical level was developed for horticultural crops, i.e. AOT40 of 6 ppm h, based on a growth period of 3.5 months. Based on the analysis of the current experimental database, the concentration-based critical level of ozone for trees has been reduced from an AOT40 value of 10 ppm h (Kärenlampi and Skärby, 1996) to 5 ppm h. Further details on the new critical levels for ozone and its application can be found in chapter 3 of the Mapping Manual. The next 'Ozone critical levels Workshop' will be held in Obergurgl (Austria) in November 2005, where further application and development of the flux-based approach will be reviewed and discussed.

By conducting experiments in ambient air, the ICP Vegetation has established a unique database for developing the flux-based approach to critical levels. Since 1996, ozone-sensitive (NC-S) and ozone-resistant (NC-R) biotypes of white clover (*Trifolium repens* cv Regal) have been grown at each of the ICP Vegetation sites according to a standardised experimental protocol. Effects of ozone are recorded as a score for visible injury, and as the ratio of the weight of the dried clippings (biomass) of the NC-S to the NC-R biotype. By exposing plants to ambient air, the reaction to ozone episodes could be considered without any confounding influence of a chamber on the flux of ozone to the plant. Trends in the impacts of ozone on clover between 1996 and 2003 and the development of a flux-based dose-response function for the effects on biomass were described previously (Harmens *et al*., 2004c). However, the flux-effect model for biomass reductions in white clover is based on flux estimates to an individual leaf and currently the single leaf flux model is being up-scaled to a whole canopy flux model (see chapter 2).

In recent years, interest in the effects of ozone on (semi-)natural vegetation has increased considerably. Setting critical levels for this type of vegetation is far more complicated than for crops because of the diversity of species and ecosystems within the UNECE region. In contrast to crops and trees, only limited experimental data are available for a small proportion of the vast range of species. For (semi-)natural vegetation the concentration-based critical level was defined as an AOT40 of 3 ppm h, based on a growth period of 3 months, which is sufficient to protect the most sensitive annual and short-lived perennial species when grown in a competitive enviroment (Mapping Manual, 2004). Further study of factors influencing the stomatal uptake of ozone is required before a flux-based critical level for ozone can be established for (semi-)natural vegetation. Data from the ICP Vegetation database are used to identify species 'at risk' from ozone damage and the communities they represent and mapping procedures are being developed indicating where such species might be at risk from ozone. Recently, ICP Vegetation has developed a new ozone biomonitoring system using the (semi-)natural species *Centaurea jacea* (brown knapweed).

Heavy metal deposition to vegetation

Concern over the accumulation of heavy metals in ecosystems, and their impacts on the environment and human health, increased during the 1980s and 1990s. The LRTAP Convention responded to this concern by establishing a Task Force on Heavy Metals (and persistent organic pollutants) under the Working Group on Abatement Techniques. In 1998, the first Protocol for the control of emissions of heavy metals was adopted and signed by 36 parties to the Convention. The Protocol stated that "an effects-based approach should integrate information for formulating future optimised control strategies taking account of economics and technological factors". Cadmium, lead and mercury emissions were targeted by the Protocol.

The ICP Vegetation is addressing a short-fall of data on heavy metal deposition to vegetation in two ways. Firstly, the clover clones used in the ozone experiments have been analysed for arsenic, cadmium, copper and lead in 2000, 2002 and 2004. Comparison of the heavy metal concentrations in white clover with measured heavy metal bulk deposition rates at these experimental sites is allowing a method for determining the level of deposition at any site to be developed. Secondly, the ICP Vegetation has taken over the coordination of a well-established programme that monitors the deposition of heavy metals to mosses. The programme, originally established in 1980 as a joint Danish-Swedish initiative, involves the collection of mosses and determination of their heavy metal concentration at five-year intervals; it included almost 7,000 samples of mosses taken from 29 European countries in the 2000/2001 survey (Buse *et al.*, 2003b). ICP Vegetation is currently coordinating the European heavy metals in mosses survey 2005/2006.

Impacts of nitrogen deposition on (semi-)natural vegetation

The ICP Vegetation agreed at its 14th Task Force Meeting (January 2001) to include consideration of the impacts of atmospheric nitrogen deposition on (semi-)natural vegetation within its programme of work. This stemmed from concern over the impact of nitrogen on low nutrient ecosystems such as heathlands, moorlands, blanket bogs and (semi-)natural grassland. The empirical critical loads for nitrogen for different ecosystems were reviewed and revised at the UNECE Workshop on 'Empirical Critical Loads for Nitrogen Deposition on (Semi-)Natural Ecosystems', Bern, Switzerland, 11-13 November 2002. Impacts of nitrogen, and the interaction with ozone, now forms part of the work programme of the ICP Vegetation. At selected sites across Europe *Centaurea jacea* has been exposed to different levels of nitrogen pollution to determine the interactive effects of nitrogen and ozone pollution on (semi-)natural vegetation. In addition, the total nitrogen concentration in mosses was determined in selected samples from the heavy metals in mosses survey from selected European countries in order to determine trends in nitrogen deposition between 1977/1980 and 2000/2001. ICP Vegetation has also collected moss samples from national herbaria from selected European countries for nitrogen analysis for establishing long-term trends in atmospheric nitrogen deposition in Europe.

Participation in the ICP Vegetation

The participation in the ICP Vegetation has increased to 35 Parties to the Convention (table 1.1). The contact details of the participants are included in Annex 2. It should be noted that in many countries, several other scientists (too numerous to mention individually) also contribute to the biomonitoring programmes, analysis and modelling procedures that comprise the work of the ICP Vegetation.

Table 1.1 Countries participating in the ICP Vegetation

Austria	Lithuania
Belarus	Netherlands
Belgium	Norway
Bosnia and Herzegovina	Poland
Bulgaria	Portugal
Czech Republic	Romania
Denmark	Russian Federation
Estonia	Serbia and Montenegro
Finland	Slovakia
France	Slovenia
FYR of Macedonia	Spain
Germany	Sweden
Greece	Switzerland
Hungary	Turkey
Iceland	United Kingdom
Ireland	Ukraine
Italy	USA
Latvia	

Web site

The ICP Vegetation web site can be found at icpvegetation.ceh.ac.uk

Aims of this report

It is the intention of this report to provide an overview of the main activities of the ICP Vegetation in 2004/2005 (chapter 2) and report in more detail on heavy metal deposition and the potential contamination of crops (chapter 3). Conclusions and future work are reported in chapter 4, together with contributions to the proposed deliverables to the WGE.

2. Overview of activities in 2004/2005

Biomonitoring of ozone impacts on vegetation

The ICP Vegetation collates information on the effects of ambient ozone episodes on crops and (semi-)natural vegetation in Europe and the USA by conducting biomonitoring experiments, and by assessing information in the scientific literature. Since 1996, participants in the ICP Vegetation have detected effects of ambient ozone at sites across Europe and in the USA by growing ozone-sensitive (NC-S) and ozone-resistant (NC-R) biotypes of white clover (*Trifolium repens* cv Regal; Heagle *et al*., 1995), and recording the occurrence of leaf injury and biomass differences between the two biotypes. Since 2002, the ozone biomonitoring programme has been extended to include brown knapweed (*Centaurea jacea*) as a representative of (semi-)natural vegetation. The response of the biomonitoring species at individual sites is compared with pollutant and climatic conditions during the experiment. The data from the 2004 experimental season of the ICP Vegetation has been added to the existing database. The ambient air experiments were the core activity for participants in 2004: 20 sites in 12 countries partcipated in biomonitoring with white clover and ten sites in eight countries participated in biomonitoring with brown knapweed. This section summarises the results from the 2004 biomonitoring experiments. A more detailed analysis of the clover biomonitoring data from 1996 – 2003 was presented by Harmens *et al*. (2004c).

The clover biomonitoring experiment in 2004

Cuttings of ozone-sensitive (NC-S) and ozone-resistant (NC-R) biotypes of white clover (*Trifolium repens* cv Regal) were distributed by the Coordination Centre to participants of the programme. A standard protocol developed at the Coordination Centre was followed for establishment and subsequent exposure of the plants (Harmens *et al*., 2004b). Individual plants were placed in individual 30 litre pots, which had an integral wick system for watering, and maintained at a field site away from local pollution sources and major roads. Plants were inspected at least weekly for ozone injury on leaves. At 28 day intervals the foliage was cut down to 7 cm above the soil surface, then dried and weighed to determine biomass. The plants were allowed to re-grow before a further harvest 28 days later. The period between the first and fourth harvest at each site equated to the three-month time period for calculation of AOT40 and other three-month based parameters. The ratio of the biomass of the NC-S biotype to that of the NC-R biotype indicated the extent of ozone damage at participating sites, with ratios of less than 1 showing that ozone was having a negative effect on the sensitive biotype. At many of the sites in 2004, a second batch of NC-S clover was grown, using an identical protocol but 14 days later than the first batch. This ensured that there was always a full canopy of leaves on some clover plants at each site and allowed a more complete assessment of the development of visible injury at each site. Participants monitored the extent of visible leaf injury on the sensitive biotype of white clover frequently (generally on a weekly basis).

A wide range of climatic and pollution conditions are found over the network of biomonitoring sites in the ICP Vegetation. The range of sites in Europe extends from Sweden to Spain and covers both urban and rural locations. The data from each experimental site were sent to the Coordination Centre for analysis. Data comprised measurements of biomass from four to five 28-day harvests, stomatal conductance measurements, assessments of plant health and weekly assessments of visible injury. Hourly means of climatic and pollution data including temperature, humidity, solar radiation, windspeed, ozone, NOx and SO_2 for a four to five-month period were also sent to the Coordination Centre for analysis.

Ozone pollution and climatic conditions in 2004

In 2004, the summer was generally colder and wetter across Europe and ozone concentrations were lower than in 2003 (table 2.1; figure 2.1). The main daily maximum ozone concentration in 2004 ranged from 35.0 ppb in UK-Bangor to 70.6 ppb in Switzerland-Cadenazzo and the AOT40 for the three-months period ranged from 0.4 ppm h in UK-Bangor to 13.7 ppm h in Switzerland- Cadenazzo. Despite lower ozone concentrations in 2004, the long-term critical level for (semi-)natural vegetation and agricultural crops (a three month AOT40 of 3 ppm h) was again exceeded at 80% of the sites where ozone was continuously monitored (Harmens *et al*., 2004c).

Table 2.1 Climatic and pollution conditions over the three-months experimental period at selected ICP Vegetation biomonitoring sites in 2004; - = data unavailable or insufficient.

