ACID DEPOSITION

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Summary

The effects of acid deposition were first (1960-1970) observed in the form of reduction of fish populations in lakes and rivers in Scandinavia, Canada and the US. In a later stage (1980-1985) effects on forests were reported, especially spruce and pine were loosing their needles too fast and tree die-back was attributed to acid-deposition.

In the same period it was shown that very high deposition fluxes of nitrogen contribute to eutrophication (exposure to too large concentrations of nutrients such as phosphorus and nitrogen) in parts of Europe and the US. Eutrophication leads to loss of species (e.g. replacement of heather by grass) and too high nitrate concentrations in ground water for use as drinking water.

Sulfate, nitrate, and ammonia/ammonium are the main contributors to acid deposition/eutrophication. Emissions of industry, power stations, transport, agriculture and households constitute most of the precursors for acid deposition. The primary emissions are in the form of sulfur dioxide, nitrogen oxides and ammonia. Sulfur

dioxide and nitrogen oxides are converted in the atmosphere to sulfuric and nitric acid. Part of these acids is neutralized by, mainly, ammonia and base cations like calcium and magnesium.

Both wet as well as dry deposition contributes to acid deposition in varying degree dependent on meteorological conditions and location.

Conversion of ammonia, ammonium and nitrate in soil and groundwater must be taken into account to derive correct acid deposition fluxes.

The effects of acid deposition on vegetation can be direct, at high fluxes or exposure levels. But the main impact is indirect by way of aluminum ions, liberated by soil interactions or causing uptake of too large amounts of nitrogen by the root system.

Based on the observed effects, vegetation and soil characteristics, critical loads can be defined. If these critical loads are exceeded, effects can be expected, dependent on the degree and period of exceedance.

Modeling of emission/exposure/effects relations provide an effective tool for the development of abatement measures.

1. Introduction: The Problem

The first signs of the effects of acid deposition were encountered when losses of fish populations in Canadian, Scandinavian and US lakes were reported in the early sixties. The common explanation in all cases was that the water in the lakes was acidified to a point where fish eggs no longer can produce young specimen. The cause of this acidification was acid deposition; precipitation had introduced so much acid in the lakes that its pH had sunk below the critical limit for egg hatching.

In the middle eighties reports came in from specifically Canada, the US and Germany that unusual damage was observed in forests. Trees would have less foliage or needles as normally encountered and this damage even progressed to the point that trees would die, a phenomenon which happened for instance in the border area of former East-Germany, Poland and former Czechoslovakia. In the case of tree-dieback the cause/effect relation was much more complicated than in the case of loss of fish in lakes. In fact, much later it was established that not only acid deposition but also increased oxidant concentrations (species as ozone, Peroxy-Acetyl Nitrate, PAN, hydrogen peroxide) contributed to tree damage.

A third type of effect of acid deposition was reported in the mid-eighties; the same deposition processes which were responsible for too high loads (load is a time integrated flux) of acid compounds also were the cause of too high nutrient concentrations in soil and groundwater. Nitrate and ammonium are beneficial, even essential, for development in vegetation but in too high concentration these species lead to the loss of diversity especially in oligotrophic (= adapted to low nutrient availability) ecosystems. Heather fields were rapidly disappearing, as result of eutrophication. Too high nitrate concentrations in groundwater were measured in the same areas, making this water unfit for human consumption. This problem was mainly encountered in The Netherlands, Belgium, and parts of Germany, Denmark and Southern Sweden.

The common factor on all these cases is that pollutants, or their precursors (substances which are converted in the atmosphere to acidifying or eutrophication causing compounds) are emitted transported in the atmosphere and deposited either by way of precipitation (wet deposition) or in dry form (dry deposition). In some cases acid deposition takes place at distances of 1000 km or more from the place were the responsible emissions have taken place.

The most important acid forming species are sulfur dioxide (which is partially converted to sulfuric acid in the atmosphere), nitrogen oxides (converted to nitric acid during atmospheric transport) and ammonia. Ammonia may act as a base in the atmosphere, neutralizing nitric and sulfuric acid, but in soil or groundwater ammonia is to a large extent converted by microorganisms to nitric acid, producing additional acid in the process.

The cycles of the most important species in acid deposition and eutrophication are given in Figures 1 to 3.

The sources for SO_x (sum of SO_2 and sulfates), NO_x (NO plus NO_2) and NH_x (NH_3 and NH_4) are both natural as well as anthropogenic.

