

AN ESTIMATION OF THE ATMOSPHERIC INPUT OF ACIDIFYING
SUBSTANCES TO A FOREST ECOSYSTEM

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ABSTRACT

Acidifying substances are compounds capable of increasing the hydrogen ion activity in the ecosystem. They are deposited to vegetation and soil in different forms (gases, particles, rain) and the deposition mechanisms are extremely complex. However, to evaluate possible effects of the deposition of acidifying substances to an ecosystem, the quality and quantity of atmospheric input must be known, as well as the pathways by which the deposition takes place.

This paper gives a brief description of the occurrence of acidifying substances in the atmosphere, the essential pathways, and the mechanisms for deposition of anthropogenic nitrogen and sulphur compounds.

The paper also presents a rough estimate of the total input, i.e. a deposition budget, of these compounds to a coniferous forest ecosystem in southern Sweden.

AN ESTIMATION OF THE ATMOSPHERIC INPUT OF ACIDIFYING SUBSTANCES TO A FOREST ECOSYSTEM ^{x)}

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INTRODUCTION

The term 'acid precipitation' gives the impression that the acid in rain and snow is the only input of acidifying substances to an ecosystem. This is wrong. Acidifying substances, i.e. compounds that might increase the hydrogen ion activity in the ecosystem, will be deposited also in other forms. Moreover, the substances are not necessarily acidifying immediately on entering the ecosystem. This means that the acidifying properties may not be developed until after deposition. Sulphur dioxide will e.g. be less acidifying than its oxidation product, sulphuric acid. To avoid misunderstandings in the following we will use the expression 'deposition of acidifying substances'.

To evaluate the effects of the deposition of acidifying substances to the ecosystem the atmospheric input must be known qualitatively and quantitatively, together with the pathways by which the deposition takes place. The deposition mechanisms for acidifying substances are extremely complex and involve different compounds, different forms for the deposition (gas, particles, rain), and different pathways for further transport, incorporation and turnover in the ecosystem. Moreover, the factors affecting these different flows vary, and a change in one factor might change the deposition flows radically. Consequently, it is extremely difficult to make a detailed deposition budget which both describes the deposition of the different acid compounds to a terrestrial ecosystem and the pathways for deposition. So far, a broad approach to this problem has not been made. Instead, most of the efforts have been concentrated on two processes only: sulphur input by precipitation and sulphur dioxide deposition to

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vegetation during dry conditions in daylight.

The aim of this contribution is:

- (1) to describe briefly the essential pathways for deposition of nitrogen and sulphur compounds, and
- (2) to give a rough estimate of the total input of these compounds to a coniferous forest ecosystem in southern Sweden.

The description will cover only man-produced nitrogen and sulphur pollutants. The input of nitrogen through nitrogen fixation or the different turnover reactions in the soil leading to e.g. reemission will therefore not be considered here.

In order to reduce the number of factors to be handled, we have chosen the coniferous ecosystem since the conifers are winter-green. Furthermore, effects of acidification may be expected to occur earlier in a coniferous forest than in a deciduous forest.

THE OCCURRENCE OF ACIDIFYING SUBSTANCES IN THE ATMOSPHERE

What compounds should be considered in a budget for deposition of acidifying substances? It is obvious that the anthropogenic nitrogen and sulphur compounds and their reaction products are the most important.¹ In addition to these compounds, hydrochloric acid seems to be the only substance that might give an acid input in the form of strong acid. The possible influence of hydrochloric acid will be discussed below.

The acidifying substances occur in the atmosphere either as gases or as suspended material (solids, liquids, or aqueous solutions). The suspended material covers a very wide size range: from the smallest particles (e.g. condensation nuclei), via larger particles, fog and mist to rain and snow. The sulphur and nitrogen compounds of interest occur in all these forms.