	Ozone			**Temperature (°C)**		**Rainfall**		**VPD (k Pa)**	
Site	Mean daily max (ppb)	24 hr mean (ppb)	AOT 40 (ppm h)	Mean	Daylight mean	Total (mm)	No. of Days	24 hr mean	Daylight mean
Austria - Seibersdorf	54.8	36.6	8.20	18.6	21.1	97	29	0.82	1.18
Belgium - Tervuren	43.7	24.5	2.98	17.2	19.4	-	-	0.46	0.69
Germany - Hohenheim	53.2	32.1	8.97	18.4	20.2	-	-	-	-
Greece - Thessaloniki	50.2	33.1	4.06	-	-	-	-	-	-
Italy - Pisa	57.2	34.5	7.26	19.3	-	69	46	-	-
Slovenia - Iskrba	55.6	29.4	9.34	16.5	19.7	391	61	0.62	0.94
Slovenia - Ljubljana	58.1	31.5	9.5	19.9	21.9	470	31	0.79	1.10
Slovenia - Rakican	53.3	28.7	6.11	18.8	21.3	175	48	0.72	1.06
Sweden - Östad	40.7	26.3	1.06	15.3	18.2	-	-	0.35	0.62
Switzerland - Cadenazzo	70.6	37.1	13.73	21.0	23.2	454	35	1.72	1.71
UK - Ascot	46.1	30.9	3.32	-	-	136	42	-	-
UK - Bangor	35.0	25.7	0.44	-	-	-	-	-	-

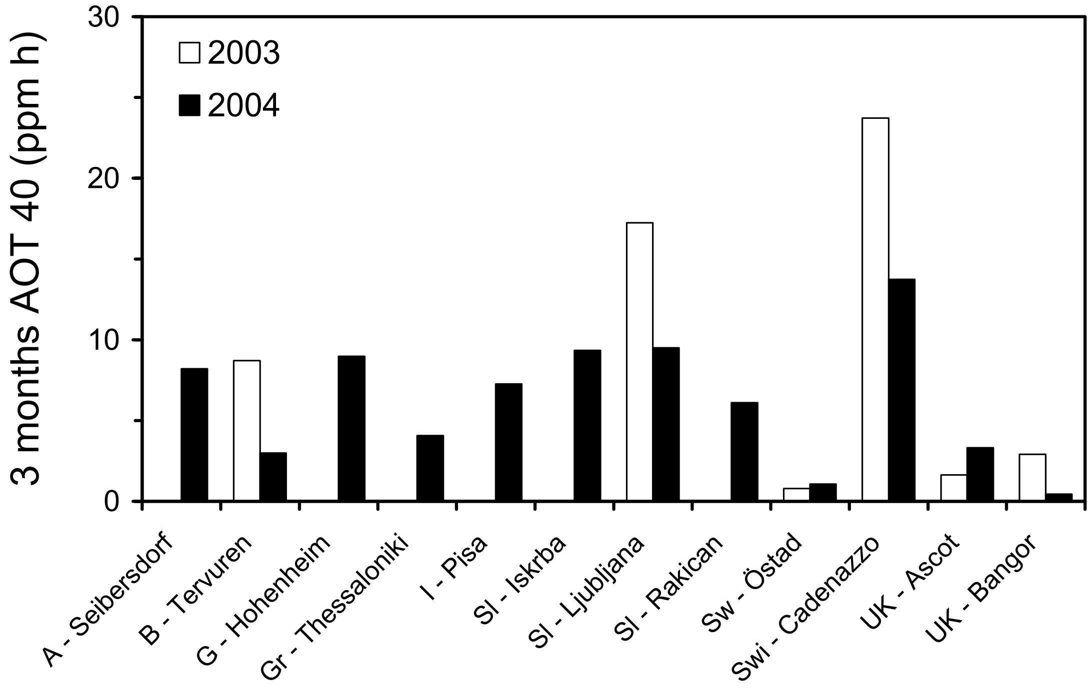

Figure 2.1 Three months AOT40 (ppm h) at selected ICP Vegetation sites in 2004. For some of 2004-sites a comparison with 2003 is available.

Effects of ambient ozone on white clover

Nine of the participarting sites carried out weekly assessments of ozone-induced leaf injury on white clover. In addition, some other sites recorded the first occurrence of ozone injury and the extent of ozone injury at harvest. By late June, approximately two-thirds of the sites had recorded visible leaf injury, although some sites had recorded ozone injury as early as 18^{th} May. The cold, wet summer with low ozone coincided with low injury scores. Usually several sites record injury scores representing 90% or more of the leaves with ozone-injury symptoms, but generally no more than 50% of the leaves showed symptoms at any of the sites in 2004 (figure 2.2). However visible injury was still widespread across the sites, if at a lower intensity than in previous years. Even some of the sites which received less than the critical level for ozone of 3 ppm h reported some visible injury symptoms over the summer (e.g. Sweden-Östad). In Italy-Rome and Spain-Ebro Delta leaf injury was recorded as late as 5^{th} October at an average score of 2.4 and 3.8, respectively and in Spain-Ebro Delta the average leaf injury score was 2.8 on 2^{nd} November. In 2004 it wasn't possible to validate the new short-term critical level for visible injury (Mapping Manual, 2004) as the vast majority of the sites providing adequate quality ozone and vapour pressure deficit data had less than 10% ozone injury at any individual assessment.

In addition to leaf injury assessments, mainly 'high-ozone sites' determined the relationship between the biomass ratio of sensitive (NC-S) to resistant (NC-R) biotypes of white clover. The decrease in biomass ratio with increasing ozone exposure from the 2004 data fits the same trend as data from 1996 to 2003 (figure 2.3).

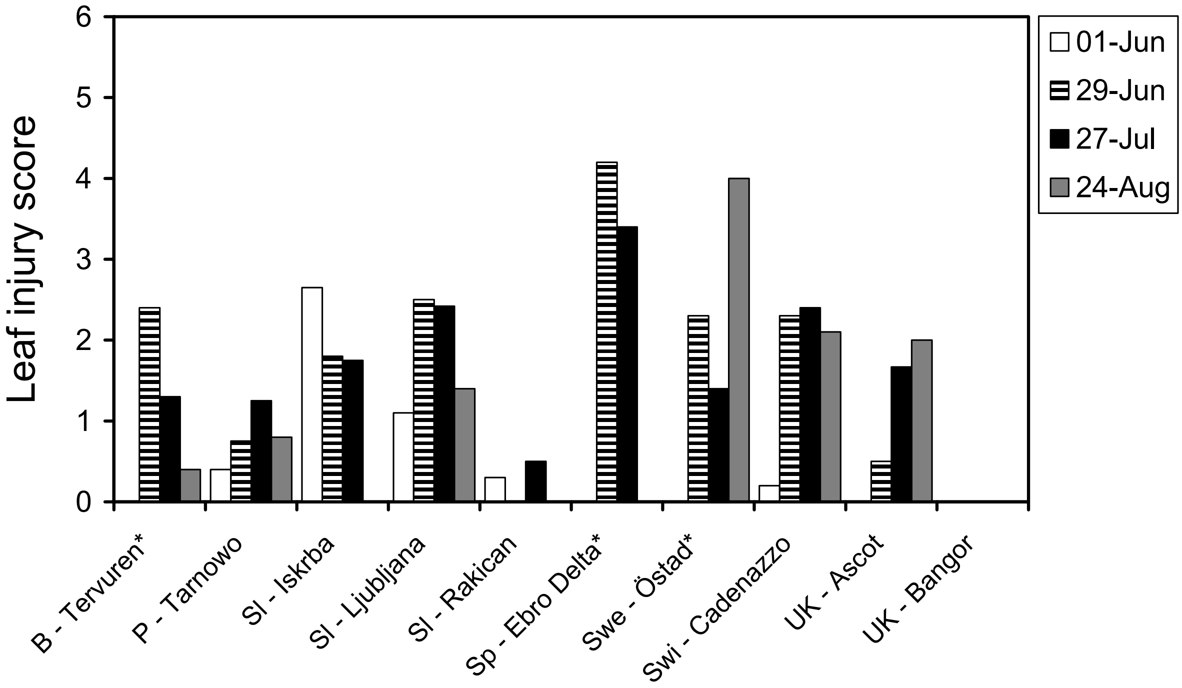

Figure 2.2 The extent of visible injury due to ozone on the sensitive biotype of *Trifolium repens* during four separate weeks in 2004 at a range of sites across Europe. Leaf injury scores: 1= <1%, 2= 1%-5%, 3= 5%-25%, 4= 25%-50%, 5= 50%-90%, 6= 90%-100% of leaves affected. * = no leaf injury score determined on 1st June; otherwise a score of 0 indicates no leaf injury.

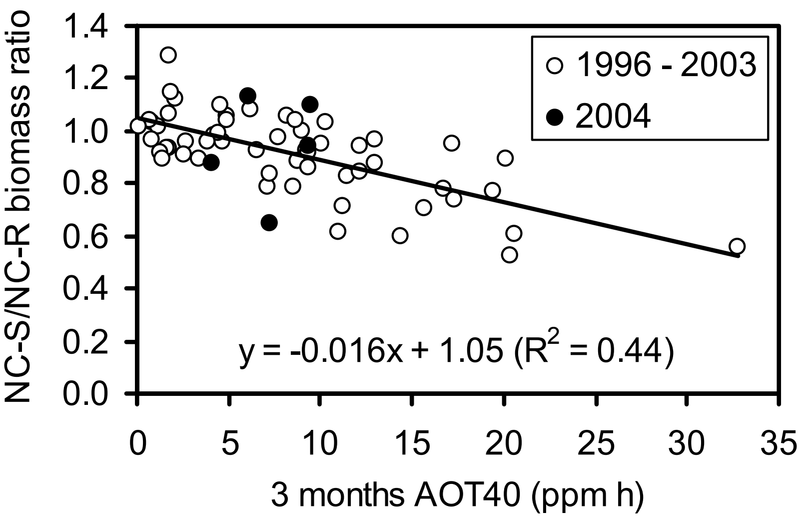

Figure 2.3 Response of the NC-S/NC-R biomass ratio of white clover to AOT40 over three months.

Effects of ambient ozone on (semi-)natural vegetation

Whilst there is considerable evidence for effects of ozone on a wide variety of crop plants, including clover, relatively few native plant species have been investigated. Existing evidence suggests that many species characteristic of (semi-)natural plant communities are at least as sensitive to ozone as the major crop plants. *Centaurea jacea* has been identified as one of several native species which is relatively sensitive to ozone, exhibiting characteristic symptoms of ozone injury following exposure (Buse *et al*., 2003a). In 2004, *Centaurea jacea* was used again as a model species to evaluate the relationship between ozone exposure and effects on the performance and injury symptoms of native plant species, along the existing gradient of ozone exposure from the north to the south of Europe.

Seeds were collected from an ozone sensitive and ozone resistant population of *Centaurea jacea* by participants from Switzerland, led by Mr Jürg Fuhrer. The seeds and wick material were distributed by the ICP Vegetation Coordination Centre to participants, who established and grew *Centaurea jacea* in glasshouses according an improved experimental protocol (Harmens *et al*., 2004b). The plants were transferred to the field site and exposed to ambient ozone concentrations when they had about 8-10 true rosette leaves. From then onwards leaf injury due to ozone was recorded weekly and photographs were taken to document the growth stage and extent of injury.