The sulfur compounds are converted eventually to sulfuric acid, NO_x to nitric acid and ammonia reacts with acids to form ammonium salts.

Precursors (SO_2, NO_x and ammonia) and products (sulfuric acid, nitric acid and ammonium) can be transported over large distances (up to 1500 km) dependent on meteorological conditions, speed of conversion, and removal by deposition processes.

To quantify the impact of emissions on the effects caused by acid deposition and eutrophication the whole chain of emissions, transport, atmospheric conversion, dry and wet deposition and the effects caused by the total deposition loads, including the role of ground water and soils must be understood.

Wet and dry deposition are not only the processes by which pollutants are transported to the earth surface and exposing humans and ecosystems to acid deposition and eutrophication, but deposition processes also play an essential role in cleansing of the atmosphere.

If removal by wet and dry deposition would not take place, the earth’s atmosphere would be unsuitable to sustain life in a relatively short period, in the order of a few months.

Adequate knowledge of the deposition processes is essential for developing environmental policy:

- Avoiding transgression of the maximal sustainable deposition load for acid deposition and eutrophication (exceedance of critical loads) is a guiding principle in the development of environmental policy in e.g. Europe.
- Emitter-receptor relations can only be derived based on sufficiently accurate descriptions of emissions, transport and deposition. These emitter-receptor relations are the basis of the sulfur and nitrogen protocols (under the guidance of UN-EMEP), which play an essential role in emission abatement policies in Europe.
- In order to derive good descriptions of other environmental problems like oxidant formation it is necessary to quantify losses of chemical constituents by deposition processes.