The only gaseous sulphur compounds occurring in significant concentrations in the atmosphere are sulphur dioxide and hydrogen sulphide. Other compounds, such as carbonyl sulphide, carbon disulphide and dimethyl sulphide may occur but in concentrations at least one order of magnitude lower.²

Hydrogen sulphide and sulphur dioxide are either deposited directly as gases or oxidized to sulphates in the atmosphere and then deposited with precipitation or particles. The sulphur dioxide oxidation will occur mainly as a photochemical or cataly-

tic reaction. The photochemical reaction appears in gas phase but the reaction product (sulphur trioxide or sulphuric acid) will rapidly take up water vapour and form a droplet. The catalytic reaction takes place in water phase only, which means that the gas has to be absorbed to a particle or a raindrop before oxidation.

The mean atmospheric concentrations of sulphur dioxide, hydrogen sulphide and particle-borne sulphate in a rural area of southern Sweden are presented in Table 1.

Table 1

Typical concentrations of acidifying substances in gas phase and on particles in the atmosphere in southern Sweden.

Compound		Concentration nmole/m ³	References
Gases	SO ₂	200	3, 4
	H ₂ S	5	5
	NO	50	6
	NO ₂	150	6
	HNO ₂	3	7
	HNO ₃	40	8
	NH ₃	10	9
Particles	SO ₄ ²⁻	60	4
	NO ₃ ⁻	20	4
	NH ₄ ⁺	100	4

The picture is more complex for nitrogen compounds. Anthropogenic nitrogen oxides are mainly emitted as nitrogen monoxide. In the atmosphere this compound is oxidized to nitrogen dioxide and further to other products of which nitric acid is predominant. Nitrogen monoxide and nitrogen dioxide exist as gases while nitric acid (nitrates) occurs both in gas phase and in suspended material (particles and precipitation). The presence of nitric acid in gas phase has been almost neglected so far.⁸ However, recent data indicate that it is important and that the concentration in rural areas in Sweden is approx. 40 n mole/m^3 ^{x)}.⁸ This means that there is more nitrate in gas phase than on particles. Fig. 1 shows the concentration of gaseous and particulate nitrates at a rural station in Sweden.

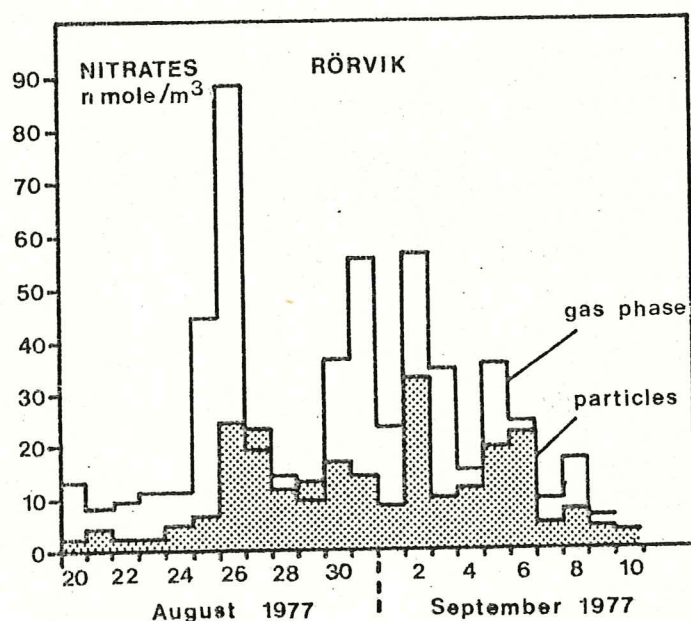


Figure 1. Concentrations of particulate and gaseous nitrates at a rural station (Rörvik) on the Swedish west coast during Aug. 20 - Sept. 10 1977.

x) In this paper concentration of atmospheric pollutants is denoted in n mole/m^3 . For conversion to ppb at STP, multiply by 0.0224.

Nitrite will probably occur in gas phase only. Measurements in England indicate that the nitrite concentration is much lower than the concentration of gaseous nitrate.⁷

In addition to the oxidized nitrogen compounds, ammonia is an important constituent of the atmosphere. By forming neutral ammonium sulphate and ammonium nitrate aerosols it will neutralize acid particles in the atmosphere. Consequently, the concentration of free ammonia in the atmosphere depends on the acidity of the particles, *i.e.* in acid atmospheres the concentration is very low (less than 1 ppb) while concentrations up to 20 ppb have been observed in alkaline atmospheres.^{9, 10}

In Table 1 typical concentrations of nitrogen compounds in gas phase and on particles in Sweden are presented.

