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UPDATING AND REVISION OF THE AIR QUALITY GUIDELINES FOR EUROPE

Report on the WHO Working Group on
Ecotoxic Effects

Les Diablerets, Switzerland
21–23 September 1994

1995

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AIR QUALITY

By the year 2000, air quality in all countries should be improved to a point at which recognized air pollutants do not pose a threat to public health.

ABSTRACT

Within the framework for the updating and revising of the WHO Air Quality Guidelines for Europe, a meeting of the Working Group on Ecotoxic Effects was held in Les Diablerets, Switzerland, from 21 to 23 September 1994. The meeting was attended by 17 experts from 7 countries, a representative each from UN/ECE and CEC-DG XI, as well as staff members of WHO-ECEH and IPCS. The group discussed ecological effects of airborne pollutants. Draft chapters dealing with sulfur dioxide (including sulfur and total acid deposition), nitrogen dioxide (and other nitrogen compounds) and ozone had been prepared by scientific experts in this field and were circulated in advance among the members of the working group. The outcome of the meeting was the finalization of ecological risk evaluations of the compounds discussed, and the decision on guideline values (critical levels and critical loads).

Keywords

AIR QUALITY
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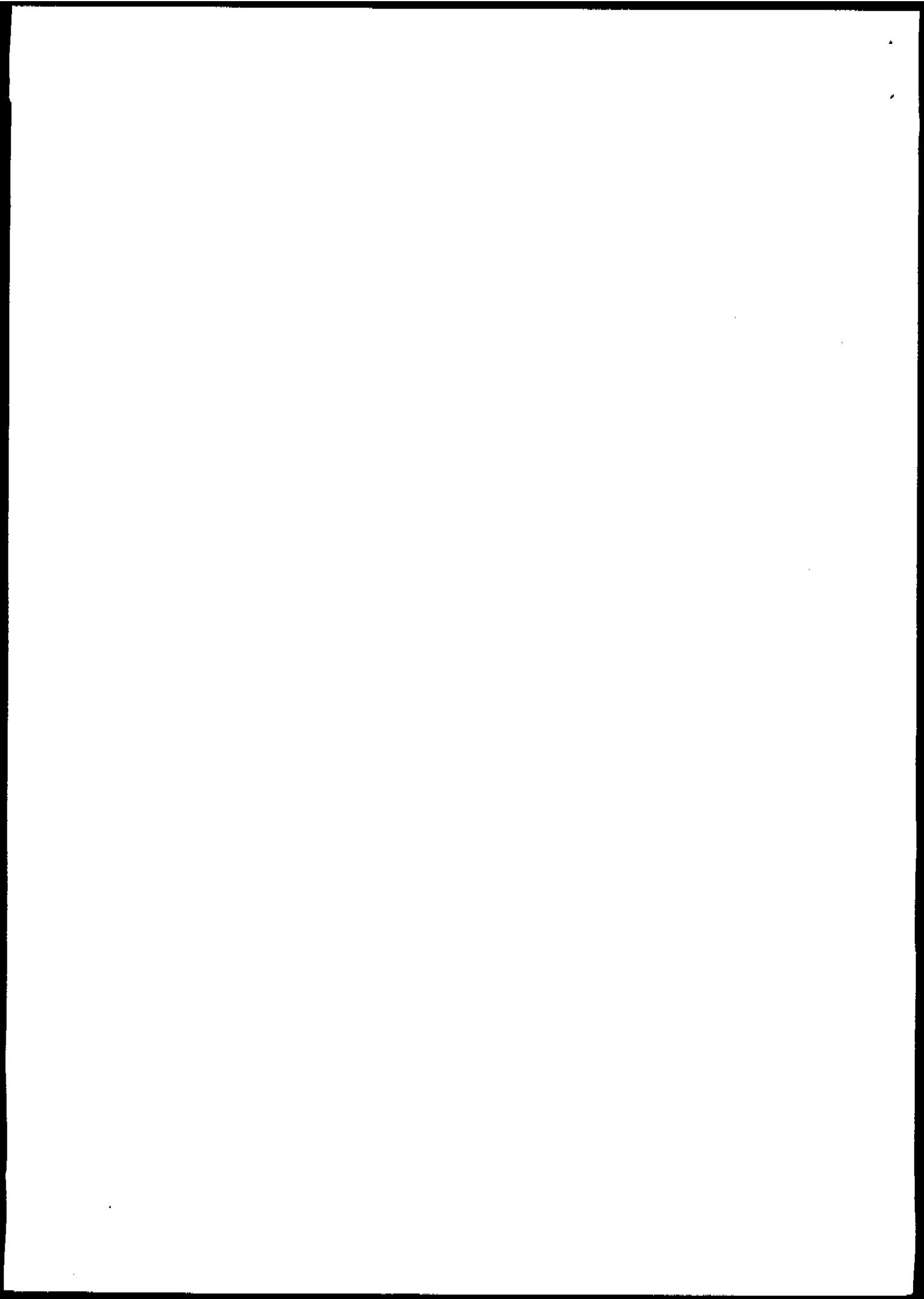
INTRODUCTION

Since the publication of the Air Quality Guidelines for Europe in 1987, new scientific data have been accumulated and new developments in risk assessment methodologies have taken place, requiring updating and/or revision of the existing guidelines. To initiate the updating procedure, which is being conducted in collaboration with the Commission of the European Communities (CEC) and the International Programme on Chemical Safety (IPCS), a planning meeting was held at the Bilthoven Division of the European Centre for Environment and Health of the World Health Organization on 11-13 January 1993. At that meeting, which set the frame for the updating and revision process, it was recommended to set up a number of specialized working groups to assess the effects of specific pollutants/groups of pollutants.

In the context of this endeavour, it was decided to consider ecological effects of major air pollutants in more detail, and to cooperate with the Working Group on Effects under the UN/ECE Convention on Long-range Transboundary Air Pollution, capitalizing on the scientific work undertaken since 1988 to formulate criteria for the assessment of the effects of air pollutants on the natural environment (critical levels/loads).

Following an informal planning meeting in January 1994, a number of scientific experts have been invited to prepare draft chapters on the ecological effects of sulphur dioxide (including sulphur and total acid deposition), nitrogen dioxide (and other nitrogen compounds including ammonia) and ozone.

Based on financial support by the Swiss Federal Office of Environment, Forests and Landscape, the meeting of the working group on ecological effects was held in Les Diablerets, Switzerland, on 21-23 September 1994. The aim of the meeting was to finalize the draft chapters and to derive consensus air quality guideline values for ecological effects of the compounds reviewed. The meeting was attended by 17 experts from 7 countries, a representative each from UN/ECE and CEC-DG XI, as well as staff members of WHO-ECEH and IPCS. Dr Robin Wilson was elected chairman and Dr Keith Bull rapporteur. Dr Maged Younes was scientific secretary.



DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

Use of the guidelines in protecting the environment

Although the main objective of the WHO Air Quality Guidelines for Europe is the direct protection of human health, the WHO "Strategy for Health for All in Europe" recognized the importance of protecting the environment in terms of benefits to human health and well being. In Resolution WHA 42.26 of the World Health Assembly and Resolutions 42/187 and 42/186 of the United Nations General Assembly the interdependence of health and the environment was recognized.

Ecologically based guidelines for preventing adverse effects on terrestrial vegetation were included for the first time in the 1987 edition of the WHO Air Quality Guidelines for Europe, and guidelines were recommended for some gaseous air pollutants.

Since that time, however, significant advances in the scientific understanding of the impacts of air pollutants on the environment have been made. The realization that soils play an important role in mediating both the direct and indirect effects of air pollutants on terrestrial and freshwater ecosystems has led to the development and acceptance of the joint concepts of critical levels and critical loads within the framework of the UN/ECE Convention on Long-Range Transboundary Air Pollution.