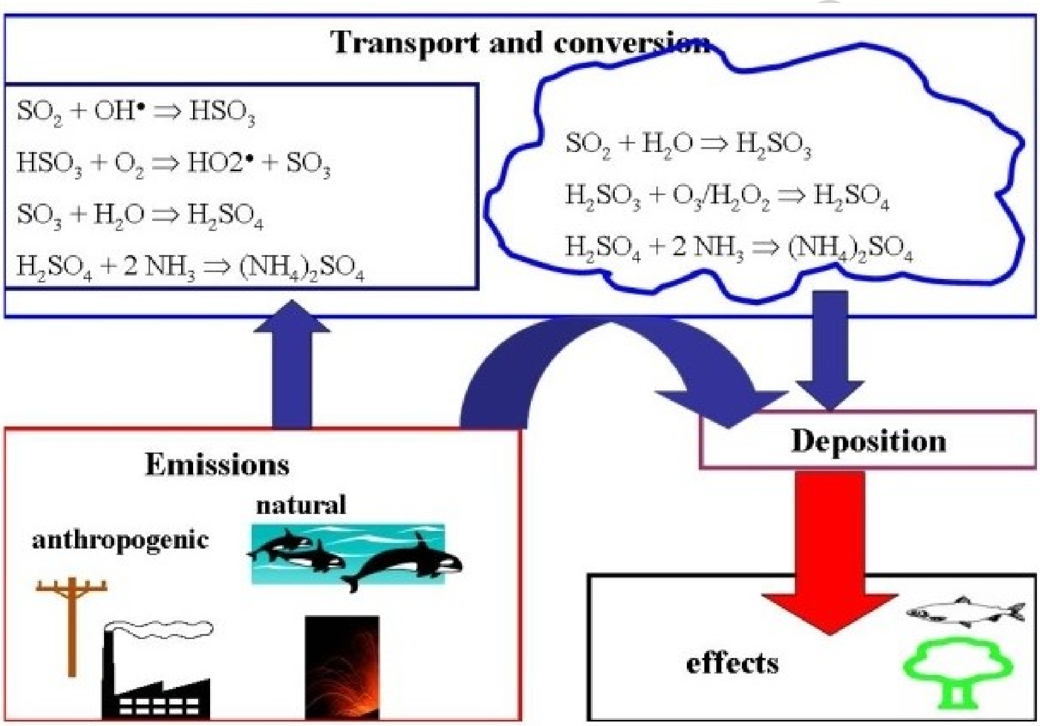

Figure 1: Emission-effect relations: central issue

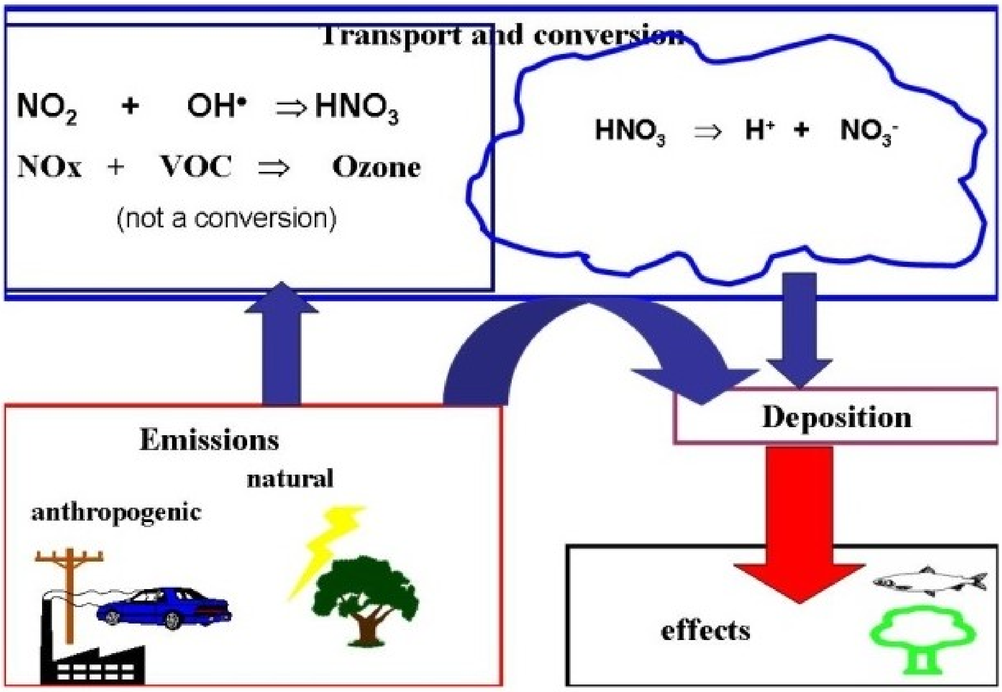

Figure 2: Conversion of NO_x

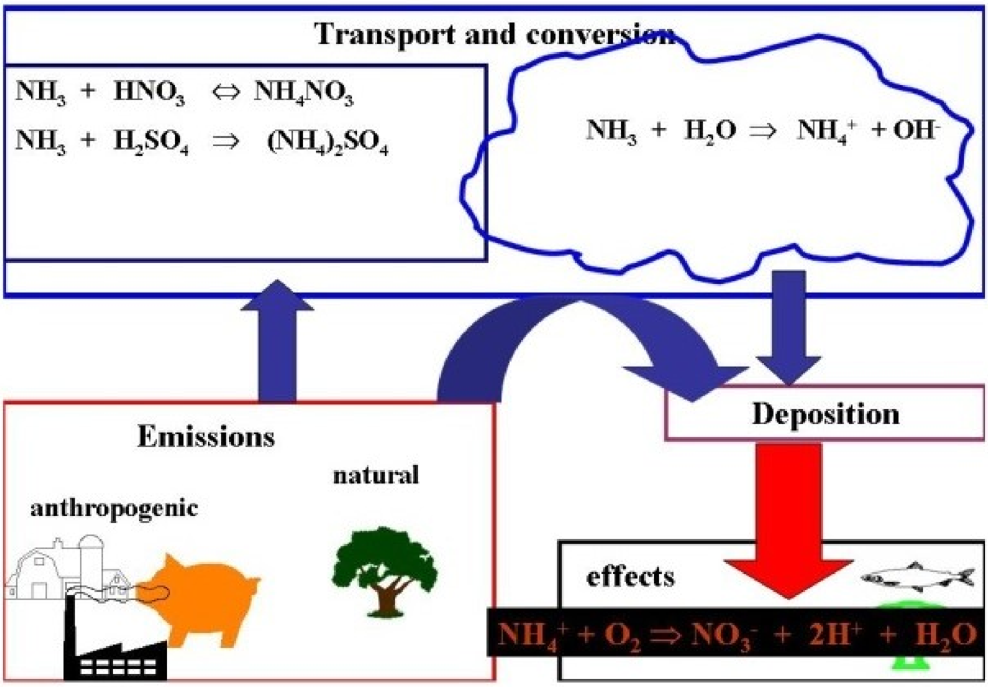

Figure 3: Conversion of NH_x

The term "adequate knowledge of deposition processes" needs defining. The uncertainties in the estimates of emissions, in description of transport and of deposition processes, contribute to the over-all uncertainty in source-receptor relations. Some of these uncertainties, especially in dry deposition fluxes, were until recently very large, often in the order of 100 to 250 %. Under conditions of large exceedance of critical loads, these uncertainties are not a problem regarding environmental policy. But as abatement measures are implemented and the costs of environmental measures increase exponentially, these uncertainties must be reduced in order to develop cost-effective environmental policy.