DEPOSITION PROCESSES

The vegetation is the primary recipient for most pollutants on their way from the atmosphere into the terrestrial ecosystem. However, the vegetation is not a passive participant in the transfer of pollutants into the ecosystem but will take an active part in the deposition process. Both the amount and the chemical composition of deposited pollutants are strongly dependent on the properties of the vegetation surfaces.

Deposition of any pollutant to vegetation is determined mainly by the following factors:

- atmospheric concentration and form of the compound
- atmospheric turbulence and wind speed
- canopy characteristics (composition, height, density, roughness, leaf area index)
- surface wetness (snow, wet, dry)
- stomates (size and number, opened or closed).

In a deposition budget it is necessary to exclude the least important factors, *e.g.* stomatal openings will not be important for deposition of particles.

Gases

Although parameters such as atmospheric turbulence and canopy density are very important for the deposition velocity of an acidifying gas, we assume that the main parameters affecting the deposition velocities are the surface wetness and the stomatal openings.

Since the deposition process for the acidifying components involves dissolution of the components in an aqueous solution, the existence of water on vegetation surfaces will strongly influence the deposition velocities.^{11, 12} However, information is scarce on the frequencies of surface wetness during a year, the amount of water on the leaves in different climatic situations, and the chemical composition of these aqueous solutions.

The importance of snow has not been considered in earlier deposition budgets. For example, in northern regions such as Canada and Scandinavia, the long duration of snow cover is probably of importance. In forest districts of southern Sweden, a typical figure of snow cover duration is 20% of the year. In northern Sweden, the corresponding figure might be 50%. These figures derive from meteorological observations and of course do not represent the time during which e.g. a forest canopy is covered with snow.

Several investigators have already concluded that the stomatal openings are limiting for the deposition velocity of sulphur dioxide during dry conditions (reviewed by 13). The influence of stomates on the deposition of other gaseous pollutants is less well known but the stomatal activity is probably of major importance also for these compounds.^{14,15,16,17}

Estimated figures of the duration of different vegetation surface situations are given in Table 2.

Table 2.

Duration in percent of the year of different vegetation surface situations of importance for the deposition of gaseous pollutants.

Vegetation surface situations	Percent of the year
Snow cover	20
No snow:	
Stomata closed	45
rain	9
wet without rain	10
dry	26
Stomata open	35
rain	3
wet without rain	2
dry	30

Particles

The smallest particles in the atmosphere behave like gases and brownian diffusion is an important process for the deposition of these particles. However, brownian diffusion becomes less important for larger particles and, instead, inertia and gravitational forces predominate. The size of the particles is, consequently, crucial for the deposition velocity. To accurately estimate the deposition of a certain compound it is therefore necessary to know both the size distribution of the particles and the deposition velocities for the different size fractions. However, the concentration of acidifying substances on particles is normally lower than in gas phase and besides, the deposition velocities are normally lower for particles than for gases.¹⁸ Consequently, in a rough deposition budget we believe it is sufficient to treat the particles as belonging to one group, i.e. it is not necessary to estimate the contribution of different size fractions.

Mist and Fog

The importance of mist and fog in deposition processes is largely unknown. Few investigations exist that deal with the amount of water deposited to a forest canopy during mist and fog situations as well as with the concentration of acidifying substances in the water. Rough estimates indicate that this deposition might be important at places where fog and mist are common.¹⁹ In Sweden, a typical figure of the fog frequency is a total of 3% of the year.

Precipitation

Deposition by precipitation (rain, snow) is the best known part of the total input of acidifying substances. Data obtained from precipitation networks are used in the deposition budget. These data normally include only sulphate and data concerning nitrogen compounds are therefore insufficient. Furthermore, the precipitation collectors are not suitable for measuring snowfall and, as a result, the data on deposition with snow are uncertain.