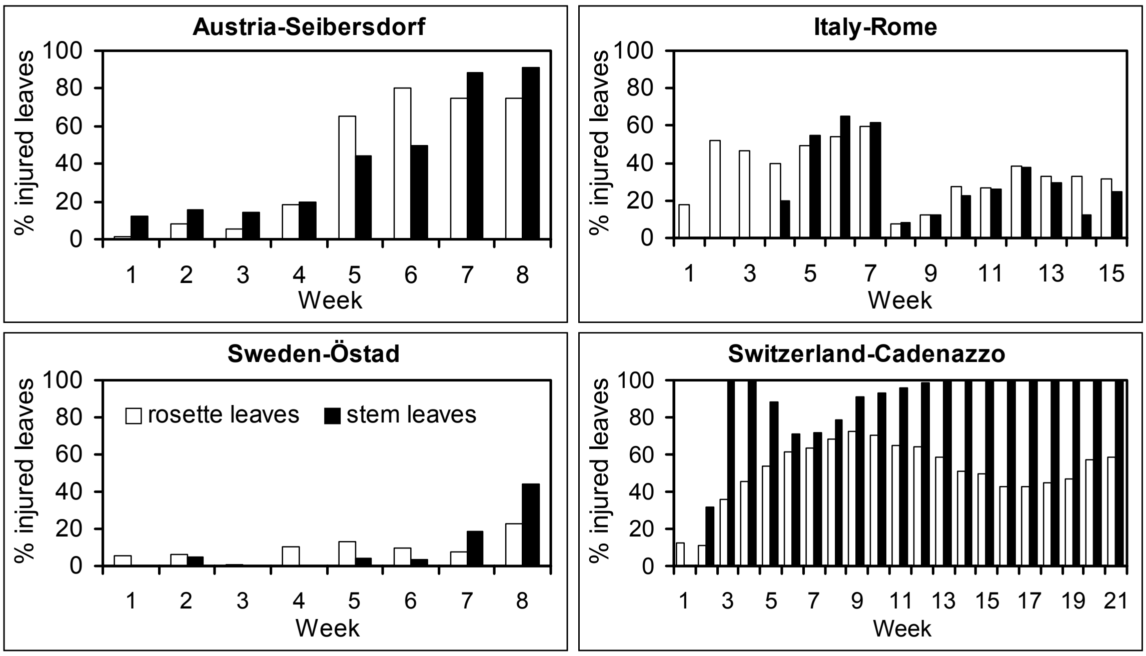

Figure 2.4 Progression of ozone injury on the stem and rosette leaves of *Centaurea jacea* at four selected sites in Europe. In Italy-Rome plants were harvested after eight weeks and allowed to regrow, whereas in Switzerland-Cadenazzo leaf injury was recorded beyond the standard eight weeks of growth.

No visible injury was observed on ambient air plants in Ireland-Carlow or UK-Bangor. Only slight injury was observed at UK-Ascot. Visible injury was recorded weekly at the other sites (Austria-Seibersdorf, Italy-Rome, Sweden-Östad, Switzerland-Cadenazzo, Slovenia-Velenje, Slovenia-Zavodnje, Spain-EbroDelta). Of the sites that observed visible injury on the plants, this injury was extensive at some sites, e.g. Switzerland-Cadenazzo observed almost 100% of leaves with visible injury (figure 2.4). Where the extent of injury on rosette leaves and stem leaves was compared, there were no significant differences.

Interaction between ozone and nitrogen pollution on (semi-)natural vegetation

Four of the European sites participating in the ozone biomonitoring study with *Centaurea jacea* exposed the plants to three levels of nitrogen: control (no added N), medium (30 kg ha^{-1} yr^{-1}) and high (80 or 120 kg ha^{-1} yr^{-1}) at fortnightly intervals during the course of an eight week exposure to ambient air and recorded visible leaf injury. The nitrogen was added in the form of NH_4NO_3 and all plants also received non-N nutrients in the form of Hoagland solution to make sure that no other nutrient was limiting plant growth.

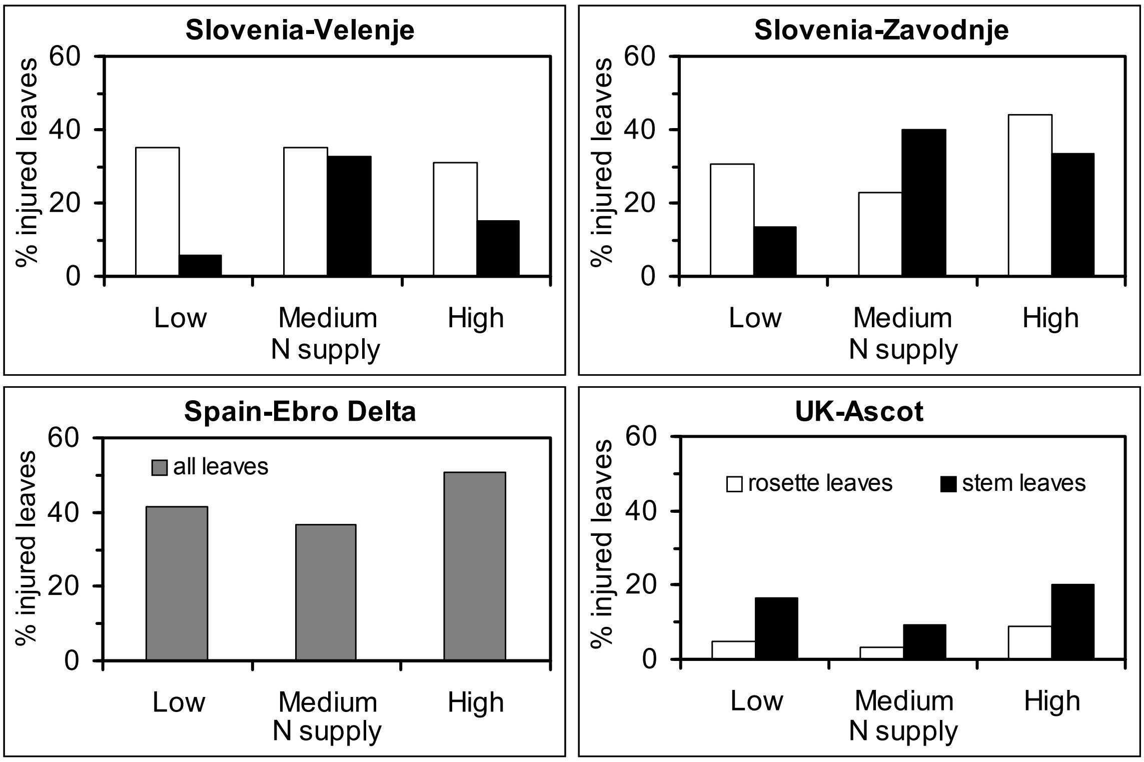

Figure 2.5 Influence of nitrogen supply on the percentage of ozone injured leaves on *Centaurea jacea* exposed to ambient ozone at four sites across Europe. Nitrogen treatments used were: 0, 30, 120 kg ha^{-1} for Slovenian sites, and 10, 30, 80 kg ha^{-1} for Spain-Ebro Delta and UK-Ascot.

There were no interactions between nitrogen supply and visible leaf injury at any site (figure 2.5). Analysis of rosette leaves showed that the nitrogen concentration and C:N ratio of the leaves were not affected by nitrogen supply. It appears that *Centaurea jacea* is very unresponsive to nitrogen as the plants grew well at all sites without added nitrogen to the recommended peat:sand soils mixture (the low nitrogen treatment). At the Task Force Meeting in February 2005 it was concluded that *Centaurea jacea* is insensitive to nitrogen and that this aspect of the biomonitoring work will not be continued.

Critical levels of ozone for crops

In the recent revision of the Mapping Manual (Mapping Manual, 2004) stomatal flux-based critical levels of ozone were included for the crops wheat and potato. Although these two crops are very important in Europe, there remains the need to expand the range of crops for which flux-effect relationships exist. The literature on effects of ozone on crops other than wheat and potato has been reviewed at SEI-York (UK) together with data on stomatal conductance-environmental parameter relationships for these crops. Five species (tomato, grapevine, sugar beet, maize and sunflower) were selected for investigation for potentially establishing robust flux models for use in future revision of the Mapping Manual. The flux models would be based on the stomatal conductance (g_s) multiplicative algorithm as described in the revised Mapping Manual. This requires a number of different g_s parameters and g_s relationships with environmental variables to be identified. Review of data available within the scientific literature has provided sufficient information for the development of robust flux models for three of the species: grapevine, sunflower and tomato. For sugarbeet and maize the current data availability is too limited to define robust flux models.

The flux-effect relationships included in the Mapping Manual relate the ozone flux to a single sun-lit leaf to the effect measured. For white clover the single leaf flux model has been up-scaled to a whole canopy flux model based on an estimation of average canopy stomatal conductance, using stomatal conductance measurements made by participants in previous years. Scaling from the leaf to the canopy level has been achieved by consideration of the penetration of irradiance into the canopy estimated using a canopy extinction algorithm, development of the leaf area index of the canopy and the fraction of leaf age populations present in the canopy throughout a growing period and their respective stomatal conductance. The canopy flux model will be applied to establish a canopy flux-effect relationship for white clover.

Preliminary maps indicating exceedance of the revised critical levels of ozone have been produced in collaboration with EMEP/MSC-W and they include for the first time exceedance of the flux-based critical levels for crops and forest trees. Work is almost finalised on the economic losses associated with exceedance of the new concentration-based and flux-based critical levels of ozone for crops. Analysis of the uncertainties in concentration- and flux-based methodologies and in the economic analysis are being made. The development of the economic assessment of ozone damage to crops includes a refinement of the model structure and considerations of approaches for dealing with impacts that cannot be described in quantitative terms (e.g. visible injury). Regarding the economic assessment, close links have been maintained with the EU programme CAFE (Clean Air For Europe). The outcome of the economic assessment will be published in a separate report.

Ozone-sensitive communities of (semi-)natural vegetation

The revised critical level of ozone for (semi-)natural vegetation was concentration-based since the methods for evaluating the risk of adverse impacts on (semi-)natural communities using flux-based methods was still at an early stage of development. However, it was recognised that progress could be made with identifying ozone-sensitive communities and predicting their response to ozone using flux-based concepts and existing single-species response information. Currently the ICP Vegetation is constructing a conceptual spatial framework that can be applied across Europe for mapping impacts of ozone on communities of (semi-)natural vegetation using the European Nature Information System (EUNIS) classification. AOT40-response functions have been defined for 70 species and the EUNIS communities they represent have been identified and sources of flux-based information have been determined. The work is focussing on grassland communities, because of their significance across Europe and because there is a greater body of experimental data on responses to ozone (Fuhrer *et al*., 2003). The framework will eventually combine information on species composition and species sensitivity for ozone-sensitive communities together with information relevant to flux modelling such as phenology, management, conductance of dominant species and soil moisture deficit (Ashmore and Franzaring, 2003).

European heavy metals in mosses survey 2005/2006

The European heavy metals in mosses survey provides data on concentrations of ten heavy metals in naturally growing mosses (Buse *et al*., 2003b; Harmens *et al*., 2004a). The next survey will be conducted in 2005/2006. So far, participants from 32 countries have indicated their willingness to participate in the survey. Of these, 20 have confirmed participation and other countries are likely to participate depending on national funding. The Manual for collecting and analysing moss samples was reviewed and revised by participants of the moss survey and can be downloaded from the ICP Vegetation web site (Harmens *et al*., 2005). Standard moss samples were distributed amongst participants for quality assurance purposes (Steinnes *et al*., 1997).