2. Emissions

A recent compilation of estimates of global sulfur emissions, by different authors can be found in Table 3 of the Chapter on sulfur. According to these estimates anthropogenic contributions are in the order of 75% of the total S emissions. Most authors agree that anthropogenic emissions exceeded the natural emissions as early as 1950.

Important natural sources are volcanoes and DMS (dimethylsulfide, $(CH_4)_2S$) emissions from the oceans. Fossil fuel use in industry, fuel production in refineries and electricity generation are the main activities responsible for the anthropogenic emissions.

According to EMEP studies, the maximum of sulfur emissions in Western Europe occurred in the period 1975 to 1980, at a level of 40 million tons of SO_2. The emissions have gone down since and are currently at a level of about 30 million tons of SO_2.

NO_x emissions were estimated on a global scale to be about equally divided between anthropogenic and biogenic sources according to former publications. Recent compilations (see emission tables in *Oxidized and Reduced Nitrogen in the Atmosphere*) argue that anthropogenic contributions are already much higher than the natural emissions. And it must be kept in mind that though biomass burning can occur due to natural causes, most of these emissions are tied in with agricultural activities in South-America and Africa.

In Western Europe and the North America traffic is the main source for NO_x, contributing 50% or more of the total NO_x emissions in these parts of the world.

Ammonia should be mentioned in the same cadre as sulfur and oxidized nitrogen compounds. Ammonia is a base but this compound is in most cases rapidly converted to nitrate in the soil due to the activities of microorganisms. So ammonia contributes to acid deposition, in fact one molecule of H^+ is produced in the soil for each molecule of ammonia, which is converted to nitrate.

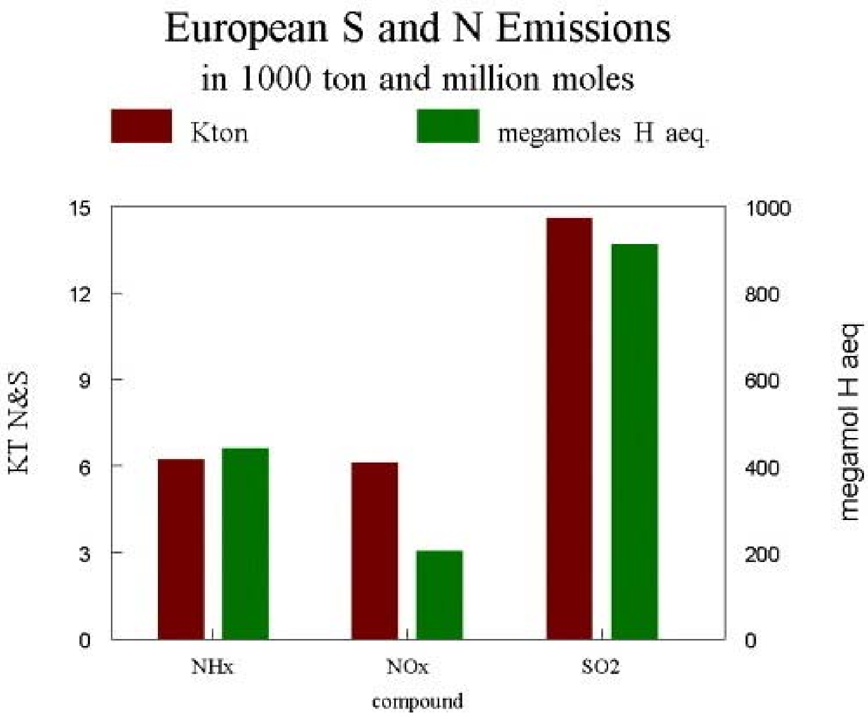

Figure 4: S and N emissions in Europe plus produced acid according EMEP

The main sources of ammonia are cattle manure and fertilizer.