At the UN/ECE Workshop on Critical Loads for Sulphur and Nitrogen at Skokloster, Sweden in 1988 critical levels and loads were defined as follows:

Critical levels means the concentrations of pollutants in the atmosphere above which direct adverse effects on receptors such as plants, ecosystems or materials, may occur according to present knowledge.

Critical loads means a quantitative estimate of an exposure, in the form of deposition, to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.

The contrasts between conventional environmental objectives, critical levels and critical loads are shown in Table 1.

Table 1: Contrasts between conventional environmental objectives, critical levels and critical loads

Conventional objectives	Critical Levels	Critical Loads
Effects generally experienced at the organism level	Effects experienced from organism to ecosystem levels	Effects usually manifested at the ecosystem level
Objectives established on the basis of laboratory tests	Established by laboratory, controlled environment and field studies	Ecosystem studies required to establish values
Lethality or physiological effects are the usual response used in setting objectives	Physiological and ecosystems effects by direct and indirect mechanisms	Ecosystem effects may be via direct (chemical change) or indirect (food chain alterations) mechanisms
Environmental objectives are set well below known effects to provide some margin of safety	Objectives are set as closely to damage levels as possible	Objectives are set as closely to damage levels as possible
No beneficial effects are likely to occur in the environment at any level	Changes may occur that are deemed beneficial although such benefits may be very subjective	Changes may occur that are deemed beneficial (such as increased productivity)
Environmental damage from exceedances is usually observed within a short time (i.e. hours up to one year)	Environmental damage from exceedances is usually short- to medium-term	Environmental damage from exceedances may occur over a long time (years - decades) and may be cumulative

The critical levels approach is essentially a further development of the guidelines in the 1987 WHO Report and relate principally to direct effects on vegetation. Critical loads relate to total deposition and to indirect effects, e.g. soil acidification and eutrophication and their impacts on productivity and freshwater acidity. Both critical levels and critical loads approaches have been used by the United Nations Economic Commission for Europe to define air pollutant emission control strategies for the whole of Europe. They are being or may be used in a series of Protocols relating to the control of sulphur dioxide, oxides of nitrogen, total nitrogen (including oxidized and reduced species) and ozone and full use has been made of the data that underpin these Protocols in this report. The proposed guidelines cover the same range of air pollutants and are aimed at a wide range of vegetation and ecosystem types. They may be used to indicate the state of existing or required environmental protection.

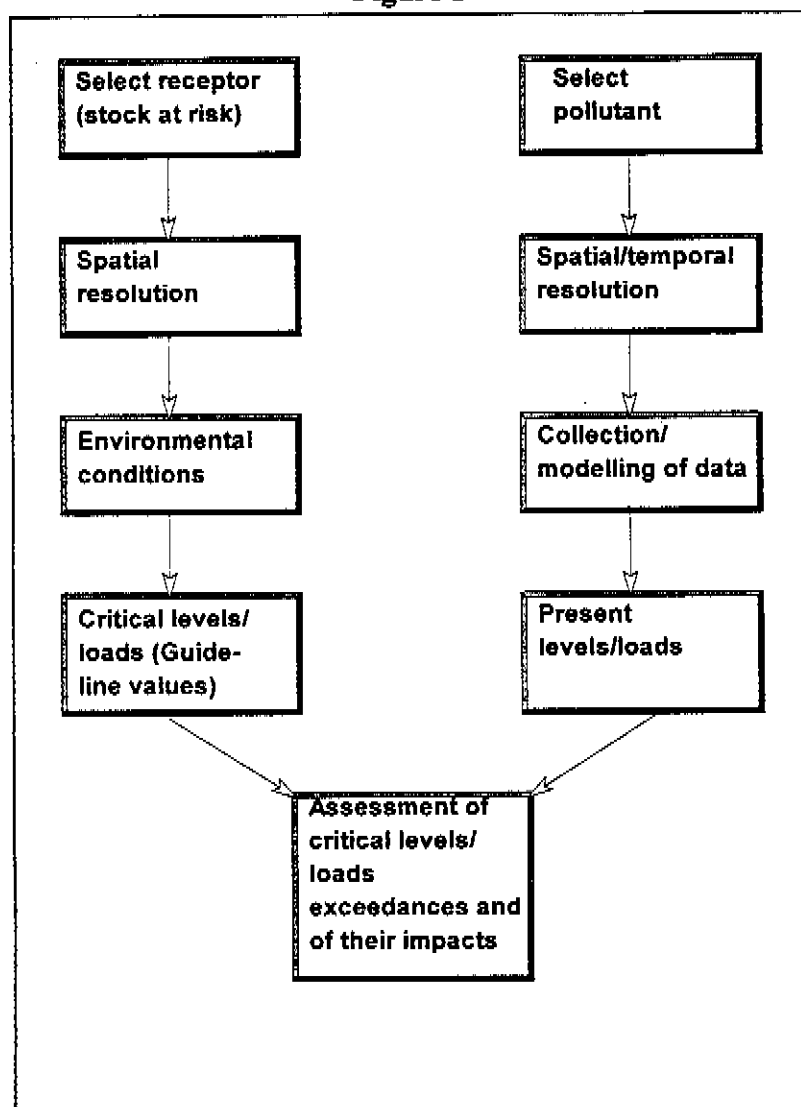
To carry out an assessment based on the guidelines due consideration has to be given to the various problems caused by air pollution and their impact on the stock

which may be at risk. The requirements for the former are often different from those needed to assess the risks to human health. Nevertheless, methodologies have been developed which can assess the risks of damage to vegetation, ecosystems and buildings and materials including cultural heritage.

A simple overview of the elements of how critical levels and critical loads can be used is shown in Figure 1.

Critical Levels/Loads Application Pathway

Figure 1



Effects of ozone on vegetation

The revision of the air quality guidelines for ozone builds upon the progress made to define critical levels to protect crops and tree species. Guidelines for other photochemical oxidants, such as peroxyacetylnitrate (PAN) and hydrogen peroxide

(H₂O₂), are not recommended because of the low levels of these pollutants observed in Europe, and because data concerning their effects on plants in Europe are very limited. Research in recent years in Europe has mainly advanced our understanding of exposure, uptake, and effects of ozone.

Ozone concentrations vary strongly both in space and in time, and in order to quantitatively relate ozone exposure to effects it is necessary to summarize the concentration pattern during the exposure period in a biologically meaningful way. Based on results from exposure-response studies with open-top chambers, it is concluded that mean concentrations are not appropriate to characterize ozone exposure. This is mainly because (a) the effect of ozone results from the cumulative exposure, and (b) not all concentrations are equally effective, i.e. higher concentrations have greater effects than lower concentrations. Therefore, ozone exposure is expressed as the sum of all 1-h mean concentrations above a cut-off concentration of 40 ppb.

The use of 40 ppb as the cut-off concentration provides good linear relationships between ozone exposure and plant response for a number of species, thus confirming its biological relevance. Furthermore, the ozone concentrations found in most areas of Europe, in the absence of photochemical pollution are in the range 10-40 ppb, except at very high altitudes. In relation to long-term effects this sum (referred to as the 'accumulated exposure above a threshold of 40 ppb', AOT40), is calculated for 3 months (e.g. May-July) in the case of crops, or 6 months (April-September) for trees. Since uptake of ozone by crops occurs only during daylight hours when stomata are open, the calculation of the AOT40 considers only those hours when radiation is higher than 50 W/m². In the case of some tree species, especially in coniferous trees, substantial ozone uptake may occur at night, and thus the AOT40 is calculated for all 24 hours of a day.

In order to define critical levels, the AOT40 is related to specific effects. A reduction in economic yield (e.g. grain yield in wheat) is considered the most relevant long-term effect of ozone on crop species, and a reduction in biomass is chosen for tree species. In mixtures of species the effect of ozone is expressed as the change in the species composition. In all these cases, the AOT40 corresponding to an effect of 10% is considered to be the critical level. The most important short term-effect of ozone is the appearance of visible leaf injury.

