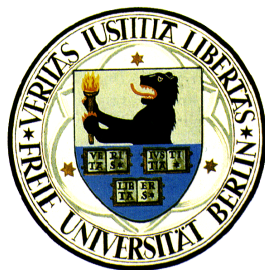


Abschlußbericht zum Forschungs- und
Entwicklungsvorhaben 298 41 252 auf dem Gebiet des
Umweltschutzes „Modellierung und Prüfung von Strategien
zur Verminderung der Belastung durch Ozon“

Aerosols in LOTOS

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16. Kurzfassung Der Bericht beschreibt die von der TNO, Niederlande, zur Bereitstellung des Aerosolmoduls MARS für das Vorhaben geleisteten Arbeiten. Es wird ein Überblick gegeben zur Physik und Chemie der anorganischen Aerosole. Das Aerosolmodul MARS wird beschrieben und in einer Boxmodellanwendung diskutiert. Erste Ergebnisse des Aerosolmoduls im Rahmen einer Anwendung im Ausbreitungsmodell LOTOS werden vorgestellt.		
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16. Abstract The report describes the work carried out by TNO, Netherlands, to deliver an inorganic aerosol module, which can be included in a large scale dispersion model. The physical and chemical properties of aerosols are reviewed. The MARS aerosol module is described. Its functioning is demonstrated in a box model application and in an application within the LOTOS dispersion model.		
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1. Introduction

Aerosols in the atmosphere have the potential to seriously affect the quality of our environment. Particles of less than 10 micrometers may after inhalation cause adverse effects on health. In addition to direct effects on the health of mankind, aerosols also affect the climate. Aerosols scatter and absorb light as a result of which they directly affect the radiation balance of the earth. Indirectly they have an effect on the radiation balance because aerosols act as condensation nuclei for clouds. The radiation balance in turn affects photochemistry. Processes on the surface of aerosols and transport of aerosols may change the chemical composition of the atmosphere. In addition the reduction of visibility by aerosols should be mentioned as a result of which for example the recreational value of nature reserves falls. Consequently, aerosols are important in issues such as climate change, air pollution and health.

By definition an aerosol is a suspension of particles in air. These particles may be solid or liquid. Cloud droplets are not classed as aerosols, although technically they meet the definition. Aerosols vary in size from ~ 1 nm to ~ 100 μm . The lower limit is arbitrary. When does a cluster of molecules behave as a gas and when as a particle? A distinction is made between three classes of particles in the size of aerosols: the Aitken mode ($d < 0.1$ μm), the accumulation mode ($0.1 < d < 1.0$ μm) and the coarse mode ($d > 1.0$ μm). Aerosols behave differently in the atmosphere depending on their size.

A distinction is also made between primary and secondary aerosols. Primary aerosols are emitted directly from the earth's surface. Wind erosion is naturally an important source of primary aerosols. These aerosols consist mainly of reasonably chemically inert substances such as quartz and minerals. Important anthropogenic sources are emissions from combustion processes, such as power stations and traffic. A lot of soot is emitted here. Secondary aerosols are formed in the atmosphere. In the conversion of gas to particle, chemical processes, nucleation and condensation play an important part. In the atmosphere the composition of an aerosol may be changed by all sorts of processes such as by chemical reactions. By particles sticking together, coagulation, the size distribution of the aerosols in the atmosphere is modified. Coagulation is the most important removal mechanism for small Aitken particles. In addition to coagulation particles are removed by dry and wet deposition and by sedimentation. Sedimentation is the most important removal mechanism for the coarse particles in the troposphere. In the stratosphere sedimentation is important for all particles, as the stratosphere is meteorologically very stable.

The purpose of this research is to incorporate aerosols in the LOTOS model of TNO. LOTOS is a photochemistry model that is used to calculate ozone concentrations in the troposphere. The stratosphere is ignored. Important secondary questions are: How are aerosols formed? How do these aerosols behave physically? Does the aerosol chemistry considered affect ozone formation?