Heavy metal deposition to white clover

As a contribution in kind to the ICP Vegetation, Mr Ludwig De Temmerman (VAR, Belgium) determined the heavy metal concentration in clover used in the ozone biomonitoring experiment. Twelve participants grew the NC-R (ozone-resistant) biotype of white clover at their site using a standard soil mixture distributed by Mr De Temmerman. Harvested foliage was analysed for cadmium (Cd), copper (Cu) and lead (Pb). Data from 2004 were combined with data from previous years and the heavy metal bulk deposition rates were plotted against the heavy metal concentrations in clover (figure 2.6).

Significant linear correlations were found between the heavy metal bulk deposition rates and the heavy metal concentrations in white clover. Further statistical analyses were conducted to determine the ‘normal’ background concentrations and pollution thresholds of heavy metals in white clover. The background concentrations were 0.065 μg Cd g^{-1} dry matter (DM), 3.50 μg Cu g^{-1} DM and 0.15 μg Pb g^{-1} DM and the pollution thresholds were 4.15 μg Cu g^{-1} DM and 0.36 μg Pb g^{-1} DM, respectively. For cadmium only a preliminary pollution threshold of 0.155 μg g^{-1} DM could be established as the calculation of this threshold was based on three data points only. Up to a bulk deposition rate of 2.5 μg Cd m^{-2} day^{-1} the cadmium concentration in clover did not differ significantly from the background concentration. For copper the background concentration and the pollution threshold are not far apart. At about half of the participating sites in Europe the pollution thresholds for copper and lead were exceeded at some time during the growth period. In general, the concentration of lead and copper in white clover was above the pollution threshold at three sites in Dunkerque (France) and at Tervuren (Belgium), and at Athens and Volos (Greece) for lead only. The preliminary pollution threshold for cadmium was only exceeded in the centre of Dunkerque (France). The heavy metal concentration in clover was below the pollution threshold for all metals in Thessaloniki (Greece), Pisa (Italy) and Bangor (UK). In conclusion, the white clover biomonitoring network is working well for the trace elements lead and copper, but more data from polluted sites are needed to establish the pollution threshold for cadmium. The use of a standard substrate low in cadmium is required to prevent confounding effects of the uptake of cadmium by the roots from the substrate.

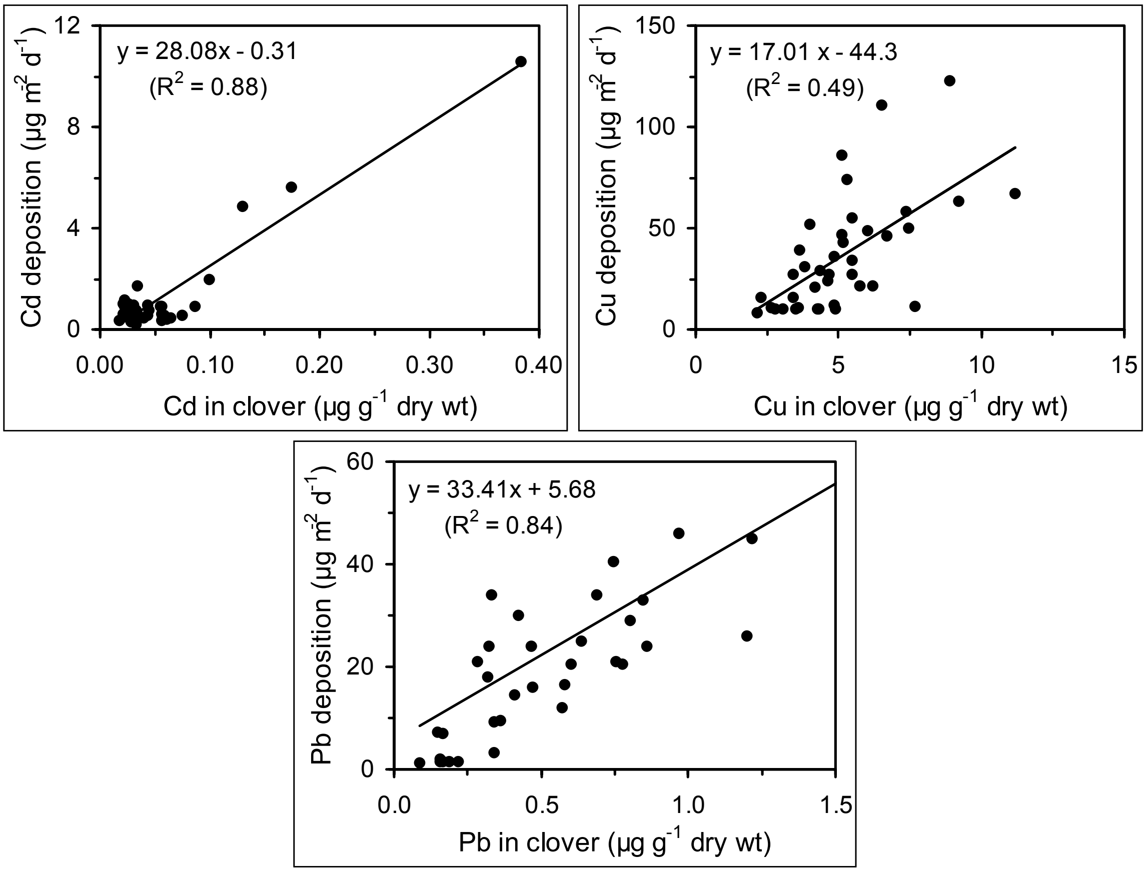

Figure 2.6 Heavy metal bulk deposition rates plotted against heavy metal concentrations in white clover for the metals cadmium (Cd), copper (Cu) and lead (Pb).

Nitrogen deposition to mosses

The European moss survey (see above) provides an excellent opportunity to test whether carpet forming mosses can be used as biomonitors of atmospheric nitrogen deposition at a European scale. Earlier studies have indicated that there is a clear relationship between atmospheric nitrogen deposition and the concentration of nitrogen in mosses (e.g. Pitcairn *et al.*, 1995; Solga *et al.*, 2005). In 2004, Scandinavian countries that have had long involvement in the heavy metals in moss survey, provided the Coordination Centre with moss samples from 20 sites per selected survey year for the determination of the total nitrogen concentration. In addition, nitrogen data were received from Germany for more recent years. Although the total nitrogen concentration in mosses was significantly different between countries, temporal trends were statistically not significant (figure 2.7). Analysis of data from Norway indicate that there was also no temporal trend in the atmospheric nitrogen deposition rates between 1977 and 2000 for the EMEP grid cells from which moss samples were taken. In addition, for Norway the nitrogen concentration in the mosses was well correlated with the atmopheric nitrogen deposition rate, independent of nitrogen speciation in deposition (figure 2.8). Therefore, the Task Force meeting recommended to include the determination of the total nitrogen concentration in mosses in the 2005/2006 European moss survey.

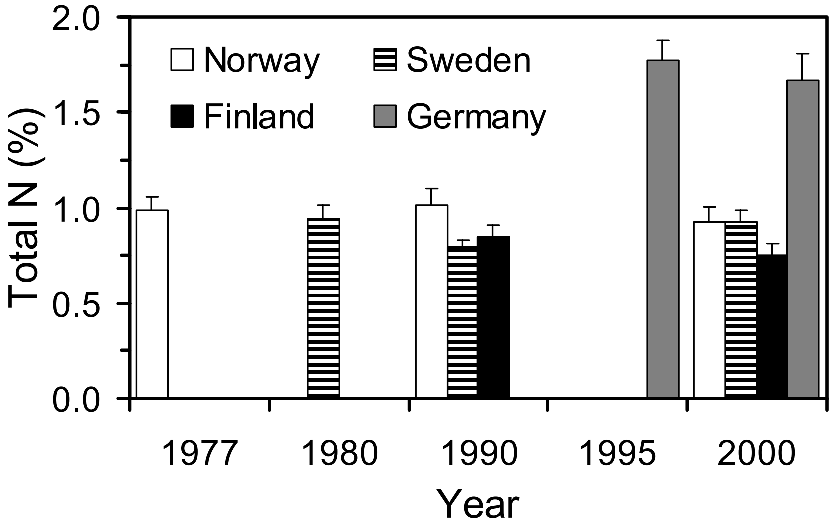

Figure 2.7 Nitrogen concentration in mosses sampled in selected years in four countries. The following moss species were sampled: Norway – *Hylocomium splendens*, Sweden and Finland – *Pleurozium schreberi*, Germany – mixture of *Pleurozium schreberi*, *Hypnum cupressiforme* and *Scleropodium purum*.

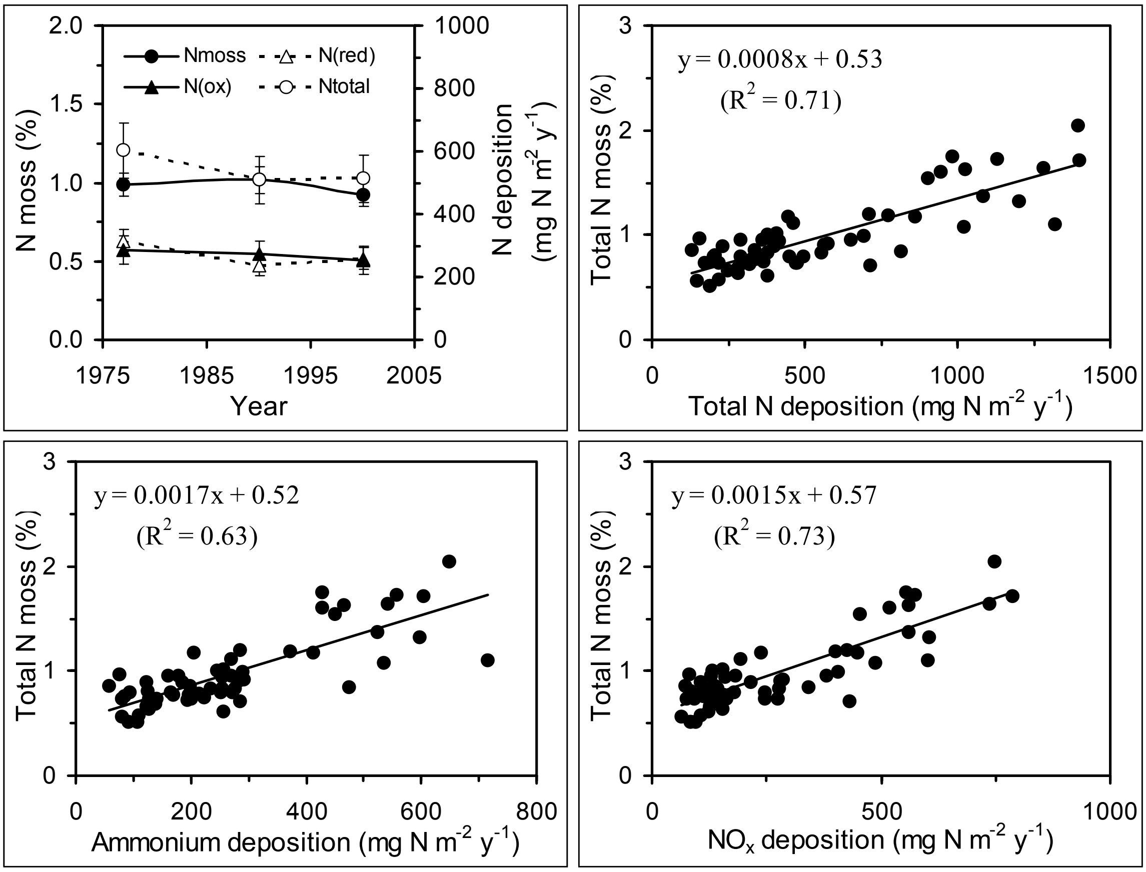

Figure 2.8 Changes in the nitrogen concentration in *Hylocomium splendens* and nitrogen deposition rates with time, and the nitrogen concentration in the moss plotted against total, reduced (ammonium) and oxidised (NO_x) nitrogen deposition rates for selected EMEP grid squares in Norway.