The species used to derive the critical levels are known to be relatively sensitive to ozone. For crops, data on grain yield of spring wheat exposed to different ozone concentrations over the growing season is used to set the critical level, since the data base is the largest (8 experiments between 1987 and 1991 in four European countries using four different cultivars) and most consistent. The data base for short-term effects of ozone on crops, i.e. visible injury, is small and the critical level must be regarded as provisional. For species mixtures, a few studies of grassland communities give evidence of significant shifts in species composition in response to ozone. For trees, finally, the data base available is small and variable. Most studies only concern physiological effects. Single data sets from three different European studies of the effects of ozone on biomass production in birch, beech, oak, silver fir, Scots pine and Norway spruce have been used.

The data used to derive critical levels are almost entirely drawn from experiments in open-top chambers in central and northern Europe, using plants that are adequately supplied with water and nutrients. There are uncertainties in using these data to define air quality guidelines for vegetation throughout Europe. Among the most important of these are:

1. The open-top chamber technique will tend to overestimate the effects because of the higher ozone fluxes within the chambers compared with outside.
2. There are a great many species which have not been investigated experimentally in Europe, especially those of the Mediterranean region.
3. The critical level is likely to be higher when water availability is limited, because ozone flux is reduced. This is a very significant factor in many areas of Europe, especially as periods of water stress often coincide with periods of high ozone concentration.
4. There may be physiological, morphological or biochemical changes induced by ozone exposures below the critical level which could be important, for example in altering sensitivity to other abiotic and biotic stresses.
5. The data on trees are more variable than those for annual crops and there is uncertainty about the extent and significance of night-time ozone uptake. Furthermore, there are uncertainties in extrapolating from experiments of limited duration with young pot-grown trees to long-term effects on forest ecosystems. For these reasons, there is greater uncertainty attached to the recommended guidelines for trees.
6. For changes in species composition, the experiments are also of limited duration, and there is great uncertainty about the long-term effects of ozone exposure.

In summary, there is a sound scientific basis for expecting that adverse ecological and economic effects may occur when the guidelines recommended below are exceeded. There is a possibility that adverse effects might also occur at exposures below these guidelines, but there is considerable uncertainty over this, and we prefer to recommend values with a sound scientific basis rather than incorporate arbitrary uncertainty factors. Therefore, critical levels fulfil the primary aim of air quality guidelines in providing the best available sound scientific basis for the protection of vegetation from significant effects. Hence, critical levels can provide a solid information basis for risk assessments.

The following air quality guidelines are recommended:

To protect agricultural crops from a yield loss above 10%, the accumulated ozone exposure over a concentration of 40 ppb (AOT40) for daylight hours (i.e. with radiation levels above 50 W/m^2) over a three month growing season (e.g. May-July) should not exceed 5 ppm.h. This guideline should also prevent changes in the composition of species mixtures. To protect agricultural crops from short-term visible leaf injury, the AOT40 for daylight hours over a 3-day period should not exceed 0.7 ppm.h.

To protect forest trees from growth reductions, the AOT40 for 24 hours per day, over a six-month growing season (e.g. April-September), should not exceed 10 ppm.h.

The effects of nitrogen containing air pollutants on vegetation - Critical levels

Human activities, both industrial and agricultural, have strongly increased the amount of biologically active nitrogen compounds in the environment, thereby causing direct phytotoxic effects, disturbing the natural nitrogen cycle, and acidifying the soil. Various forms of nitrogen pollute the air, mainly nitrogen monoxide (NO), nitrogen dioxide (NO₂) and ammonia (NH₃) as dry deposition, and nitrate (NO₃⁻) and ammonium (NH₄⁺) as wet deposition. Other contributions are from occult deposition (fog, clouds, aerosols), PAN, N₂O₅, N₂O and amines. Since the publication of the WHO AQG in 1987 there have been significant advances in knowledge of the impacts of oxides of nitrogen and ammonia on vegetation.

In the present evaluation, attention is mainly paid to direct effects on plants, caused by exposure durations from one hour to one year. The long term impact (more than one year) on vegetation and the nitrogen cycle is discussed in the section on critical loads for nitrogen deposition (see below), while the contribution of nitrogen containing air pollutants to soil acidification is evaluated in the section on acidification (see below). The properties of PAN are discussed in the section on O₃ (see above). The role of NO_x and N₂O in atmospheric chemistry (formation and depletion of O₃ in the troposphere and stratosphere, respectively) and relations with climate change are not considered.

The reason to define critical levels for NO, NO₂ and NH₃ is the recent evidence from monitoring and mapping that these are the dominant forms of N deposition in many parts of the world and that several important effects of these compounds are not covered by the critical loads for nitrogen or acidity.

The critical levels are based on a survey of published evidence of physiological and ecologically important effects on plants. Biochemical changes have only been used as additional indicators of potentially relevant ecological responses. The survey has considered that in an ecological context growth stimulations and reductions are both potentially negative responses.

The impact of a pollutant on plants is determined by its rate of adsorption, rate of uptake and the plants' reaction. Foliar uptake is of particular importance for NO_x and NH₃, while the pathway via soil and roots is the major route for nitrogen in wet deposition. Foliar uptake of NH₃ and NO_x is driven by the concentration gradient between atmosphere and mesophyll, and mostly, but not always is directly determined by stomatal conductance and thus depends on factors influencing stomatal aperture. Although in higher plants uptake through the stomata strongly dominates, there are indications that penetration through the cuticle is not negligible. Lower plants like

bryophytes and lichens do not have stomata and a waxy waterproof cuticle, and thus the potential of direct uptake of pollutants in the form of wet or dry deposition is greater, perhaps resulting in the greater sensitivity of these organisms.

The solubility of NO, NO₂ and NH₃ differs, but at low concentrations their solution products are readily metabolised by the normal nitrogen assimilation processes in the shoots. High concentrations of these gases may lead to the accumulation of toxic NO₂⁻ and NH₄⁺ concentrations and to alteration of cellular acid: base regulation. Thus, depending on concentration the assimilation of these gases can be both beneficial and detrimental, and this may be modified by the presence of other toxic gases e.g. SO₂ and O₃. Beneficial effects include the stimulation of photosynthesis and the growth of plants. Both NO_x and NH_y generally cause an increase in the shoot: root ratio which may or may not be beneficial.

Responses to nitrogenous pollutants can be further modified and exacerbated by interactions with other environmental factors including frost, drought and pest organisms. Generally these include increased susceptibility to these factors which may in turn lead to major ecological changes.

The following gaps in knowledge were identified:

There have been important developments in the use of critical levels and critical loads approaches to AQGs. However, with regard to the critical levels of nitrogen-containing air pollutants there are several areas where improvements are urgently required.

- (i) the guidelines for the critical levels of NO_x and NH₃ are intended to apply to all classes of vegetation and under all environmental conditions. However, more information is needed to quantify the range of sensitivity.
- (ii) the guidelines are based largely on research performed in temperate climates on a limited range of soil types. Caution is required when critical levels are considered for plants in very different conditions - for example in tropical and sub-tropical zones.
- (iii) there is a need to understand further the long term impacts on growth of changes in biochemical parameters.
- (iv) there is growing awareness of the physiological importance of NO and this is reflected in the new incorporation of this compound in the guideline for NO_x. Comparisons of the phytotoxicity of NO and NO₂ are scarce and still not conclusive with regard to their relative degree of toxicity.
- (v) the relevance of NH₃ emissions from plants should be investigated in more detail in order to establish its potential importance in nitrogen budgets.

The recommendations for guidelines are based on the following:

Evidence exists that NH_4^+ (and NO_3^-) in rain, clouds and fog can have significant direct impact on vegetation, however, current knowledge is still insufficient to arrive at critical levels for those compounds.

NO and NO_2 should be assumed to act in an additive manner.