This research only considers secondary aerosols as from a chemical point of view they are the most interesting. Unlike secondary aerosols primary aerosols are reasonably chemically inert. In aerosol chemistry only the following gases are considered: H_2SO_4 , HNO_3 and NH_3 . From these aerosols are formed consisting of (bi)sulphate, nitrate, ammonium and water. These aerosols account for around 30% of the total PM_{10} . All the other aerosols, inorganic or organic, are ignored. Aerosol physics will be discussed briefly. Clouds and cloud formation will not be included in this study. Firstly cloud formation is described diagnostically in LOTOS. In that model then no clouds condense onto aerosols. Secondly it would be too complicated to describe in a simple way.

In the research first of all the gas phase reaction mechanism will be made suitable for the implementation of aerosols. The CBM-IV mechanism used by TNO serves as a basis for this mechanism. The behaviour of the aerosol module will then be examined, after which this will be linked with the gas phase reaction mechanism. This chemistry will be put into LOTOS. In addition to chemistry, physical processes will also be described.

The most important physical processes added to LOTOS are the wet and dry deposition of particles. The aerosol concentrations in August 1997 will be simulated with LOTOS.

In the next chapter general properties of aerosols will be discussed. The aerosol cycle will be covered. In addition the chemical composition and the log-normal distribution will be discussed. Chapters 3 and 4 cover respectively the chemistry and aerosol physics. Chapter 5 discusses the box model developed and the model results. The implementation of aerosols in LOTOS and the model results are discussed in chapter 6. This report ends with conclusions and recommendations.

2. Aerosols: general properties

In this chapter a few general properties of aerosols are discussed. First of all the aerosol cycle in the atmosphere is discussed. As the size of an aerosol has a great effect on its behaviour in paragraph 2.2 the size distribution of aerosols is discussed. Surface and volume distributions are also described. In the third paragraph the chemical composition of aerosols is covered. Depending on its chemical composition and the relative humidity an aerosol is liquid or solid. This dependence is discussed for ammonium (bi)sulphate and ammonium nitrate in the last paragraph. The terms deliquescence and hysteresis will be explained.

2.1 Aerosol cycle

The particles in the Aitken mode are produced mainly by reactions between gases. A small proportion are emitted directly in the atmosphere. The products of these reactions have a low vapour pressure, as a result of which homogenous or heterogenous condensation occurs. During homogenous condensation a gas condenses from itself, unlike heterogenous condensation where a gas condenses onto an existing particle. The Aitken particles can coagulate with other Aitken particles or with bigger aerosols to thus form bigger particles. Coagulation is the most important removal mechanism for Aitken particles and the most important source of particles in the accumulation mode. In addition to coagulation of or with Aitken particles, heterogenous condensation plays a part in the formation and growth of particles in the accumulation mode. Particles may also coagulate with one another in the accumulation mode. We shall later see however that coagulation with Aitken nuclei is more effective. Particles from the accumulation mode are least effectively removed from the atmosphere. Wet deposition plays a big part in the removal of these particles. Dry deposition and sedimentation are less important for the removal of particles in the accumulation mode.

Aerosols from the coarse mode are largely emitted directly from the earth's surface. These are primary aerosols. Wind erosion is the most important source. Coarse particles consist mainly of quartz and minerals and are reasonably chemically inert. These big particles are mainly removed from the atmosphere by sedimentation. Sedimentation is the removal of aerosols under gravity. An example of the sedimentation of coarse aerosols in the Netherlands is the deposition of loess in the last ice age.

An aerosol may be transported over great distances through the atmosphere before it is removed. During its residence in the atmosphere the composition of an aerosol may be changed by chemical reactions, condensation and evaporation or by interaction with clouds.

2.2 The size distribution of aerosols

The atmosphere always contains a significant quantity of aerosols. The particle concentrations may amount to 10^8 particles cm^{-3} . Since the behaviour of aerosols, both chemical and physical, is dependent on their dimensions, it is important to know the size distribution of aerosols.