The global emissions of ammonia are very uncertain. The European emissions are estimated to be around 6000 kiloton per year. In some parts of Europe, e.g. Denmark but especially The Netherlands, the ammonia emissions are very high (about 215 kt of ammonia for The Netherlands) and the contribution to acid deposition of ammonia in The Netherlands is nearly 50 %).

An overview of European emissions for SO_x, NO_x, and NH_x, both expressed in kiloton and in million moles H^+ equivalent is given in Figure 4. In terms of emitted moles or H^+ equivalents, sulfur is still the dominating species, but expressed as moles, the contribution of NH_x already outweighs the NO_x emission.

The future global development of SO_x, NO_x, and NH_x emissions will be dominated, if emission patterns do not change, by the emissions of developing countries and especially of East Asia. It is a reasonable assumption that Chinese NO_x emissions will equal the American emissions within 20 to 25 years if the fast economic development of China goes on at the present rate.

3. Atmospheric Transport and Chemical Conversion

Most of sulfur dioxide is emitted through the stacks of industries, refineries and power plants. SO_2 in the emission plumes is diluted by turbulent diffusion. High surface concentrations of sulfur dioxide in the vicinity of large sources constitute a health problem and this situation is e.g. encountered in cities of developing countries, especially where coal is used as fuel.

Sulfur dioxide is converted both in the gas phase in the atmosphere as well as in dissolved state in mainly cloud and fog droplets.

An over view of the most important processes is given in *Sulfur Dioxide and Sulfur Cycles*
.
The most important reactions are given below:

The gas phase conversion starts with reaction with the OH-radical followed by formation of a HO_2 radical

$$SO_2 + OH\cdot \Rightarrow HOSO_3 + O_2 \Rightarrow HO_2\cdot + SO_3$$

$$SO_3 + H_2O \Rightarrow H_2SO_4$$

The speed of gas phase conversion can vary from a few tenths of percent to a 10 percent per hour, depending on OH-radical concentrations and other factors.

The really critical point is the initial and rate determining reaction of SO_2 with OH-radicals. As will be shown later, the conversion of NO_2 also starts with a reaction with the OH-radical, so sulfur and nitrogen compounds compete with each other leading to non-linear behavior of conversion as function of the concentrations of sulfur dioxide and nitrogen oxide compounds.

The conversion in the water phase starts with uptake of SO_2 in droplets and the formation of sulfurous acid.

$$SO_2 \Leftrightarrow SO_{2(aq)} + H_2O \Leftrightarrow H_2SO_3 \Leftrightarrow H^+ + HSO_3^-$$

So, SO_2 uptake is dependent on the next equilibria. If the H^+, formed by dissociation of sulfurous acid is taken away, e.g. by reaction with ammonia or carbonates, more sulfur dioxide is dissolved. If on the other hand high H^+ concentrations are present, e.g. by uptake of nitric or hydrochloric acid or the formation of sulfuric acid, the uptake of SO_2 is inhibited.

Next H_2SO_3 is oxidized:

$$H_2SO_3 + O_3/H_2O_2/O_2 \Rightarrow H_2SO_4 \Rightarrow 2H^+ + SO_4^{2-}$$

Oxidation by oxygen is only possible when suitable catalysts such as Fe (III) or MN(II) species are present. The reaction with ozone is fast at low H^+ concentrations but slow in acid conditions. Sulfur dioxide reacts fast with hydrogen peroxide independent of the pH of the drop.

Two points are in general critical: The pH of the cloud droplets determines the uptake of SO_2 in the droplet as lower pH means that the equilibrium is displaced towards SO_2 .

The next critical stage is the oxidation of sulfite to sulfate and the question whether sufficient hydrogen peroxide and ozone is available.

Nitrogen dioxide is oxidized in the gas phase only (see *Oxidized and Reduced Nitrogen in the Atmosphere*) as both NO and NO_2 are very sparingly soluble in water.

The basic reaction in daytime is:

$$NO_2 + OH\cdot \Rightarrow HNO_3$$

The reaction rate of NO_2 with OH-radicals is higher compared to SO_2 in summer time.