A strong case can be made for the provision of critical levels for short-term exposures. There are insufficient data to provide these with confidence at present, but current evidence suggests values of c. $75 \mu\text{g}/\text{m}^3$ for NO_x and $270 \mu\text{g}/\text{m}^3$ for NH_3 as 24 hour means.

Interactive effects between NO_2 and SO_2 and/or O_3 have been reported frequently, but from a review of recent literature it was concluded that the lowest effective levels for NO_2 are approximately equal to those for combination effects (although, generally, at concentrations near to its effect threshold, NO_2 causes growth stimulation if NO_2 is the only pollutant, while in combination with SO_2 and/or O_3 it results in growth inhibition).

Critical levels for a 1 year period are recommended to cover relatively long-term effects.

The following guidelines are recommended:

The critical level for NO_x (NO and NO_2 , added in ppb and expressed as NO_2 in $\mu\text{g}/\text{m}^3$) is $30 \mu\text{g}/\text{m}^3$ as an annual mean.

The critical level for NH_3 is $8 \mu\text{g}/\text{m}^3$ as an annual mean.

The effects of air-borne nitrogen pollutants on vegetation - Critical loads

Most of earth's biodiversity is found in (semi-)natural ecosystems, both in aquatic and terrestrial habitats. Mans activities pose a number of threats to the structure and the functioning of these ecosystems, and thus to the natural variety of plant and animal species. One of the major threats is the increase in air-borne nitrogen pollution (NH_y and NO_x) in recent decades. Nitrogen is the limiting nutrient for plant growth in many of the (semi-)natural ecosystems. Most of the plant species from these (semi-)natural habitats are adapted to nutrient-poor conditions, and can only compete successfully on soils with low nitrogen levels. Nitrogen is the only nutrient of which the cycling through the ecosystem is almost exclusively regulated by biological processes. To establish reliable critical loads for nitrogen, it is essential to understand the effects of nitrogen upon these ecosystem processes. The critical loads for nitrogen depend on (i) the type of ecosystem; (ii) the land use and management in the past and present and (iii) the abiotic conditions, especially those which influence the nitrification potential and immobilization rate in the soil. The impacts of

increased nitrogen deposition upon biological systems are diverse, but the most important effects are: (i) short-term direct effects of nitrogen gases and aerosols to individual species (see chapter on CLE); (ii) soil-mediated effects; (iii) increased susceptibility to secondary stress factors and; (iiii) changes in (competitive) relationships between species, resulting in loss of biodiversity. The empirical approach has been used to establish guidelines for excess N deposition on natural vegetation. It was decided not to include the results of the mass balance approach with nitrogen as a nutrient for non-forest ecosystems, because essential data are missing. The acidifying effects of air-borne nitrogen are incorporated in the guidelines for excess acidity based upon steady state mass balance models (see section on effects of acidifying compounds below).

The main aim of this evaluation was to update the 1987 WHO air quality guideline for air-borne nitrogen deposition on vegetation, which was estimated at $30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for sensitive vegetation. At that moment only few evidence was available to establish critical nitrogen deposition. Since then significant progress had been made upon the ecological effects of nitrogen deposition (both NH_y and NO_x) in several types of vegetation. The published effects of increased airborne nitrogen supply have been reviewed with respect to changes in vegetation in terrestrial and aquatic (semi-)natural ecosystems. Observed and validated changes are used as an indication for the impacts of nitrogen deposition. Based upon these data, guidelines for nitrogen deposition (Critical loads CLOs) have been presented. CLOs are presented within a range per ecosystem, because of genuine spatial differences in ecosystems. The following natural ecosystems have been treated: freshwater ecosystems (shallow soft-water bodies, lakes and streams) and terrestrial ecosystems (wetlands & bogs, species-rich grasslands, heathlands and forests) (table 2).

Table 2:
Guidelines for nitrogen deposition ($\text{kg N ha}^{-1} \text{ yr}^{-1}$) to (semi-)natural freshwater and terrestrial ecosystems.
reliable; # quite reliable and (#) best guess*.

	CLO	Indication
Soft-water lakes	5-10 ##	Decline isoetid species
Mesotrophic fens	20-35 #	Increase tall graminoids, decl. diversity
Ombrotrophic (raised) bogs	5-10 #	Decrease Sphagnum and subordinate species, increase tall graminoids
Calcareous species-rich grassland	14-25 ##	Increase tall grass, decline diversity
Neutral-acid species-rich	20-30 #	Increase tall grass, decline diversity
Montane-subalpine grassland	10-15 (#)	Increase tall graminoids, decl. diversity
Lowland dry-heathland	15-20 ##	Transition heather to grass
Lowland wet-heathland	17-22 ##	Transition heather to grass
Species-rich heaths/acid grassl.	7-20 #	Decline sensitive species
Arctic and alpine heaths	5-15 (#)	Decline lichens, mosses and evergreen dwarf-shrubs, increase in grasses and herbs
Coniferous forests (acidic; managed)	10-15 #	Tree health; Nutrient imbalance (low nitrification rate)
Coniferous forests (acidic; managed)	20-50#	Tree health; Nutrient imbalance (mod-high nitrification)
Coniferous forests (acidic; managed)	15-20 #	Changes ground flora
Deciduous forests (acidic; managed)	15-20 #	Tree health; Nutrient imbalance; shoot-root ratio
Deciduous forests (acidic; managed)	15-20 #	Changes ground flora
Forests (acidic unmanaged)	unknown	unknown
Calcareous forests	15-20 (#)	Changes ground flora

- * - reliable: when a number of published papers of various studies show comparable results;
 - quite reliable: when the results of some studies are comparable;
 - best guess: when no data are available for this type of ecosystem. The CLO is than based upon knowledge of ecosystems which are likely to be more or less comparable with this ecosystem.

Critical loads for nitrogen are formulated to as reliable an extent as possible. As most of the research efforts have focused on acidification in forestry, serious gaps in knowledge exist on the effects of enhanced nitrogen deposition on (semi-)natural terrestrial and aquatic ecosystems. The following gaps in knowledge are most important:

- more research is needed in Mediterranean, tropical and subtropical vegetation zones;
- quantified effects of enhanced nitrogen deposition on fauna in all reviewed vegetations are extremely scarce;
- the critical load for nitrogen deposition to Arctic and alpine heathlands and forests are largely speculative;
- more research is needed on the nitrogen effects on forest ground vegetation and (ground) fauna, because most research had focused on the trees only;

- a serious gap in knowledge is the effects of nitrogen in neutral/calcareous forests, which are not sensitive to acidification;
- more long-term research is needed in montane/subalpine meadows, species-rich grasslands and ombrotrophic bogs;
- the long-term effects of enhanced atmospheric nitrogen in grassland and heathland of high nature conservation importance under different management regimes are insufficiently known and may affect the critical load value;
- the possible differential effects of the deposited nitrogen species (NO_x or NH_y) are insufficiently known to make a differentiation between these N species for critical load establishment;
- long-term effects of nitrogen eutrophication in (sensitive) aquatic ecosystems (freshwater and marine) needs further research.

Nitrogen is the only nutrient for which the cycling through ecosystems is almost exclusively regulated by biological processes. To establish reliable guidelines, it is crucial to understand the long-term effects of increased nitrogen deposition on these processes in a representative range of ecosystems. It is thus very important to quantify the effects of nitrogen loads on (semi-)natural terrestrial and freshwater ecosystems by manipulation of nitrogen inputs in long-term ecosystem studies in unaffected and affected areas. These data are essential to validate the presented critical loads and to develop robust dynamic ecosystem models, which are reliable enough to calculate critical loads for nitrogen deposition in (semi)natural ecosystems.

Recommended guidelines:

Guidelines for nitrogen deposition to specific ecosystems are given in table 2. The most sensitive ecosystems for which effects thresholds can be estimated show critical loads of 5-10 kg N·ha⁻¹·yr⁻¹. A more average value for the limited range of ecosystems studied is 15-20 kg N·ha⁻¹·yr⁻¹.