Figure 2.1 shows the size, surface and volume distributions for a typical urban aerosol. The Figure clearly shows that the largest numbers of aerosols are in the Aitken mode. If however we look at the surface or the volume, the maxima are found to be in the accumulation or in the coarse mode.

For the size distribution a log-normal distribution is often assumed for each mode. This log-normal distribution looks like the following:

$$\frac{dN}{d \ln(d_p)} = \frac{N_t}{\sqrt{2\pi \ln(\sigma_g)}} * e^{-\frac{(\ln(d_p) - \ln(d_g))^2}{2 \ln^2(\sigma_g)}}$$

Here N_t is the total particle concentration, d_p the diameter, d_g the mean diameter and σ_g the geometric standard deviation. The form of the distribution is determined by the mean diameter and the geometric standard deviation.

This size distribution can be converted into other distributions such as the surface distribution and the volume distribution:

$$\text{surface distribution: } \frac{dS}{d \ln(d_p)} = \frac{dN}{d \ln(d_p)} * \pi d_p^2$$

$$\text{volume distribution: } \frac{dV}{d \ln(d_p)} = \frac{dN}{d \ln(d_p)} * \frac{\pi}{6} d_p^3$$

In Figure 2.1 the log-normal distributions are extended with a dotted line. The mass distribution can be calculated by multiplying the volume distribution by the density of the aerosol.

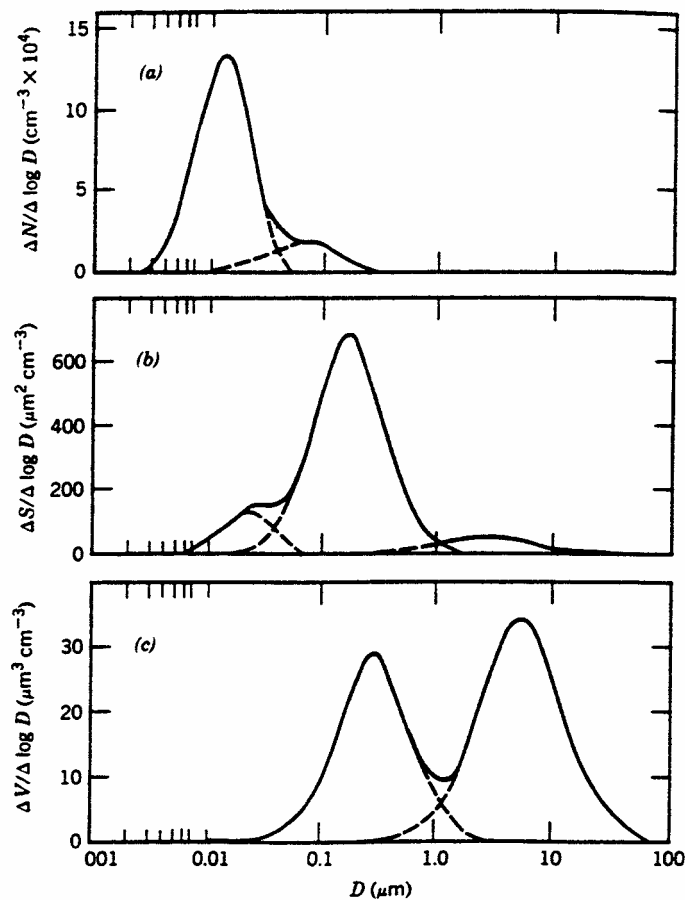


Figure 2.1 Size-, surface and volumedistributions of a typical urban aerosol.
Source: Witby and Sverdrup, 1980.

2.3 The chemical composition of aerosols

The chemical composition of aerosols is complex and not completely known. The literature makes a distinction between three groups of substances: soluble salts, insoluble minerals and organic substances, soluble and insoluble. This relates to solubility in water. The composition of marine aerosols differs from that of continental aerosols. Continental aerosols are often broken down into rural and urban aerosols.