DEPOSITION BUDGET

Based on the inventory of acidifying substances and the deposition processes discussed above, a deposition budget for a coniferous forest ecosystem was made including all known sulphur and nitrogen compounds of expected significance. The yearly deposition in molar terms ($\text{m mole/m}^2 \text{ yr}$) as well as the total amounts of nitrogen and sulphur (kg/ha yr) are summarized in Table 3.

Table 3

Typical quantities of atmospheric sulphur and nitrogen compounds deposited to a coniferous forest ecosystem in rural areas of southern Sweden.

		Deposition mmole/m ² yr	S-deposition kg/ha yr	N-deposition kg/ha yr
Gases	SO ₂	32	10.2	
	H ₂ S	<0.5	<0.2	
	NO	<3		<0.4
	NO ₂	24		3.4
	HNO ₂	<0.5		<0.1
	HNO ₃	8		1.1
	NH ₃	<2		<0.3
Particles	SO ₄ ²⁻	9.5	3.0	
	NH ₄ ⁺	16		2.2
	NO ₃ ⁻	3.2		0.4
Mist and fog	SO ₄ ²⁻	2.5	0.8	
	NH ₄ ⁺	1.7		0.2
	NO ₃ ⁻	1.7		0.2
Precipitation	SO ₄ ²⁻	30	9.6	
	NH ₄ ⁺	20		2.8
	NO ₃ ⁻	20		2.8
			23.6-23.8	13.1-13.9

To obtain values of the yearly deposition of the different gases, we started with sulphur dioxide for which literature data on deposition velocities during different situations are available.¹³ From the different vegetation surface situations in Table 2 we have obtained five "deposition classes". For each class given in Table 4, a deposition velocity is assumed, based on literature data. The deposition velocities are presented in Table 4. These data are "qualified guesses" of probable deposition velocities.

When treating the other gaseous compounds, in cases where no literature data exist, we have assumed that their deposition velocities depend on their solubilities in water.¹⁴ Moreover, we have assumed that there is a fixed relation between their deposition velocities and the deposition velocity of sulphur dioxide independent of deposition class. The ratios chosen are 0.5 for hydrogen sulphide, 0.06 for nitrogen monoxide,¹⁷ 0.67 for nitrogen dioxide,¹⁷ 0.67 for nitrous acid, 1.0 for nitric acid, and 0.5 for ammonia.

When calculating the yearly deposition of gaseous compounds we determined the deposition for each vegetation surface situation (see Table 2) using vertical deposition velocities according to Table 4 and mean concentrations for the different situations when such data were available. The different contributions to the total deposition are presented in Table 3.

Table 4

Estimated vertical deposition velocities for sulphur dioxide to a forest canopy.

"Deposition class"	Deposition velocity, m/s	References
Snow cover	0.005	20
Stomata closed, dry canopy	0.001	
Stomata closed, wet canopy	0.10	
Stomata open, dry canopy	0.008	11, 21
Stomata open, wet canopy	0.15	11

Concerning particles, we have not gone into details as very little is presently known about how the deposition velocities depend on different parameters. We have used a deposition velocity of 0.005 m/s for all particles and typical concentration data for the southern parts of Sweden (see Tables 1 and 3).

For fog and mist, we have used the calculations of Unsworth¹⁹ but translated them to the situation in Sweden. We used the fog frequency 3% and a deposition velocity of 0.20 m/s.²² The deposition of sulphate, nitrate, and ammonium is presented in Table 4.

For precipitation, we used representative rainwater data for southern Sweden.⁴

DISCUSSION

From this presentation it is clear that the different atmospheric transformations and the different pathways through which the deposition takes place give a very complex picture. The chemistry of deposition to a leaf surface is presented in Figure 2. As will be seen from this figure, we are not dealing with flows only from the atmosphere to the vegetation but, under certain conditions, some compounds will be reemitted to the atmosphere. Some of the flows are speculative, e.g. the flow of nitrogen dioxide to the surface and further through the cuticle has not been confirmed. Furthermore, the flows of ammonium and ammonia have so far not been thoroughly investigated.