Task Force Meeting

Each year, the ICP Vegetation holds a Task Force Meeting in one of the participating countries to consider recent results and to plan the future work programme. The 18th Task Force Meeting of the ICP Vegetation was held in Almería, Spain, from 1-4 February 2005, and was hosted by Mr Ben Gimeno (CIEMAT, Madrid) and Javier Tello and Reyes Blanco (University of Almería, Almería). Sixty two participants from 17 parties to the Convention attended the meeting, including the Chairman and Secretary of the Working Group on Effects (WGE) and representatives of the ICP Forests and EMEP/MSC-West.

Poster sessions, presentations and discussions addressed the following topics:

- biomonitoring of ozone pollution using crops and (semi-)natural vegetation;
- recent developments in modelling ozone fluxes;
- further development of ozone critical levels and their application;
- developing a new framework for mapping (semi-)natural vegetation at risk from ozone;
- interactions between the impacts of ozone and nitrogen on (semi-)natural vegetation;
- biomonitoring of heavy metal pollution using mosses and crops;
- biomonitoring of nitrogen pollution using mosses;
- preparations for the next European heavy metal in mosses survey 2005/2006.

Presentations and discussions for the further development of the programme included:

- impacts of nitrogen deposition on vegetation;
- ozone and climate change (i.e. CO_2 enrichment) interactions;
- links with air pollution effect networks in Asia and southern Africa.

The short and medium-term objectives of the ICP Vegetation were revised (see Annex I) and the medium-term workplan was updated.

Publicity

Reports

Harmens, H., Mills, G., Hayes, F., Williams, P., De Temmerman, L. and the participants of the ICP Vegetation (2005). Air Pollution and Vegetation: ICP Vegetation Annual Report 2004/2005. Centre for Ecology and Hydrology, Bangor, UK. ISBN 1 870393 80 5

Mills, G., Harmens, H., Hayes, F., Williams, P., Emberson, L., Cinderby, S., Terry, A., Ashmore, M., Holland, M., Green, E., Power, S. (2005). The UNECE International Cooperative Programme on Vegetation. Progress report. Defra contract EPG1/3/205.

Working Group on Effects (2005). An overview of the impacts of ambient ozone on white clover at ICP Vegetation sites (1996 – 2003). Technical Report prepared by ICP Vegetation (EB.AIR/WG.1/2005/8).

<u>Contributions were made to the following reports:</u>

Working Group on Effects (2005). Joint Report of the International Cooperative Programmes and the Task Force on Health Apects of Air Pollution (EB.AIR/WG.1/2005/3 and add. 1).

Papers

Harmens, H., Buse, A., Büker, P., Norris, D., Mills, G., Williams, B., Reynolds, B., Ashenden,, T.W., Rühling, Å., Steinnes. E. (2004). Heavy metal concentration in European mosses: 2000/2001 survey. Journal of Atmospheric Chemistry 49: 425-436.

Web site

The web site has been updated during the year and can be found at: icpvegetation.ceh.ac.uk

3. Heavy metal deposition and potential contamination of crops

(text provided by Ludwig De Temmerman as a contribution in kind)

Background

Atmospheric deposition of heavy metals can cause accumulation of trace elements in the topsoil up to toxic levels for different components of the terrestrial ecosystem. Some of these elements can be taken up and accumulated by crops, resulting in elevated concentrations in specific plant parts. Depositions of trace elements can also accumulate on the surface of crops and as such contaminate the crops directly. Effects of rain and cleaning before consumption of the crops can reduce the concentration of heavy metals, but it won't entirely remove the accumulated particulates. It was demonstrated that atmospheric concentrations of mercury and dust depositions contaminate above-ground plant parts and contribute to the ingestion of mercury through vegetables (De Temmerman *et al*., 1986), but it is not yet known whether this is a threat for consumers. Other transfer ways are probably more important.

Whereas the soilborne accumulation of trace elements such as cadmium, copper and zinc is extensively studied, this not the case for the airborne accumulation. However, it was demonstrated that even at low atmospheric deposition rates (< 1 µg m^{-2} day^{-1}), airborne cadmium contributes to 20-60% of the total plant cadmium content (Hovmand *et al*., 1983). Root uptake and accumulation is low to very low for elements such as arsenic, lead and mercury. The origin of the elements in above ground plant parts – primarily in the leaves – is largely atmospheric. Dalenberg and Van Driel (1990) figured out that atmospheric deposition contributed considerably (73-95%) to the lead concentration in leafy material of grass, spinach and carrot. Most of the pollutants reach the plant as particulates, although mercury is mainly occurring in gaseous form. This has consequences for leafy vegetables as they are usually thoroughly washed prior to consumption. This procedure is removing an important part of the accumulated dust, but not all. On the contrary, gaseous mercury is taken up by the plant and consequently less can be removed by washing the vegetables. For cadmium, there is surely a contribution of atmospheric deposition on the contamination status of above-ground plant parts, but that is normally much lower than the soilborne cadmium concentration in the plant. Fodder crops are not washed prior to consumption and they are important for the transfer pathway to animal products. Fortunately, the transfer in the animal to milk, meat, and eggs is rather low. Animal organs, however, can cause a substantial risk to human health through the accumulation of heavy metals.

The aim of this chapter is to establish whether there is a direct impact of atmospheric deposition of metals on the metal concentration in food and whether this has any implications for food quality and safety. The focus is on arsenic, cadmium, lead and mercury, trace elements that are known to be toxic for humans. Other trace elements are not included because there is lack of information about their transfer in the food chain and their toxicity for humans.

Biomonitoring of atmospheric metal deposition

Atmospheric deposition of trace elements is mostly studied as the main source of soil contamination. Indeed in areas influenced by pollution sources long-term accumulation is leading to increased soil concentrations. As such, the soil becomes a potential source of pollution through uptake and accumulation of mobile elements such as cadmium, or as a source of pollution by generating particulates loaded with trace elements that are re-suspended and contaminate vegetation. Although atmospheric deposition is not the only source of soil contamination, it is the most difficult one to control.

Mosses can be used to monitor atmospheric deposition of heavy metals (Rühling and Tyler, 1968; Tyler, 1970; Berg and Steinnes, 1997; Harmens *et al*., 2004a). It is based on the fact that mosses, especially the carpet-forming species, obtain most of their nutrients directly from precipitation and dry deposition; there is little uptake of metals from the substrate. However, the accumulation of heavy metals by mosses is not comparable to the accumulation by crops. For crops, there is always an effect of soilborne trace elements, which can be important for one element but negligible for another. The great advantage of biomonitoring is that the impact of atmospheric deposition can be measured for some crops (clover, grass, leafy vegetables) in a way that can serve as a model for other leafy crops. Correlations between atmospheric deposition of cadmium and lead and accumulation in plants have been calculated for grass (Vandermeiren *et al*., 1986), leafy vegetables (De Temmerman and Hoenig, 2004) and clover (Buse *et al*., 2003a). In recent years a limited biomonitoring network with clover was established within the ICP Vegetation (see chapter 2). In 2004, the same peat based soil substrate was used at each site to prevent confounding effects caused by soilborne cadmium.

Crops at risk

Atmospheric deposition of particulate and gaseous pollutants has primarily an effect on the above-ground plant parts. The accumulation of dust is a function of the specific area of the plant part that is exposed to atmospheric deposition. Primarily the leaf blades accumulate particulates as they have the largest specific area compared to the petioles, stems, fruits or seeds. Crops at risk from atmospheric deposition of trace elements and gaseous mercury are leafy vegetables (spinach, lettuce, endive, celery, lamb's lettuce, etc.) and leafy fodder crops (grass, clover, maize, etc.). The use of leafy vegetables for biomonitoring, in combination with atmospheric deposition measurements, allowed to establish a relationship between the concentration of cadmium and lead in the vegetables and the average deposition rates during their exposure (De Temmerman and Hoenig, 2004). Those data are useful in models for risk assessments. Clover is a very good model as a fodder crop and the results of the European monitoring network with clover contribute to the fodder crop pathway (Buse *et al*., 2003a).

It is not clear yet whether atmospheric deposition contributes to the trace element levels in roots. This implies that the elements are taken up and transported in the plants. Harrison and Chirgawi (1989) studied the accumulation of different elements in the storage roots of radish and carrot and found important atmospheric contributions up to 50% for cadmium and 88% for lead. However, Dalenberg and Van Driel (1990) did not confirm these findings and it remains doubtful whether there is any contribution of airborne trace elements to the contamination of storage roots.

Potential risks caused by airborne trace elements

Arsenic

Arsenic is a toxic element and is largely present in seafood, however, mainly in organic form. The methylated forms of the element have a low level of toxicity and the principal arsenic species found in fish and crustaceans, arsenobetaine, is considered virtually non-toxic. Inorganic arsenic, present as arsenite As (III) and arsenate As (V), found in food are the most toxic forms (SCOOP, 2004). Problems with arsenic poisoning are related to the inorganic forms in ground water. Some geological aquifers contain a high arsenic level. There is a

Provisional Tolerable Weekly Intake (PTWI) for arsenic in drinking water (15 µg kg^{-1} body weights) in the form of inorganic arsenic, but not for food (WHO, 1993). The intake by the mean adult population in Europe is 880 µg $week^{-1}$ (SCOOP, 2004).

In plants arsenic concentrations are rather low and arsenate is predominantly present in roots and leaves of plants (Bohari *et al*., 2002). About 87% of the weekly arsenic intake (adults) in the EU is from fish and seafood, mostly in less toxic organic forms. Half of the remaining 13% arsenic is originating from fruits, vegetables and cereal products primarily in the inorganic form (SCOOP, 2004). The most important contribution comes from storage roots and cereals, which is most likely to some extent soilborne. The contribution of airborne arsenic to the contamination of plants at rural sites is rather low, even for leafy vegetables. This is mainly due to the relatively low deposition rates in areas that are not directly influenced by pollution sources. However, at industrial sites with arsenic pollution, airborne arsenic will be the main source of plant contamination. Even the contribution of soilborne arsenic to the contamination status of leafy vegetables is considered to be low, except on heavily contaminated soils (Amonoo-Neizer and Amekor, 1993). At a deposition rate less than 5 µg $m^{-2}day^{-1}$, the arsenic concentration in leafy vegetables is less than 0.02 mg kg^{-1}. The concentration in unwashed vegetables increases to about 0.55 mg kg^{-1} at deposition rates in the range of 20-100 µg $m^{-2}day^{-1}$ (De Temmerman, 2004). An increase in atmospheric deposition can have an important effect on the arsenic concentration in vegetables.