The effects of SO₂ on vegetation - Critical levels

Since the publication of the first edition of the WHO Air Quality Guidelines in 1987, the relative importance of SO₂ as a phytotoxic pollutant in Europe has diminished to some extent, due to falling emissions in many areas and the recognition of O₃ and nitrogen compounds as being of much greater significance than realized hitherto. In terms of understanding of the basic mechanisms of direct SO₂ injury the statements in the original chapters are still valid. However, advances have been made with respect to demonstrating the significance of very low concentrations of SO₂ on growth and yield, and on changing plant sensitivity to other environmental stresses. New work has also provided information which can be utilized to introduce new guidelines for protection of lichens against SO₂ and forests against acid mists.

A number of studies have provided valuable data for several major agricultural crops, based on fumigations, filtrations and transect studies. These new data confirm the annual guideline value of 30 µg/m³ as an annual mean. However, it is recommended that this value should not be exceeded as a mean for the winter months, October - March, inclusive, in view of the abundant evidence for increased sensitivity

of crops growing slowly under winter conditions. The only evidence for any adverse effect of SO₂ below the guideline comes from filtration studies in open-top chambers in Belgium and Scotland, with small decreases in root growth and grain yield in the presence of 9 µg/m³ and 26 µg/m³ SO₂, respectively. However, in both cases NO₂ was present and in the Belgian study there was an 8 hour mean of 39 µg/m³ over the growing season. In view of the small effects and the presence of other pollutants, a reduction of the guideline below 30 µg/m³ cannot be justified. In the first edition of the AQG, concern was expressed over the possible validity of the guidelines in the presence of other pollutants. The new studies involved NO_x and O₃ at or below their guidelines, as probably did the key study used in setting the 1987 guideline. Thus, given present knowledge, the presence of other pollutants is taken into account by the current recommendations. It is recommended that the 24 hour guide value for all species is abandoned, in view of further evidence confirming that peak concentrations are not significant compared with accumulated dose for SO₂.

A lower guideline of 20 µg/m³ is now recommended for forests and natural vegetation, as both annual and winter means. This is based on new evidence of periods of high sensitivity of conifers during needle elongation and the longevity of many of the species concerned as well as their being unmanaged or minimally managed which renders them more sensitive to pollution stress. The only example reported in the literature which makes a case for a lower guideline for natural vegetation is a Dutch study involving SO₂ fumigation of a range of heathland species. On the basis of probability distribution of species numbers injured in relation to pollutant dose, it was suggested that 8 µg/m³ SO₂ as an annual mean would be sufficient to protect all but 5% of the species concerned. While this represents an approach worthy of consideration which is compatible with some other ecotoxicological recommendations, on the basis of present knowledge and the generally accepted criteria for setting air quality standards it cannot be recommended as a basis for lowering the recommended guidelines.

The potential importance of extreme environmental conditions in reducing air quality standards has been recognized since at least 1978, when the International Union of Forestry Organisations established these for forests. This was acknowledged in the 1987 AQG chapter on SO₂ but not used to set a guideline applicable to such conditions. New data have confirmed concerns over low temperature stress contributing to greater SO₂ sensitivity in forests. In particular, a field study of Norway spruce at different altitudes in the polluted Ore Mountains of Czechoslovakia has demonstrated a relationship between low winter temperatures and the time in which stands start to disintegrate. This has been used to develop a model in which effective temperature sum of <1000° C days above +5° C is used as a threshold for lowering annual and winter SO₂ means for protection of forests and natural vegetation to 15 µg/m³. This lower concentration is now recommended for WHO Air Quality Guidelines for temperatures below this threshold. Further justification for this approach is given by field evidence from elsewhere in Europe and from evidence of sulphate mists enhancing frost sensitivity. It should be recognized, however, that this guideline is based on field studies where the temperatures recorded were above those pertaining in some forested areas of Europe, such as northern Finland. Thus it is possible that in even more extreme environments a lower guideline is required. As in

the case of crops, these guidelines have been established primarily on the basis of observations at field sites where NO_x and O_3 will also have been present and thus are applicable to pollutant mixtures.

The 1987 edition of the WHO Air Quality Guidelines only considered the effects of SO_2 on higher plants, thereby ignoring the extensive evidence of the ultra-sensitivity of certain lichen and bryophyte species. Many sensitive species have disappeared from vast areas of Europe with only moderately elevated SO_2 concentrations. Winter and annual means of $30 \mu\text{g}/\text{m}^3$ SO_2 are sufficient to eradicate the most sensitive taxa. Examination of the available information indicates that a careful field study shows community changes occurring at concentrations below $10 \mu\text{g}/\text{m}^3$. It is recommended on this basis that a guideline value of $10 \mu\text{g}/\text{m}^3$ annual mean be established for lichens. However, this level may have to be reduced further as more detailed information becomes available for the most sensitive species.

In the 1987 AQG chapter on SO_2 , recognition was given to the issue of soil acidification, but no deposition guidelines were set. However, no mention was made of direct impacts of acid precipitation on above ground plant organs. It is now recognized that mists can contain solute concentrations up to ten times those of rain and thus cause direct impact to vegetation. Since mist and cloud occur most frequently at high altitudes and are intercepted with particular efficiency by forests, trees are likely to be the most sensitive receptors. Experiments on young trees, backed up by field observations, show significant effects of acid mists on leaf surface structure at pH 3.5, which is equivalent to $150 \mu\text{mol}/\text{l}$ sulphate. Visible lesions occur at pH 3.0, equivalent to $500 \mu\text{mol}/\text{l}$ and have been recorded on sensitive species at the lower value (pH 3.5). The difficulties of measuring sulphate concentrations in cloud water can be overcome by translating these into an atmospheric concentration for particulate sulphate. On this basis a guideline for acid mists of $1.0 \mu\text{g}/\text{m}^3$ particulate sulphate as an annual mean is recommended for trees where ground level cloud is present 10% or more of the time. However, this guideline only applies when calcium and magnesium concentrations in cloud do not exceed hydrogen and ammonium ion concentrations, because no data exist to establish a guideline under these conditions. This restriction excludes areas such as the Mediterranean, Eastern Europe and the Alps.

The following guidelines are recommended:

<u>Vegetation category</u>	<u>Guideline ($\mu\text{g}/\text{m}^3$)</u>	<u>Time period</u>
Agricultural crops	30	Annual and Winter (Oct. - March) mean
Forests and natural vegetation	20	Annual and Winter (Oct. - March) mean
Forests and natural vegetation (effective temperature sum <math><1000^\circ\text{C}</math> days $>+5^\circ\text{C}$)	15	Annual and Winter (Oct. - March) mean
Lichens	10	Annual mean
Forests (where ground-level cloud is present >10% of time)	1.0 sulphate particulate (equivalent to 150 $\mu\text{mol}/\text{l}$ non-marine sulphate in mists, when Ca^{2+} and Mg^{2+} concentrations <math><\text{H}^+</math> and NH_4^+ ion concentrations)	Annual mean

The above guidelines do not take into account SO_2 increasing sensitivity to other stresses, with the exception of low temperatures for forests and natural vegetation. Given further knowledge on the effects of SO_2 on stresses, such as drought, pathogens and pests, it is possible that they may require further modification in the future. The 24 hour mean guideline has been abolished, but this is on the basis of knowledge on higher plants. The inclusion of lichens in these new guidelines may warrant future considerations of a short-term guideline for these organisms, if knowledge indicates the necessity for this. The new guide value for acid mists has similarly been applied to forests only on the basis of the available experimental evidence and field observations. The effects of acid mist on other receptors may also warrant future attention.