As shown in Figure 2 and in the budget (Table 4) it is obviously not possible to simplify the deposition of acidifying substances to include only sulphur dioxide or the sulphate content in the precipitation. To adequately estimate the total deposition it is necessary to include several other parts of the input. The nitrogen compounds will probably give an input that, on a molar basis, is somewhat higher than that of sulphur (100 m mole/m² yr for nitrogen and 75 m mole/m² yr for sulphur).

An important question is if there are any compounds in the atmosphere, apart from the nitrogen and sulphur compounds, that can give a significant input of acid to a coniferous forest ecosystem. If we consider strong acids only, hydrochloric acid is probably the only compound of interest. However, the anthropogenic emission of hydrochloric acid is small compared to emissions of sulphur and nitrogen, and since most of the chloride existing in the atmosphere comes from neutral sea salt, it does not give any input of acids.

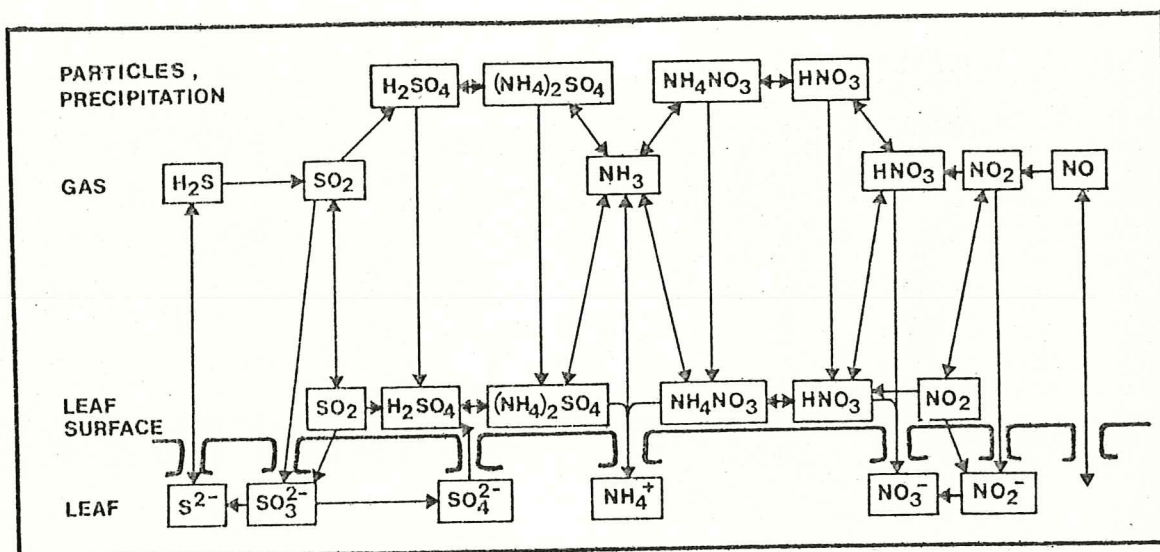


Figure 2. The flows of different nitrogen and sulphur compounds between the atmosphere and a leaf surface.

The budget includes only one part of the deposition problem: the deposition routes for different compounds and the quantities deposited to the vegetation surfaces. To improve our knowledge on the effects of acid precipitation it is probably necessary to include also the different ways of incorporation and the fate in the ecosystem of these compounds. This means that factors such as erosion on leaf surface, reemission, uptake and exudation of different compounds have to be considered in a complete model. The ability of the vegetation surfaces to absorb different compounds will change drastically depending on the amounts of water deposited on the leaves; this mechanism will probably also make it possible for volatile compounds such as ammonia and nitric acid to be reemitted.

For deposition models, the influence of a water phase on the canopy is in fact one of the most important issues to be solved. The problem is not only how to define the situation and how to calculate the duration of water covering the leaves, but parameters such as pH of the water phase and hygroscopy of the salts on the surfaces will also affect the deposition velocity.

There are several other factors in addition to the factors in our budget that must be considered in a complete deposition model. Among these we can mention atmospheric turbulence, canopy characteristics and surface chemistry. However, it is always necessary to make "best estimations" of the deposition in order to give priority and feed-back to deposition research and to produce input data for research on ecosystem effects and modelling.

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