Animal feed
Atmospheric deposition of arsenic containing dust can contaminate animal feed. Primarily soilborne dust can be important, as arsenic is a rather important natural component of the soil. The natural concentration of arsenic in soil is at least ten times higher than those of cadmium. Moreover, animal feed is not washed before consumption by the animals. In addition, during unfavourable harvest conditions the fodder crop can be contaminated with soil particles. If arsenic concentrations of 4 mg kg^{-1} fodder (lucerne or clover meal) at 12% moisture are tolerated (ca. 4.55 mg kg^{-1} dry weight (DW)) in some countries, it corresponds with an atmospheric deposition of about 120 µg m^{-2} day^{-1} (table 3.1). This was calculated from a preliminary correlation between atmospheric deposition of arsenic and its accumulation in clover (De Temmerman, unpublished). Such high deposition values are only reached in the vicinity of non-ferrous metal smelters emitting arsenic. At rural sites the atmospheric deposition is mostly lower than 5 µg m^{-2} day^{-1}.

Table 3.1 Corresponding bulk deposition rates of arsenic (As) at two different arsenic concentrations in green fodder.

[As] in green fodder (µg g^{-1} DW)	Tolerable deposition (µg As m^{-2} d^{-1})	Tolerable deposition (g As ha^{-1} y^{-1})
1.14	28	102
4.55	120	438

If there is a problem of arsenic accumulation, it will primarily be for animal feed, and it will be limited to heavily polluted areas or areas with dust, originating from soils with high (natural) arsenic concentrations. The transfer through the animal food chain towards humans is low. In Europe, only 2.5% of the daily intake of total arsenic by the mean adult population comes from milk and dairy products, meat, offal and eggs. In addition, the majority of arsenic in those animal products is of the less toxic organic form as it is the case for total daily intake (Schoof *et al*., 1999).

Cadmium

A PTWI of 7 µg kg^{-1} body weight was decided for cadmium (WHO-FAO, 1993). This is equal to 490 µg $week^{-1}$ for a person weighing 70 kg. The average weekly intake by the mean adult population of the EU is 27% of the PTWI and the most important sources of cadmium in food are cereals, fruits, vegetables, meat and fish, due to their relatively large proportion in the average food basket (SCOOP, 2004). Important foodstuffs are fruit and vegetables, and cereals and bakery wares, together 15.8% of the PTWI for adults. Meat, fish and fish products represent 5% of the PTWI, offal can be contaminated but it reaches only 0.25% of the PTWI (SCOOP, 2004). However, averages are not the best way to compare with the PTWI and 95 or 99 percentiles would be better to estimate the potential risk.

The large majority of cadmium present in food is soilborne. Airborne cadmium can be a surplus but it will not be the major source, except in specific heavily polluted areas which often have a historical soil contamination too. The minimum atmospheric deposition to cause a significant increase in the concentration in unwashed leafy vegetables is at least 5 µg Cd m^{-2} day^{-1} in spring and summer and 2.5 µg Cd m^{-2} day^{-1} at the end of the growing season (18 and 9 g ha^{-1} y^{-1} respectively; De Temmerman and Hoenig, 2004). There is an EU guideline (EU, 2001) for tolerable concentrations in leafy vegetables, fruits and cereals:

Brassica and leafy vegetables: 300 µg kg^{-1} fresh weight;
berries and small fruits: 200 µg kg^{-1} fresh weight;
other fruits: 100 µg kg^{-1} fresh weight;
cereals and pulses: 200 µg kg^{-1} fresh weight.

The differences in tolerable concentrations are linked to the sensitivity towards accumulation of cadmium deposition. In table 3.2 correlations were made with atmospheric deposition for the main accumulators, i.e. leafy vegetables (De Temmerman and Hoenig, 2004). Due to the large uptake of soilborne cadmium, only a minor part of the accumulated cadmium can be removed by thoroughly washing the vegetables. For the leafy vegetables studied about 15, 35, 50 and 20% could be removed for spinach, lettuce, endive, and lamb's lettuce respectively (De Temmerman, 2004). It is not stated in the European Guideline, but it is assumed that the leafy vegetables are washed, however, there is no description of a standard washing method available.

Washing the crops has a limited effect on the tolerable cadmium deposition rate, at least for crops growing on a soil containing a low level of cadmium and a relatively low deposition of cadmium (table 3.2). It is not clear yet whether cadmium can be taken up by the leaves and transported to other plant parts as suggested by some (Harrison and Chirgawi, 1989), as the results are not fully convincing because of possible errors in the method used, i.e. isotope dilution. Uptake and transport through the plant cannot be excluded, but the chemical form that is determining the solubility of cadmium might be a prerequisite for cadmium uptake. Soluble cadmium salts could probably be absorbed but cadmium from non-ferrous metal smelters is mainly in the less soluble oxide form. For crops growing on a non-contaminated soil the tolerable depositions are rather high. Those deposition levels will cause problems for accumulation in the soil after some years of exposure. As such, it can be concluded that with the current depositions in Europe exceedances of the European guideline for cadmium are unlikely, except in polluted areas but even there the problem is mainly be due to soilborne cadmium.

Table 3.2 Tolerable bulk deposition rates of cadmium (Cd) in order to meet the maximum tolerable cadmium concentration in vegetables grown on soils with low cadmium (i.e. low concentration and/or low availability).

Vegetable crop	Tolerable deposition (μg Cd m^{-2} d^{-1}) for unwashed crops	Tolerable deposition (μg Cd m^{-2} d^{-1}) for washed crops
Spinach	45	58
Lettuce	75	122
Endive	30	67
Lamb's lettuce	25	33

Animal feed

Animals appear to be a very efficient filter for cadmium, avoiding accumulation of cadmium in muscles (meat), fat and animal products such as milk and eggs. The maximum tolerable concentration in meat is 0.05 mg kg^{-1} fresh weight. Exceptions are, however, offal such as kidney and liver. In kidney cadmium is accumulated in the renal cortex. As these foodstuffs are less important in the average food consumption by humans, rather high concentrations are tolerated (0.5 and 1 mg kg^{-1} fresh weight in liver and kidney respectively) (EU, 2001). It must be stressed that cadmium accumulation in animals is a function of time and therefore the concentrations are higher in older animals. That is probably the reason why the tolerable cadmium concentration in horsemeat is 0.2 mg kg^{-1} fresh weight, much higher than for other animals. Indeed meat production is not the principal reason for raising horses and as such they are older when they enter the food chain. The tolerable concentrations of cadmium in animal feed are safe towards accumulation in meat as far as young animals are concerned and when offal is not taken into account.

As for vegetable crops, soil contamination will be the main source of cadmium accumulation in fodder crops. Moreover, they are not washed before the animals are fed and in addition unfavourable harvest conditions increase contamination with soil particles. This is also the case for grazing animals in bad weather conditions. For fodder crops, atmospheric deposition originating from long- and mid-range transport and from re-suspended soil dust will be more important than for vegetable crops, but still soilborne cadmium will remain the main source of contamination.

From table 3.3 it can be derived that the impact of cadmium deposition on the concentration in green fodder is rather low. If the soilborne concentration is as low as for clover and grass, rather high deposition rates are needed to increase the cadmium concentration in green fodder substantially. In rural areas the deposition rate is rather low (< 5 μg m^{-2} d^{-1}) and as such the airborne contribution will be comparably low. At very low deposition rates (< 1 μg m^{-2} d^{-1}) the concentrations found in grass and clover will be close to the soilborne concentration. A comparison of the deposition flux measured with grass cultures (using clean peat based soil substrate) and the total deposition measured with bulk collectors revealed that about 25 to 30% of the total cadmium deposition is captured and accumulated by grass. This is only true when the soilborne uptake of cadmium is subtracted. If not, the false impression is generated that grass accumulates cadmium 5 to 10% more efficient compared with lead. Hence, 25-30% of the total cadmium deposition is entering the animal food chain (De Temmerman, 2004).

Table 3.3 Corresponding bulk deposition rates of cadmium (Cd) to clover and grass at different cadmium concentrations in green fodder. The soilborne part was estimated at 0.02 μg g^{-1} DM for clover and 0.10 μg g^{-1} DM for grass and was taken into account when calculating the tolerable deposition rate (see chapter 2; Vandermeiren *et al*., 1986).

Maximum [Cd] in green fodder (μg g^{-1} DW)	Maximum tolerable atmospheric deposition rate of Cd	
	For clover μg m^{-2} d^{-1} (g $ha^{-1}y^{-1}$)	For grass μg m^{-2} d^{-1} (g $ha^{-1}y^{-1}$)
0.57	15 (55)	9 (32)
1.14	31 (113)	29 (105)
4.55	127 (464)	148 (540)

Lead

Lead is a very general pollutant present in the different compartments of the ecosystem. Over the past decades, the lead level in food has decreased significantly due to source-related efforts to reduce the emission of lead. Lead is present in low concentrations in most foods, although offal and molluscs may contain higher levels. A PTWI of 25 μg kg^{-1} body weight was decided for lead (WHO-FAO, 1993). This is equal to 1750 μg $week^{-1}$ for a person weighing 70 kg. The average weekly intake by the mean adult population of the EU is 17% of the PTWI and the most important food groups (not taking into account beverages and drinking water) are fruits, vegetables, cereals and bakery wares. Together they represent 8.9% of the PTWI by the mean adult population, meat and offal represent 1.2% of the PTWI (SCOOP, 2004).

As the uptake of soilborne lead is very low, the large majority of lead in vegetables and fruits is airborne. Soilborne lead is found in below-ground plant parts but the lead concentrations remain low in those parts. For cereals the contamination is also to a large extent airborne and occurs during seed development or during harvest. As there is a substantial contribution of atmospheric deposition to the average PTWI in Europe, plants such as leafy vegetables and fodder crops that are most exposed to atmospheric deposition are the most at risk. There is an EU guideline (EU, 2001) for tolerable lead concentrations in leafy vegetables, fruits and cereals, which is the same as for cadmium (see cadmium). The difference in tolerable concentrations is linked to the sensitivity to accumulation of lead deposition. For the main accumulators, i.e. leafy vegetables, correlations were made with atmospheric deposition (De Temmerman and Hoenig, 2004). However, a large part of the accumulated dust can be removed by thoroughly rinsing the crop. For leafy vegetables about 70, 80, 70 and 60% can be removed from spinach, lettuce, endive, and lamb's lettuce, respectively (De Temmerman, 2004). Washing the crops has an important effect on the tolerable lead deposition.