The indirect effects of acidifying compounds on natural systems - Critical loads

Acidifying deposition and ecosystem damage

Historical data provide evidence of increasing transport of SO_4^{2-} , up to a factor of 2 and 3.5 in 1950 and 1980 respectively in comparison to preindustrial levels in Europe. Emissions of SO_2 in the air are transformed to sulfate (SO_4^{2-}) which constitutes the major compound of acid deposition. The effects and risks of SO_2 emissions and resulting deposition are described for soils in general and forest soils and surface waters in particular.

Soil acidification is defined as a decrease in the Acid Neutralizing Capacity (ANC) of the inorganic fraction of the soil including the solution phase, and is directly dependent of the net supply of base cations (by weathering and deposition) and the net supply of anions (deposition minus retention) in the mineral soil. Deposition of acidifying compounds such as SO_2 , NO_x , and NH_3 leads to soil acidification by oxidation to H_2SO_4 and HNO_3 and leaching of SO_4^{2-} and NO_3^- respectively.

The dynamics of forest soil acidification is very site specific and depends on soil characteristics such as weathering rate, sulfate adsorption capacity and CEC. The acidification of soils ultimately leads to an increase in the soil solution of the aluminum concentration which increases the risk of vegetation damage. By defining the relationship between the chemical status (base cation and aluminum concentrations in the soil solution) and vegetation response, the so called critical load for that particular ecosystem can be derived. Damage to forests in Europe including defoliation, discoloration, growth decrease and tree dieback have been reported over the last decade, and have to a large extent been attributed to soil acidification, but also to eutrophication and photochemical oxidant effects.

Acidic deposition has caused acidification of surface waters, fish mortality and other ecological changes in large areas of northern Europe and eastern parts of North America.

Sulfate is normally a mobile anion in catchments located in glaciated areas. Increased sulfate concentrations in runoff due to increased acidifying inputs are accompanied by an increase of base cations and a decrease in bicarbonates, resulting in a acidifying effect on surface waters.

For most of the sensitive soils in Europe, the sulphate deposition is directly related to the acidifying load of sulphate in watershed run-off. The deposition/run-off relationship for nitrogen is not as well defined. The nitrate concentrations in run-off, and hence the contribution to the total acidity loading, is due to a combination of factors including the amount of deposition, the ability of vegetation to take up nitrogen and denitrifying processes. Even in cases of substantial nitrogen run-off, models calculate a deposition/run-off ratio greater than one due to denitrification. Determining the nitrate run-off response to a change in nitrogen deposition requires site specific information.

Under natural conditions, most of the nitrogen deposited on terrestrial catchments is taken up by vegetation leading to low concentrations of ammonia and nitrate in the run-off. However, in some areas in Europe, including southernmost Norway, Denmark and southern Sweden nitrogen concentrations in runoff water appear to be above background values. This excess nitrate in runoff is mostly due to a disruption of the nitrogen cycle and not only due to increased nitrogen deposition. In such cases, nitrogen deposition exceeds the rate of nitrogen retention mechanisms, i.e. growth uptake, denitrification, and immobilization. When nitrate is leached from the soil solution and appears in surface waters, it will contribute to soil and surface water acidification in the same manner as sulphate.

In cases of low soil pH, excess nitrogen deposition leads to acidification of natural vegetation systems other than trees. Plant species from poorly buffered habitats are adapted to nitrate uptake while plants from acid environments are generally adapted to ammonia uptake. Therefore, a low pH may lead to a shift of these systems from a nitrate dominated to an ammonia dominated system. Such a disruption of the nitrogen cycle in combination with low pH ultimately leads to acidification by nitrogen.

The critical loads

The critical load is defined as "the highest deposition of compounds that will not cause chemical changes leading to harmful effects on ecosystem structure and function".

A relationship has been established between increased aluminum concentrations in the soil solution and adverse effects to roots and growth of trees. For example, it has been shown that the tree growth of Norway spruce decreases as the base cation (i.e. calcium) to aluminum ratio is smaller than a critical limit of 1. Laboratory results of aluminum damage indicate that tolerance to aluminum varies among tree species. For example a growth reduction of 80% has been demonstrated at BC/Al of 0.1 for the northern white cedar (*Thuja occidentalis*) and of 4 for the masson pine (*Pinus massonii*). It has been found that a BC/Al ratio exceeding or equal to 1 seems to provide appropriate sustainability for European forests. However, species which grow in on aluminum oxide-rich, non-glaciated old soils, for example Teak, guapira, orange and cotton seem to be accustomed more to aluminum than trees from the temperate zone. Therefore, computation of critical loads in Europe have generally applied a BC/Al of 1.

Other critical limits for forest soils are based on aluminum concentration and pH in soil solution.

For surface waters, ANC has been considered as a chemical criterion that is used to explain the increasing risk for fish damage. The critical chemical value, ANClimit = 20 µeq/l, has been derived from the information on water chemistry and fish status obtained from the 1000 lake survey carried out in Norway in 1986. The selected ANClimit has been assessed by examining the relationship between the critical load exceedance and the damage to fish on the basis of data from the

Norwegian 1000 lake survey can again be used. The probability of damage to fish populations increases clearly as a function of the critical load exceedance.

Table 3 gives an overview of average limits that have been established to compute critical loads.

Table 3. Critical limits for chemical compounds in forest soils and freshwater systems.

Compound	unit	Forest soil	Freshwater	Groundwater
Aluminum	$\text{mol}_c \text{ m}^{-3}$	0.2	0.003	0.02
BC/Al	mol mol^{-1}	1	-	-
pH		4.0 ^a	(5.3, 6.0) ^b	6.0
[ANC]	$\text{mol}_c \text{ m}^{-3}$	-	(0.02, 0.08) ^b	0.14
[NO ₃]	$\text{mol}_c \text{ m}^{-3}$	-	-	0.8

^aAssuming $\log K_{\text{gibb}}$ of 8.0 and $[\text{Al}] = 0.2 \text{ mol}_c \text{ m}^{-3}$

^bA pH of 6.0 relates to peak flow situations and is associated with $[\text{ANC}] = 0.08 \text{ mol}_c \text{ m}^{-3}$.

Calculation of critical loads is based on the Steady State Mass Balance Method (SSMB) which assumes a time independent steady state of chemical interaction involving an equilibrium between the production and the consumption of acidic compounds.

Current UN/ECE protocols concentrate on distinctive acidifying compounds i.e., Sulphur and Nitrogen, rather than on acidity as a whole. It was necessary to subdivide the critical load of acidity between the acidifying share of sulphur and the acidifying share of nitrogen. For the purposes of the guidelines no subdivisions are performed.

Recommended guidelines

In Europe, critical loads have been established at the resolution of EMEP to allow for comparisons between critical loads and (sulphur-) deposition values and identify areas where critical loads are exceeded. Critical loads of acidity as computed by the steady state mass balance method are predominantly dependent on the rate of base cation weathering. For terrestrial ecosystems the weathering rate can be estimated by combining information on soil parent material and texture properties. Table 4 lists the ranges of critical loads of acidity in relation to combinations of parent material and texture classes.

Table 4: Critical load ranges of acidity used for the various combinations of parent material and texture in terrestrial ecosystems.

Guideline range of critical loads of acidity (eq ha ⁻¹ yr ⁻¹)	parent ¹ material	texture
< 250	acidic	coarse
250 - 500	acidic intermediate basic	coarse-medium coarse coarse
500 - 1000	acidic intermediate basic	medium, medium-fine coarse-medium, medium coarse-medium
1000 - 1500	intermediate basic	medium-fine medium
> 1500	intermediate basic	fine medium-fine

¹ Acidic :	Sand (stone), gravel, granite, quartzine, gneiss (schist, shale, greywacke, glacial till)
Intermediate:	Gronodiorite, loess, fluvial and marine sediment (schist, shale, greywacke, glacial till)
Basic :	Gabbro, basalt, dolomite, volcanic depositifs

Additional factors, such as vegetation cover, further modify the value of the critical load. To calculate precise critical loads for a given geographical area it is recommended that the mass balance equation be used.