Table 2.1 shows for rural and urban aerosols the distribution over the classes mentioned. The samples for this determination were taken in Germany. A large fraction appears to be insoluble in water. The inorganic soluble and the organic soluble fraction contribute equally to this. An aerosol consists of approx. 30% insoluble minerals. Compared with this the insoluble organic fraction is small. These values are average values. The composition of an individual aerosol varies considerably.

Table 2.1 Classification of European continental aerosols
Source: Warneck, 1988

Component	Massfraction (%) Urban (Mainz)	Massfraction (%) Rural (Deuselbach)
Soluble fraction (total)	58	68
Soluble salts	30	43
Soluble organics	28	25
Insoluble organics	5	6
Insoluble minerals	35	25

Figure 2.2 shows for rural aerosols the ratio between the soluble and the insoluble fraction as a function of the diameter of the aerosols. The diameter classes used in the figure cover the accumulation mode and the coarse mode. As the aerosol becomes smaller, the soluble fraction seems to get bigger. If this trend is extrapolated to the Aitken mode a particle with a diameter of less than $0.1 \mu\text{m}$ would consist for more than 90% of soluble substances.

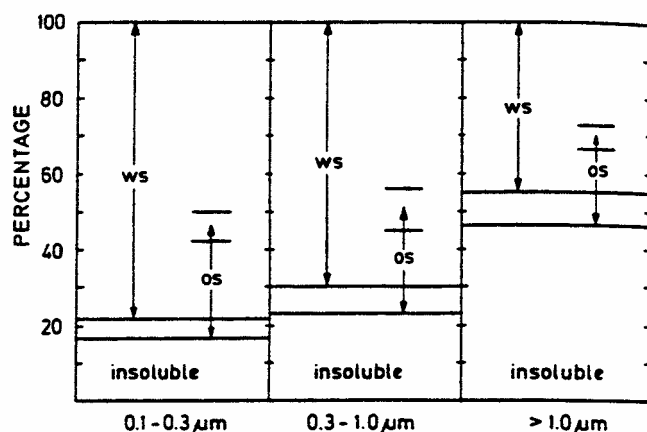


Figure 2.2 Distribution of soluble and in-soluble fraction of rural aerosols (Deuselbach, Germany)
ws: soluble in water, os: soluble in organic solvents. Source: Warneck, 1988.

Sulphate is the commonest component of aerosols. Maritime aerosols are the only exception to this. Maritime aerosols consist largely of sodium chloride. In soluble continental aerosols the mass fraction of sulphate varies between 22 and 45% (Warneck, 1988). Figure 2.3 gives the mass distribution of a few water-soluble components. Sulphate is concentrated in the particles smaller than $1 \mu\text{m}$. Figure 2.3 also shows that ammonium is the most important cation that is associated in continental aerosols with sulphate.

The peak at $0.3 \mu\text{m}$ can be explained by the fact that at this size, accumulation by coagulation and condensation is most effective (see chapter 4). From this one can conclude that the sulphate and ammonium come from gas-particle conversions,

namely the neutralisation of sulphuric acid by ammonia. The degree of neutralisation depends on the quantity of ammonia with respect to the quantity of sulphuric acid. When there is an excess of ammonia, nitric acid is also neutralised. Mass fractions of nitrate in soluble aerosols vary between 6 and 22% (Warneck, 1988). Figure 2.3 shows that nitrate in Deuselbach is much more homogeneously distributed over the aerosol spectrum. Ammonium neutralises around 80% of the sulphuric acid and nitric acid in aerosols.

In the right hand illustration in Figure 2.3 the load balance is given. There is a deficit of cations at the point where ammonium and sulphate concentrations show a maximum. This deficit is filled up by protons. The deficit thus indicates the degree of acidity of the aerosols.