From table 3.4 it can be derived that for the most sensitive group of leafy vegetables, those harvested in late autumn or winter, the maximum tolerable lead deposition is 75 μg m^{-2} d^{-1} or 274 g $ha^{-1}y^{-1}$. In areas with a comparable deposition, the production of late season leafy vegetables is at risk. As the uptake and transport of lead in plants is very low, it is not expected that uptake of atmospheric deposition of lead by the leaves and transport through the plant is important. For this reason the lead concentrations in vegetable roots (carrots) and tubers (potato) are low as they are protected from atmospheric deposition. An exception is wheat grain; in spite of the protection by the glumes during exposure in the field the grain can be contaminated. The most plausible explanation is that the grains get contaminated during the harvest. The deposited lead that accumulated on leaves, stems and ears is re-suspended during harvest and probably deposited onto the grains.

Table 3.4 Tolerable bulk deposition rates of lead (Pb) in order to meet the maximum tolerable concentration of lead in vegetables.

Vegetable crop	Tolerable deposition (μg Pb m^{-2} d^{-1}) for unwashed crops	Tolerable deposition (μg Pb m^{-2} d^{-1}) for washed crops
Spinach	130	485
Lettuce	140	670
Endive	105	280
Lamb's lettuce September	70	130
Lamb's lettuce October	40	75

Animal feed
Lead in feed is important for animal health, as some species are rather sensitive to lead poisoning. As for cadmium the transfer to meat, fat and animal products such as milk and eggs is rather low. The maximum tolerable lead concentration in meat is 0.1 mg kg^{-1} fresh weight. Higher concentrations can be found in offal and the maximum acceptable concentration is 0.5 mg kg^{-1} fresh weight (EU, 2001). Green fodder is the most important source of lead in feed for cattle, sheep, and horses. Most of the European countries have their own legislation and the tolerable concentrations are rather high. A tolerable concentration of 40 μg g^{-1} in green fodder at 12% moisture is rather common. This high level is taking into account the risk of contamination with soil as the (natural) lead concentrations are generally high in soils. Evidently, the corresponding tolerable atmospheric depositions are also rather high and the highest tolerable lead concentration is even ca. 4 kg Pb ha^{-1} $year^{-1}$ (table 3.5). However, in reality a much lower level of atmospheric deposition can be tolerated, due to the inevitable contamination with soil during harvest or during grazing in bad weather conditions.

Table 3.5 Corresponding bulk deposition rates of lead (Pb) to clover and grass at different lead concentrations in green fodder. The soilborne part was estimated at 0.2 μg g^{-1} DM for clover and grass and was taken into account when calculating the tolerable deposition rate (Vandermeiren *et al*., 1986; Buse *et al*., 2003a).

Maximum [Pb] in green fodder (μg g^{-1} DW)	Maximum tolerable atmospheric deposition rate of Pb	
	For clover μg m^{-2} d^{-1} (g $ha^{-1}y^{-1}$)	For grass μg m^{-2} d^{-1} (g $ha^{-1}y^{-1}$)
11.4	170 (625)	180 (660)
22.7	540 (1859)	470 (1730)
45.5	1270 (4350)	1070 (3890)

A comparison of the deposition flux measured with grass cultures and the total deposition measured with bulk collectors revealed that about 25 to 30% of the total lead deposition is captured by grass and accumulated. For clover it was estimated to be 31% (Buse *et al*., 2003a). This proportion is in reality entering the food chain. Thanks to the low transfer rate of lead in feed to animal products there is no immediate risk for increased exposure to lead. Moreover dairy products, meat and offal, and eggs represent only 11.5% of the weekly intake by the mean adult population in Europe.

Mercury

Mercury is a toxic element found mostly in fish and derived products. Methylmercury, the main form in which mercury is present in seafood, is the most toxic form among mercury species. Inorganic mercury species occur in plants and are less toxic than the organic form. For mercury, a PTWI of 5 $\mu g\ kg^{-1}$ body weight was decided for total mercury (WHO-FAO, 1993). The average weekly intake by the mean adult population of the EU is 38.7 $\mu g\ week^{-1}$ and the most important food group is fish (49% of total). However, fruits, vegetables and cereal products represent 30% of the weekly intake by the mean adult population of Europe. This is an important part of the exposure, although the mercury form in vegetables and cereals is the less toxic inorganic form (SCOOP, 2004).

As root uptake of mercury is very low, atmospheric deposition is the main source of mercury in vegetables, at least in the above-ground parts. Most important and most widely spread are gaseous forms of mercury (metallic mercury and mercury chloride). Plants absorb and accumulate those forms in their leaves and as a consequence less is removed by washing the leafy crops. Particulate atmospheric mercury is less important, only in some very specific circumstances where mercury-containing dust is generated, it can become important. This can happen in mining areas or sites with high soil concentrations, but it is not a general problem. As gaseous forms of mercury are the most important and widespread forms of the pollutant in ambient air, it is reasonable to compare tolerable concentrations in above-ground plant parts with ambient air concentrations. There is no European legislation for tolerable concentrations in vegetables and fruits. As an example the tolerable ambient air concentrations for total mercury can be calculated on the basis of preliminary correlations calculated for leafy vegetables (lettuce, spinach and endive) and for curly kale based on three levels of mercury in vegetables (table 3.6; De Temmerman, 2005).

Table 3.6 Corresponding ambient air concentrations of mercury (Hg) at different mercury concentrations in vegetables.

Maximum level of [Hg] in vegetables ($\mu g\ g^{-1}$ FW)	Maximum tolerable ambient air concentration of Hg: For leafy vegetables ($ng\ Hg\ m^{-3}$)	For curly kale ($ng\ Hg\ m^{-3}$)
0.01	25	4
0.03	78	9
0.05	132	14

Concentrations of total gaseous mercury in ambient air of about 25 $ng\ m^{-3}$ are only occurring at sites close to pollution sources. Even there, the accumulated mercury in most of the leafy vegetables remains rather low (0.01 $\mu g\ g^{-1}$ FW). Some vegetables like curly kale and some herbs accumulate much more mercury (De Temmerman *et al.*, 1986), but away from industrial sites polluted with mercury, the risk for excessive accumulation remains low. Typical for remote areas are total gaseous mercury concentrations below 5 $ng\ m^{-3}$.

Animal feed
Like leafy vegetables, green fodder crops also accumulate mercury from airborne origin. In table 3.7 the corresponding ambient air concentrations were calculated for three different concentrations of mercury in grass. The relations were derived from biomonitoring experiments with permanent (exposure during 28 days) and alternating cultures (exposure during 14 days) of grass (De Temmerman, 2005).

Table 3.7 Corresponding ambient air concentrations of mercury (Hg) at different mercury concentrations in green fodder (i.e. grass).

Maximum tolerable [Hg] in grass $\mu g\ g^{-1}$ DW	Maximum tolerable ambient air concentration of Hg	
	Permanent cultures ($ng\ Hg\ m^{-3}$)	Alternating cultures ($ng\ Hg\ m^{-3}$)
0.055	6	8
0.11	11	15
1.10	110	150

At a rather low pollution level in ambient air (< 6 ng Hg m^{-3}), the grass concentrations remain as low as 0.055 µg g^{-1} DW, which is lower than the lowest level for leafy vegetables (per unit fresh weight). Moreover, the transfer pathway to meat and animal products is rather restricted. There doesn't appear to be much accumulation of mercury in animal products such as milk, eggs, meat and even offal (SCOOP, 2004).

Conclusion

Atmospheric deposition of metals has a direct effect on the contamination of crops used for human and animal consumption. Leafy vegetables are particularly vulnerable to the atmospheric impact of arsenic, lead and mercury. Away from pollution sources the deposition of arsenic is rather low but atmospheric deposition remains important as a main source of contamination of leafy vegetables. Vegetables, fruits and cereals are the main source of the more toxic inorganic forms of arsenic in human food. A decrease of atmospheric deposition will have a beneficial effect on the weekly intake of arsenic. The transfer through terrestrial animals is low and consequently there is less arsenic in animal products. The contribution of atmospheric cadmium to the accumulated level in crops is often less important than that of soilborne cadmium. There is limited transfer of cadmium to humans via consumption of animal products, except for offal. Lead is a widespread pollutant having a direct impact on above-ground plant parts. Even at remote sites there is still a clear impact of lead deposition on its concentration in leaves and wheat grain. A decrease in atmospheric deposition will have a beneficial effect on the daily intake by humans. Being a toxic element, lead is also important for animal health, but fortunately transfer to foodstuffs from animal origin is rather low. Contrary to arsenic, the inorganic forms of mercury, predominantly present in crops, are much less toxic than the organic forms. In crops, atmospheric deposition is the main source of inorganic mercury. However, most crops have a rather low accumulation rate although some crops (curly kale, some herbs) are able to accumulate considerably more. An increase of atmospheric mercury would result in an increased mercury load for humans. The food chain through animals and animal products appears to be less important when aquatic organisms are excluded.

4. Conclusions and further work

In recent years, the ICP Vegetation has focussed on two air pollution problems of particular importance in the UNECE region: quantifying the risks to vegetation posed by ozone pollution and the atmospheric deposition of heavy metals to vegetation. Two further pollution problems are being considered: plant responses to pollutant mixtures, in particular ozone and nitrogen pollution, and the impacts of nitrogen pollutants on vegetation. Over 180 scientists from 35 countries of Europe and North America contribute to the programme by conducting experiments, sampling vegetation or modelling pollutant deposition and effects. The most recent 18th Task Force Meeting of the ICP Vegetation (Almería, Spain, February 2005) attracted 62 participants representing 17 parties to the Convention.

Biomonitoring of ozone impacts on vegetation

Monitoring of the impacts of ambient ozone on vegetation in Europe continued during 2004 using the NC-S (ozone-sensitive) and NC-R (ozone-resistant) biotypes of white clover. A major component of the biomonitoring work was to monitor the incidences of visible leaf injury for the ozone-sensitive biotype by weekly recordings. In 2004, the AOT40 for the three-months period ranged from 0.4 ppm h in the UK (Bangor) to 13.7 ppm h in Switzerland (Cadenazzo). The long-term critical level for (semi-)natural vegetation and agricultural crops (a three month AOT40 of 3 ppm h) was exceeded at 80% of the biomonitoring sites. However, visible injury was also recorded at sites where the critical level of ozone for yield reduction was not exceeded. The reduction in biomass associated with ozone over the three-month experimental period in the sensitive biotypes relative to that in the resistant biotypes was similar to previous years. A review of results from the clover biomonitoring experiment from 1996 to 2003 has shown that O_3 injury occurrence is widespread across Europe following O_3 episodes, and occurred every year at most of the sites (Harmens *et al*., 2004c).

Biomonitoring studies were continued in 2004 on the effects of ozone on (semi-)natural vegetation using ozone-sensitive and ozone-resistant biotypes of *Centaurea jacea* (brown knapweed). Ten sites participated in the *Centaurea* biomonitoring experiment in 2004, representing all regions of Europe. Ozone-specific injury was observed on the *Centaurea jacea* plants at eight out of the ten participating sites. The production of clonal material is currently being investigated by participants from Switzerland (Mr Jürg Fuhrer) with the aim of reducing the genetic variability between plants.