For surface waters the weathering rate can be estimated on the basis of water quality and quantity variables of which base cation concentrations and runoff are the most influential ones. Table 5 lists the ranges of critical loads in relation to combinations of base cation concentration and runoff classes. For each critical load class, at least 50% of the critical load values computed on the basis of lake data from Finland (1450 lakes), Norway (), and Sweden () fall within the class boundaries, given the ranges for present base cation concentrations and run-off. Only in two cases the boundaries for the base cation concentration classes overlapped between two critical load classes, when the class boundaries were set on the basis 25th and 75th percentile base cation concentrations for given run-off classes. For those cases the critical loads

are determined more by other factors than base cation levels and run-off, and the guideline value set is therefore more uncertain than those without overlap.

Table 5: Critical load ranges of acidity used for various combinations of Base cation concentration and run-off for surface waters

Guideline range of critical loads of acidity (eq ha ⁻¹ yr ⁻¹)	Base cation concentration (meq m ⁻³)	run-off (m)
< 250	< 45	> 1
	< 100	0.3 - 1
	< 270 ^a	< 0.3
250 - 500	45 - 70	> 1
	100 - 190	0.3 - 1
	250 - 400 ^a	< 0.3
500 - 1000	70 - 103	> 1
	190 - 290	0.3 - 1
	400 - 650	< 0.3
1000 - 1500	103 - 170	> 1
	290 - 465 ^b	0.3 - 1
	650 - 1300	< 0.3
> 1500	> 170	> 1
	> 350 ^b	0.3 - 1
	> 1300	< 0.3

a,b The class boundaries overlap

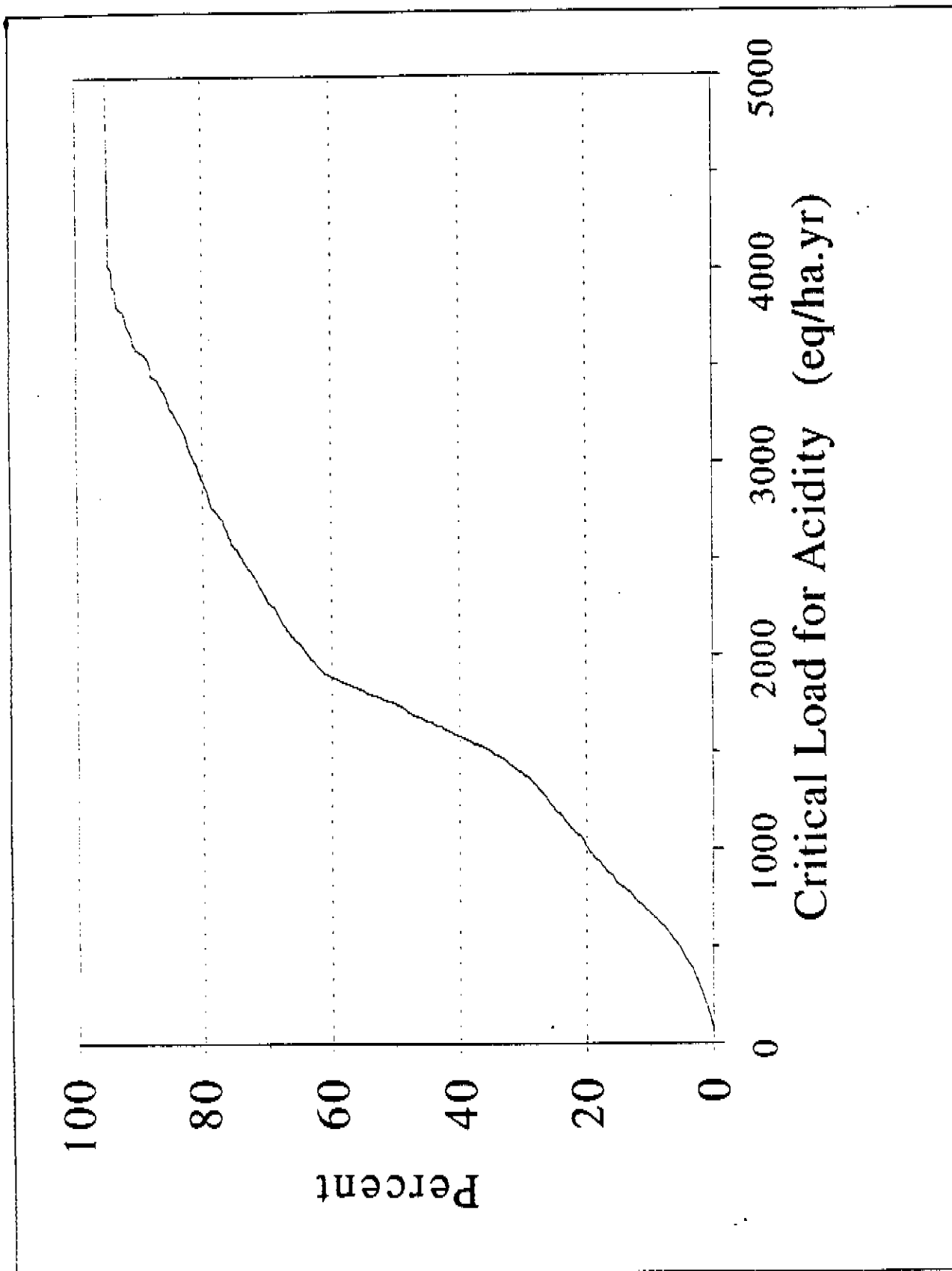
Figure 2 shows the cumulative distribution of critical load data available for terrestrial ecosystems and surface waters in Europe as collected in the framework of the UN/ECE mapping programme. The graph shows that about 1% of the natural systems have critical loads lower than 250 eq ha⁻¹ yr⁻¹ (at a median of 170 eq ha⁻¹ yr⁻¹). The range between 250 and 500 eq ha⁻¹ yr⁻¹ covers about 3% (at a median of 414 eq ha⁻¹ yr⁻¹). An areal percentage of about 11% (at a median of 821 eq ha⁻¹ yr⁻¹) has critical loads between 500 and 1000 eq ha⁻¹ yr⁻¹. Thus about 15% of terrestrial and surface water ecosystems have critical loads for sulphur which are lower than 821 eq ha⁻¹ yr⁻¹.