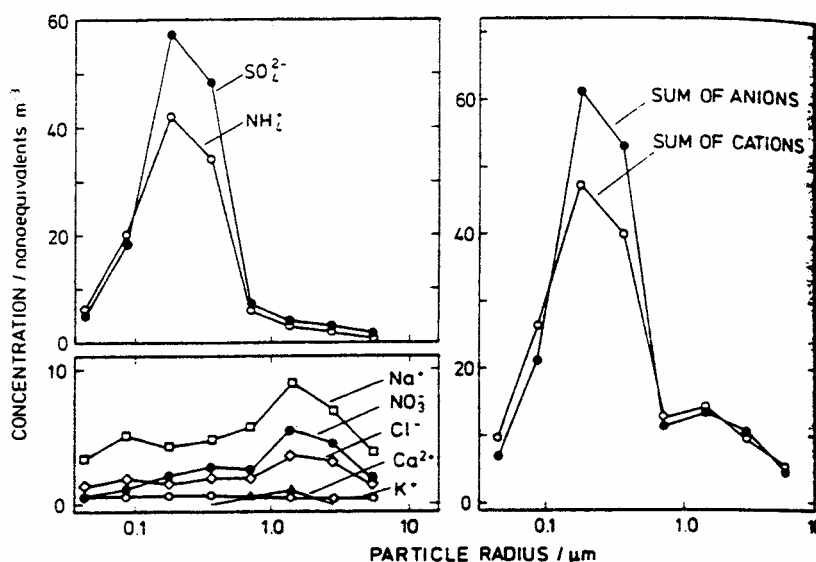


Figure 2.3 Mass-distribution of individual anions and cations of rural aerosols in Deuselbach, Germany.

Left: Contribution of individual ions. Right: Load balance.

Source: Warneck, 1988.

In the above an impression is given of the mass fractions of sulphate, ammonium and nitrate in soluble aerosols. To give an impression of the aerosol concentrations in the Netherlands, in Table 2.2 for 1996 the annual mean concentrations of sulphate, ammonium and nitrate and where possible PM_{10} are set out (RIVM, 1998 (RIVM: Dutch National Institute of Public Health and the Environment)). These measurements come from the National Air Quality Monitoring Network (Landelijk Meetnetwerk Luchtkwaliteit - LML). Nitrate and sulphate concentrations in the Netherlands are of the same order of magnitude. On average the nitrate concentration is even greater than that of sulphate. The measurements show also that sulphate, ammonium and nitrate account for a substantial part of the total PM_{10} .

Table 2.2 Yearly averaged concentrations ($\mu\text{g}/\text{m}^3$) of the components in 1996 at 7 LML-stations

Station	SO ₄	NO ₃	NH ₄	PM ₁₀	SO ₄ +NO ₃ +NH ₄ /PM ₁₀
Bilthoven	4,9	5,9	3,1		
De Zilk	4.6	4,8	2,8	41	0,30
Huijbergen	3.2	3,1	2,0		
Kolummerwaard	4.2	4,8	2,6		
Vredepeel	3.2	3,9	2,1	43	0,21
Wieringerwerf	4.4	5,0	2,8	43	0,28
Witteveen	3,4	3,6	2,1	35	0,26

In the early nineties Ten Brink (1997) measured the composition of continental aerosols as a function of the diameter on summer days in Petten. Figure 2.4 shows the measured average concentrations of sulphate, nitrate and ammonium. The size distributions of sulphate and ammonium correspond well with the distribution measured in Deuselbach. The nitrate distribution in the Netherlands is however completely different from that in Deuselbach. It can be concluded from the size distribution of nitrate and ammonium that in the Netherlands nitrate is mainly associated with ammonium. The available measurements also showed that ammonium sulphate and ammonium nitrate accounted for around 50% of the total particle mass smaller than 1 μm (Ten Brink, 1997).

In short, if one only considers secondary aerosols of sulphate, nitrate and ammonium, one covers a large proportion of the secondary aerosols smaller than 1 μm in the atmosphere and also a substantial part of total PM₁₀. This system also seems to be a good first approximation for the secondary aerosol load of particles in the Aitken and the accumulation mode.