Critical levels of ozone

In the recently revised Mapping Manual flux-based exposure indices were added to the concentration-based critical levels for ozone that use AOT40 as the exposure index. There is a sound scientific reason for moving towards the use of flux-based exposure indices. Whereas AOT40 is based on the ozone concentration in the air at the top of the plant canopy, ozone flux calculations take into account the influence of climatic, pollutant and plant factors on the amount of ozone that enters the plant through the stomatal pores and reaches the sites of action inside the leaf. For example, for a given ozone concentration, ozone uptake in dry air is much less than that for the same plants exposed to ozone on a humid day because plants reduce the aperture of their stomatal pores in dry air to reduce water loss. The effect of ozone on the plant is correspondingly reduced in dry air.

In the new Mapping Manual (Mapping Manual, 2004) stomatal flux-based critical levels of ozone were included for the crops wheat and potato. Although these two crops are very important in Europe, there remains the need to expand the range of crops for which flux-effect relationships exist. Review of data available within the scientific literature has provided sufficient information for the development of robust flux models for three other crop species: grapevine, sunflower and tomato. The flux-effect relationships included in the Mapping Manual relate the ozone flux to a single sun-lit leaf to the effect measured. For white clover the single leaf flux model has been up-scaled to a whole canopy flux model based on an estimation of average canopy stomatal conductance. Scaling from the leaf to the canopy level has been achieved by consideration of the penetration of irradiance into the canopy estimated using a canopy extinction algorithm, development of the leaf area index of the canopy and the fraction of leaf age populations present in the canopy throughout a growing period and their respective stomatal conductance. The canopy flux model will be applied to establish a canopy flux-effect relationship for white clover.

Heavy metal deposition to vegetation

Two approaches to monitoring heavy metal deposition to vegetation are adopted by the ICP Vegetation, one using clover plants from the ozone biomonitoring experiment and the other a long-term, European-wide survey of the concentration of heavy metals in naturally growing mosses. Significant linear correlations were found between the bulk deposition rates and concentrations of heavy metals in white clover for cadmium, copper and lead. 'Normal' background concentrations and pollution thresholds could be determined for copper and lead. Whilst a 'normal' background concentration for cadmium could be determined in 2004 by using a standard plant growth substrate across Europe, only a preliminary pollution threshold could be established due to a lack of data from sites with high levels of atmospheric cadmium deposition. At about half of the participating sites in Europe the pollution thresholds for copper and lead were exceeded at some time during the growing period. The next European heavy metals in mosses survey will be conducted in 2005/2006. Participants from 32 countries have indicated their willingness to participate in this survey and so far 20 countries have confirmed participation. The Manual for collecting and analysing moss samples was reviewed and revised by participants of the moss survey and can be downloaded from the ICP Vegetation web site. Standard moss samples were distributed amongst participants for quality assurance purposes.

In 2005, a special study was conducted on heavy metal deposition and the potential contamination of crops. Atmospheric deposition of metals has a direct effect on the contamination of crops used for human and animal consumption. Leafy vegetables are particularly vulnerable to the atmospheric impact of arsenic, lead and mercury. Away from pollution sources the deposition of arsenic is rather low but atmospheric deposition remains important as a main source of contamination of leafy vegetables. Vegetables, fruits and cereals are the main source of the more toxic inorganic forms of arsenic in human food. A decrease of atmospheric deposition will have a beneficial effect on the weekly intake of arsenic. The transfer through terrestrial animals is low and consequently there is less arsenic in animal products. The contribution of atmospheric cadmium to the accumulated level in crops is often less important than that of soilborne cadmium. There is limited transfer of cadmium to humans via consumption of animal products, except for offal. Lead is a widespread pollutant having a direct impact on above-ground plant parts. Even at remote sites there is still a clear impact of lead deposition on its concentration in leaves and wheat grain. A decrease in atmospheric deposition will have a beneficial effect on the daily intake by humans. Being a toxic element, lead is also important for animal health, but fortunately transfer to foodstuffs from animal origin is rather low. Contrary to arsenic, the inorganic forms of mercury, predominantly present in crops, are much less toxic than the organic forms. In crops, atmospheric deposition is the main source of inorganic mercury. However, most crops have a rather low accumulation rate although some crops (curly kale, some herbs) are able to accumulate considerably more. An increase of atmospheric mercury would result in an increased mercury load for humans. The food chain through animals and animal products appears to be less important when aquatic organisms are excluded.

Nitrogen deposition to vegetation

The European moss survey provides an excellent opportunity to test whether carpet forming mosses can be used as biomonitors of atmospheric nitrogen deposition at a European scale. Selected moss samples from Scandinavian countries with a long involvement in the heavy metals in moss survey were analysed for total nitrogen. Although the total nitrogen concentration in mosses was significantly different between countries, temporal trends over recent decades were statistically not significant. Analysis of data from Norway indicate that there was also no temporal trend in the atmospheric nitrogen deposition rates between 1977 and 2000 for the EMEP grid cells from which moss samples were taken. In addition, for Norway the nitrogen concentration in the mosses was well correlated with the atmopheric nitrogen deposition rate, independent of nitrogen speciation in deposition.

Pollutant mixtures

It is likely that the responses of vegetation to one pollutant are modified by the responses to others. Four of the European sites participating in the ozone biomonitoring study with *Centaurea jacea* exposed the plants to three levels of nitrogen. There were no interactions between nitrogen supply and visible leaf injury. Analysis of rosette leaves showed that the nitrogen concentration and C:N ratio of the leaves were not affected by nitrogen supply. It seems likely that *Centaurea jacea* is very unresponsive to nitrogen as the plants grew well at all sites without added nitrogen. It was concluded that *Centaurea jacea* is insensitive to nitrogen, therefore this aspect of the biomonitoring work will not continue in the future.

Future work

Ozone

The ICP Vegetation will continue to monitor the extent of ozone damage to vegetation by conducting standardized experiments with ozone-sensitive species of crops and (semi-) natural vegetation. The formulation and parameterisation of the canopy stomatal conductance model for white clover will be further improved with the ultimate aim to produce a canopy flux-effect model for clover for both ozone injury and biomass reduction. Ultimately, a comparison of the predictive abilities of the single leaf and canopy flux-effect relationships will determine which approach will be the most appropriate to use in future assessments of ozone damage to clover at the pan-European scale. In addition, work will focus on the validation of flux-based critical levels for additional agricultural crop and tree species by reviewing the literature on effects of ozone together with data on stomatal conductance-environmental parameter relationships for these species. The next 'Ozone critical levels Workshop' will be held in Obergurgl (Austria) in November 2005, where further application and development of the flux-based approach will be reviewed and discussed. Biomonitoring of the impact of ozone on (semi-)natural vegetation, using *Centaurea jacea* as a model species, will continue with the ultimate aim of completing a flux-effect model for this species.

The ICP Vegetation is constructing a conceptual spatial framework that can be applied across Europe for mapping impacts of ozone on communities of (semi-)natural vegetation using the European Nature Information System (EUNIS) classification. AOT40-response functions have been defined for 70 species and the EUNIS communities they represent have been identified and sources of flux-based information have been determined. The work is focussing on grassland communities and the framework will eventually combine information on species composition and species sensitivity for ozone-sensitive communities together with information relevant to flux modelling. The ultimate aim is to map (semi-)natural communities at risk from ozone damage, including the link to flux-effect modelling. Maps of the exceedance of the revised critical levels of ozone will be refined in collaboration with EMEP/MSC-W.

Heavy metals

In several countries the European heavy metal in mosses survey 2005/2006 has started. The concentration of heavy metals in mosses in the 2000/2001 survey is currently being compared with EMEP heavy metal deposition data for cadmium, mercury and lead for validation purposes. In addition, temporal trends in the existing European data set between 1990 and 2000/2001 are being conducted and these trends will be compared with trends in EMEP heavy metal deposition data.

Nutrient nitrogen

Based on the outcome of a pilot study in selected European countries, the Task Force recommended to include the determination of the total nitrogen concentration in mosses in the 2005/6 European moss survey to test whether carpet forming mosses can be used as biomonitors of atmospheric nitrogen deposition at a European scale. In addition, long-term trends in the nitrogen concentration in mosses using herbarium samples (dating back to the end of the 19^{th} century) will be determined for selected European countries.

Pollutant mixtures

It is likely that the responses of vegetation to one pollutant are modified by the responses to others. Hence, ICP Vegetation will conduct a literature review on the modifying effect of nitrogen pollution on the response of crops and (semi-)natural vegetation to ozone.

Ozone and climate change

The global climate is changings with increases in temperature and carbon dioxide levels and changes in precipitation patterns being predicted. These changes in the future climate will affect the stomatal flux of ozone into leaves. ICP Vegetation will conduct a literature review regarding the impacts of ozone on vegetation in a changing climate.

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Annex 1. Objectives of the ICP Vegetation

Agreed at the 18th meeting of the Programme Task Force, Almería, Spain, 1-4 February 2005.

Long-term objectives

1. To meet the requirements of the Convention on Long-range Transboundary Air Pollution for information on the responses of (semi-)natural vegetation and crops to atmospheric pollutants.
2. To evaluate experimental data on the responses of (semi-)natural vegetation and crops to air pollutants to validate the critical levels defined in the Mapping Manual and to show the effects of exceedance.
3. To provide information for the further development of effects-driven protocols with respect to (semi-)natural vegetation and crops.

Short- and medium- term objectives

1. To monitor the impacts of ambient ozone on various crops and (semi-)natural vegetation.
2. To further develop and apply the concept of concentration-based and flux-based critical levels of ozone for crops, (semi-)natural vegetation and trees.
3. To produce maps of exceedance of the revised critical levels (in collaboration with ICP Forests, EMEP MSC-W and the ICP on Modelling and Mapping).
4. To provide further information on response functions and land cover for use in an economic assessment of crop losses due to ozone.
5. To conduct literature reviews and specific experiments to provide further information on the critical levels of air pollutants for selected plants, plant communities and biodiversity.
6. To conduct literature reviews and experiments on the accumulation of atmospheric deposition of heavy metals by vegetation and the transfer of heavy metals into the human food chain (in collaboration with TF Health).
7. To prepare for and conduct the 2005/2006 survey of heavy metal concentrations in mosses in Europe.
8. To investigate methods for estimating and mapping heavy metal deposition from the heavy metal concentration in mosses data (in collaboration with EMEP MSC-E).
9. To study the spatial and temporal trends in the atmospheric deposition of nitrogen by determining the nitrogen concentration in mosses.
10. To review the literature on, and conduct studies of, the interactions between ozone and nitrogen.
11. To review the literature on the effects of ozone in a changing climate (including rising CO_2 concentration) and to consider the possibility of including experimental and modelling work within the programme.
12. To consider the feasibility of including nutrient nitrogen effects on (semi-)natural vegetation within the programme of work.
13. To consider the feasibility of collaborating on air pollution effects outside the UNECE region (e.g. Asia and southern Africa).

Annex 2. Participation in the ICP Vegetation

Those participants named in bold are members of the Steering Committee of the ICP Vegetation. In many countries, several other scientists (too numerous to include here) also contribute to the biomonitoring programmes, analysis and modelling procedure that comprise the work programme of the ICP Vegetation.

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