The main atmospheric reaction of ammonia is to form ammonium salts with sulfuric acid and under the right conditions with nitric acid.

$$2\ NH_3 + H_2SO_4 \Rightarrow (NH_4)_2SO_4$$

Respectively

$$NH_3 + HNO_3 \Leftrightarrow NH_4NO_3$$

The latter equilibrium is influenced by NH_3 and HNO_3 concentrations, the stability of ammonium nitrate increases at lower temperatures and higher relative humidities

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Bibliography

Commission of the European Community (2005) Report on The Communication on Thematic Strategy on Air Pollution and The Directive on “Ambient Air Quality and Cleaner Air for Europe” (Café Report) [this reports discusses effects of acid deposition in detail plus different abatement scenarios. Latest estimates of exceedances can be found here]

Coordination Centre of Effects (EU) (2005) European Critical Loads and Dynamic Modeling. [The reader finds here the latest information and background material on critical loads. At the site www.rivm.nl/cce/ There are a number of reports available explaining how critical loads are calculated in great detail].

EMEP, (2000) Summary Report: Transboundary acidification and eutrophication in Europe, ; Det Norske Meteorologiske Institutt; Norwegian Meteorological Institute; Research Report no. 101 [here complete information regarding deposition loads is found**. At** www.emep.int or www.dnmi.no (web site of EMEP) the reader can find a lot of general information on atmospheric chemistry, emissions in Europe, deposition and exceedance of critical loads etc.].

Finlayson-Pitts, B. J., and J. N. Pitts (2000), *Chemistry of the Upper and Lower Atmosphere* Academic Press, New York. 969 pp. [General information and education in atmospheric chemistry]

J.P. Hettelingh, R.J. Downing and P.A.M. de Smet, editors, (1991), Mapping critical loads for Europe, CCE technical Report No 1, [explaining in detail the approach for calculating critical loads , the site

Slanina, J. (ed) (1997).Biosphere – *Atmosphere Exchange of Trace Gases and Pollutants in the Troposphere.* Springer-Verlag, Berlin, 528 pp. [This book contains a number of scientific contributions from the EUROTRAC project, addressing natural emissions from the biosphere, dry-deposition, and their measurement. Behavior of selected sulfur compounds as well as a number of other important trace gases is described.]

T. E. Graedel, P.J. Crutzen, (1993) *Atmospheric Change; An Earth System Perspective*, W.H. Freeman and Company, New York, 446 pp. [General information and education in atmospheric chemistry. The reader should not be deterred by the unorthodox ordering of the subject in this book]

Biographical Sketches

J. Slanina , born 22-4-1942 in Heerlen, The Netherlands, studied analytical chemistry at the University of Utrecht in the period 1962 to 1968. He held a position as scientist at the same university between 1968 and 1972 and obtained his PhD there. He worked from 1972 to 2004 at the Netherlands Energy Research Foundation as project leader and head of the department of Environmental Research. He was from 1994 to 2005 a part-time full Professor at Wageningen University, The Netherlands, and holds now a Professorate in Air Pollution at Peking University, China.

Prof. Slanina has written over a hundred articles on air pollution problems, he has participated in scientific coordination of many international research projects and Dutch National Programs.

Anton Eliassen was born 16 November 1945. He graduated from the University of Oslo in 1970. After compulsory army service he started his professional career at the Norwegian Institute for Air Research (NILU) in 1972, where he studied physical and chemical processes related to the long range transport of sulfur in the atmosphere as part of a major project initiated by OECD. In 1978 he came to the Norwegian Meteorological Institute (DNMI) to lead the Meteorological Synthesizing Centre West (MSC-W) of EMEP.

Eliassen directed the research department at DNMI from 1983. In 1984 he was appointed professor (adjunct) in meteorology at the University of Oslo, where he lectures in turbulence and diffusion processes. In 1989 he became Director of the Meteorological Department at DNMI, a department which carries the operative responsibilities. In 1997 he was appointed Deputy Director General of DNMI and presently he serves as Director General. From 1995 he is a member of the board of directors of NILU.

Prof. Eliassen has led Norwegian research council committees on Geophysical sciences and on Acid rain, and has served on the Main committee for natural sciences. From 1997 he chairs the Norwegian Climate Research Committee. Since 1986 he has also led a Nordic Council of Ministers (NMR) committee on transboundary air pollution. He is currently Vice President of the Commission of Atmospheric Sciences (CAS) of the World Meteorological Organization. He was elected to the UNEP Global 500 Honour roll in 1989, in recognition of outstanding practical achievements in the protection and improvement of the environment.