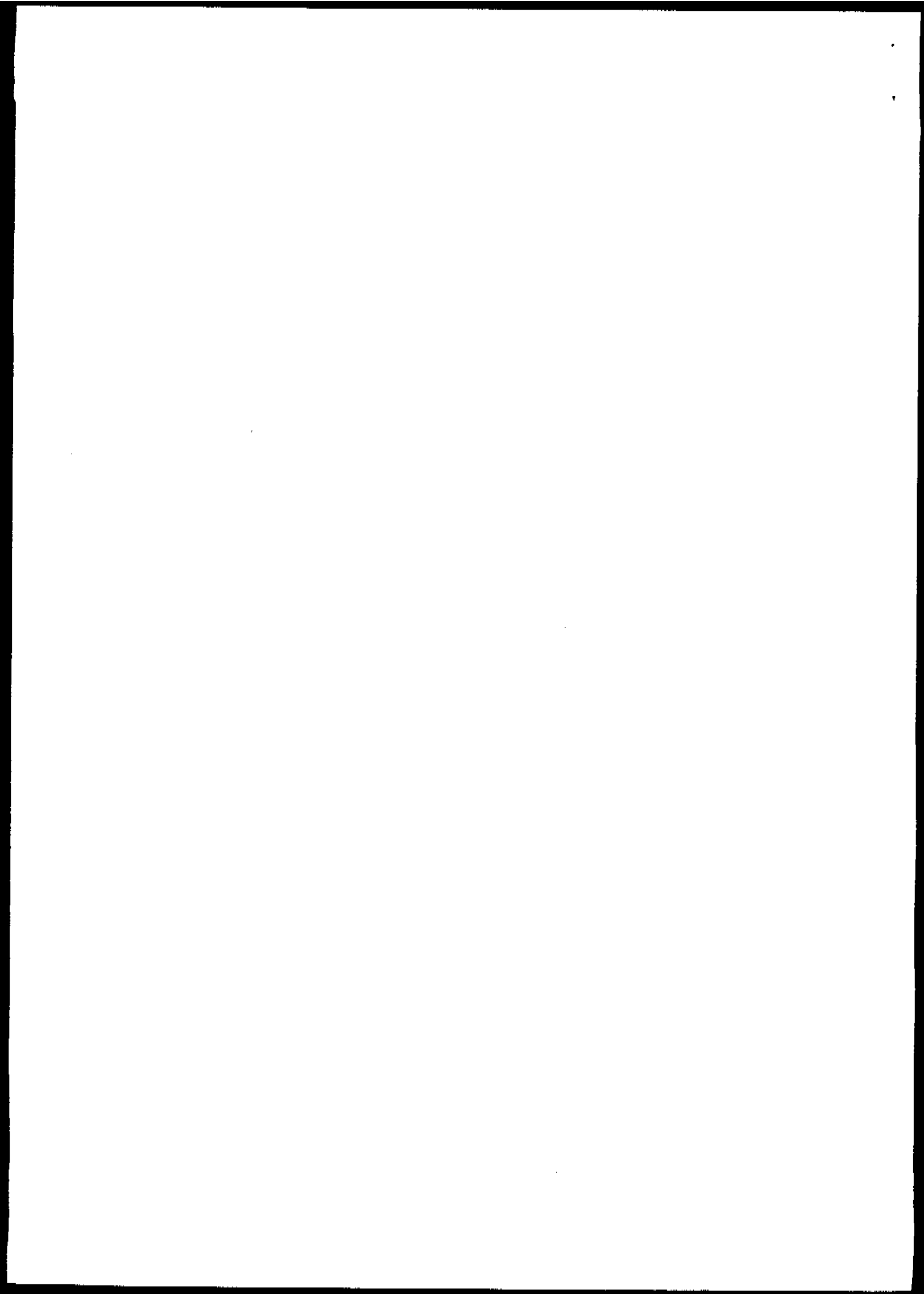
The median critical load of acidity of each of the ranges, i.e. 0-250, 250-500, 500-1000, 1000-1500 and higher, is proposed as representative value for these ranges. Table 6 lists the median values for each range including the related protection percentage of the total European natural area.

Table 6: Median values of critical load ranges of acidity for terrestrial and surface water systems.

Guideline range of critical loads of acidity (eq ha⁻¹ yr⁻¹)	median (eq ha⁻¹ yr⁻¹)	percentage of ecosystem area protected
< 250	170.0	99.2
250 - 500	414.0	96.2
500 - 1000	821.0	85.3
1000 - 1500	1269.0	73.7
> 1500	2295.0	29.9

Figure 2

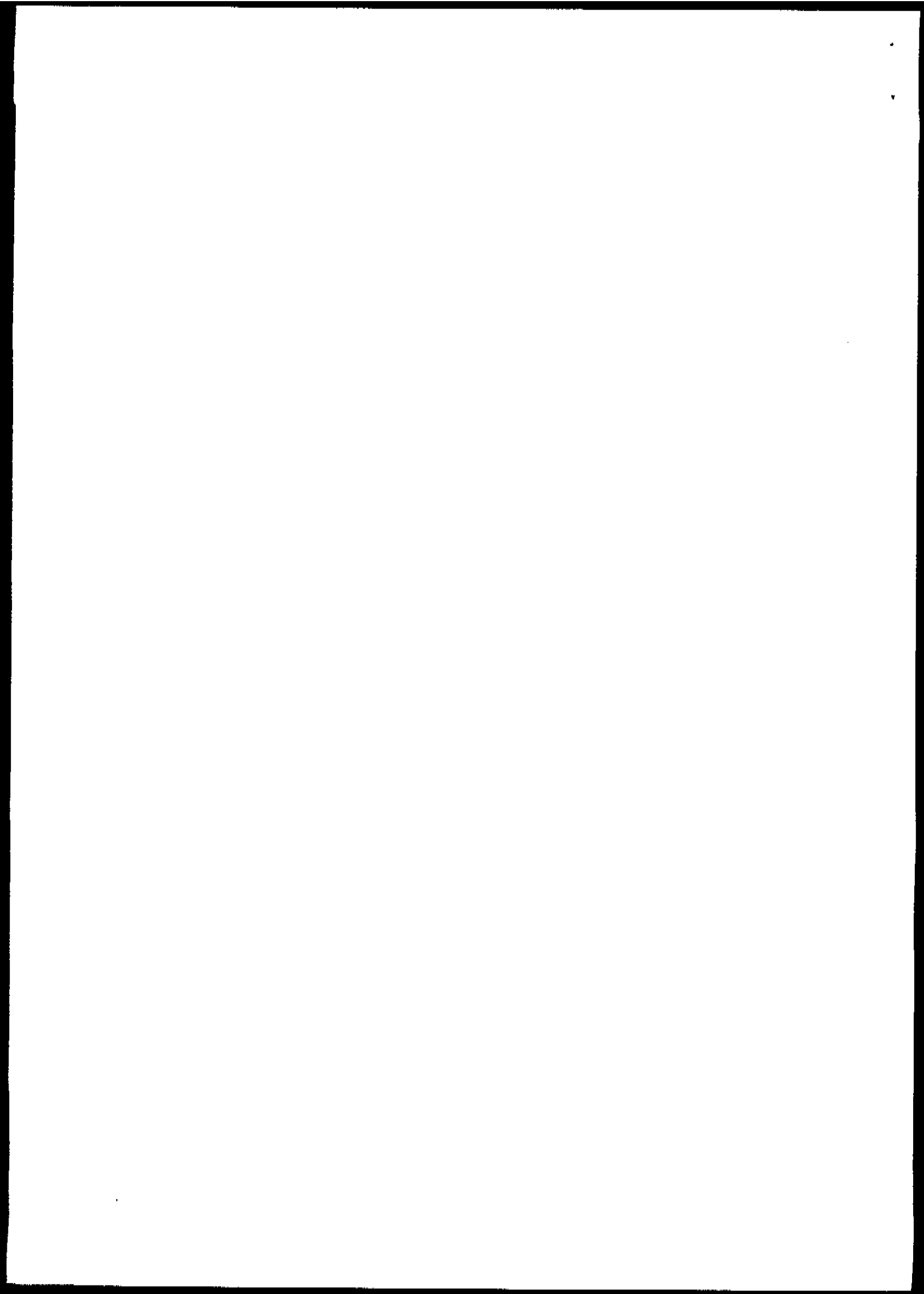




Annex 1

WORKING PAPERS

- ICP/CEH 239/6 *Draft chapter on ozone to cover effects on crops and forests,*
by Dr Mike Ashmore, Dr Jürg Fuhrer and Dr Lena Skärby
- ICP/CEH 239/7 *Draft chapter on sulphur dioxide which is to cover ambient*
levels, by Professor J. Nigel B. Bell and Dr Peter H. Freer-Smith
- ICP/CEH 239/8 *The indirect effects of sulfur compounds on natural systems,*
by Dr Jean-Paul Hettelingh and Dr Juha Kämäri
- ICP/CEH 239/9 *The effects of air-borne nitrogen pollutants on vegetation -*
critical loads, by Dr Roland Bobbink, Professor Michael Hornung and Dr Jan G.M. Roelofs
- ICP/CEH 239/10 *Critical levels for the effects of nitrogen containing air*
pollutants on vegetation, by Dr Simon J.M. Caporn,
Dr Ludger J.M. van der Eerden and Professor John A. Lee



Annex 2

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