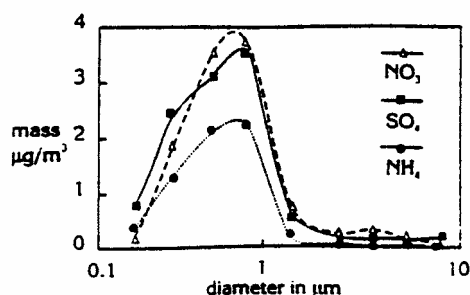


Figure 2.4 Averaged sulphate, nitrate and ammonium concentrations as function of size for continental aerosols in the Netherlands under summer conditions

2.4 Deliquescence and hysteresis

Ammonium sulphate and ammonium nitrate are hygroscopic. Aerosols that contain these substances will absorb water under wet conditions. Because of this absorption the aerosol will grow. The hygroscopicity of an aerosol has a great influence on its

physical properties and on cloud formation and thus on its life time in the atmosphere.

At low relative humidities an aerosol is dry and crystalline. By increasing the humidity a small quantity of water will be adsorbed on the surface of the particle. The quantity of water is too small to dissolve the particle and the particle remains largely crystalline. The size of the particle will increase little.

If however a certain relative humidity is reached, aerosols, consisting of non-infinitely soluble components, are subject to deliquescence. Infinitely soluble substances are miscible in all ratios with water and are thus not subject to deliquescence. These substances, for example sulphuric acid, absorb water at any degree of humidity.

Deliquescence is a rapid phase transition from a solid particle to a liquid droplet, when a certain relative humidity is reached. As much water is taken up as is necessary to achieve a saturated solution. This humidity is called the relative humidity of deliquescence (RH_d). The relative humidity of deliquescence of a substance is the relative humidity above a saturated solution of this substance and is hence a substance property.

An aerosol consisting of several salts also behaves as described above. When the humidity is increased first the relative humidity of the most soluble component is reached. Water is taken up until a saturated solution of this component has been created. The other salts will partly dissolve, so that they meet the thermodynamic equilibrium. When the humidity is increased further the relative humidity of deliquescence of a second component is reached, as a result of which the above process is repeated. The relative humidity of deliquescence of a substance in a mixture is lower than that of the same pure substance.

After deliquescence upon further increase in the relative humidity the droplet will grow in accordance with Köhler's equation.

When the relative humidity falls again, the water content will decrease. However, at the relative humidity of deliquescence the particle does not crystallise, where one would theoretically expect that. An unsaturated droplet remains. Only with a relative humidity far below the relative humidity of deliquescence does crystallisation occur. This phenomenon is called hysteresis. The relative humidity at which crystallisation occurs (RH_c) is also a substance property. Table 2.3 includes a few values for the RH_d and the RH_c .

Due to hysteresis it is possible to predict which phase a particle is in. For a good prediction it is necessary for the history of the particle and the relative humidity to be known.

Table 2.3 RH_D and RH_c -values at roomtemperatures
Source: Pilinis e.a. 1989.

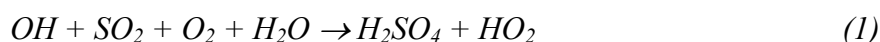
Zout	RH_d (%)	RH_c (%)
$(NH_4)_2SO_4$	80	39
$(NH_4)HSO_4$	39	2
NH_4NO_3	62	<10

3. Secondary aerosol formation

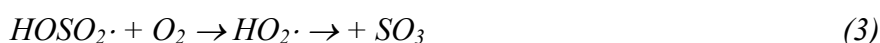
Reactions between gases in the atmosphere cause the formation and growth of secondary aerosols. An important source of aerosols is the neutralisation of (gaseous) sulphuric acid and nitric acid by ammonia. In particular ammonium (bi)sulphate and ammonium nitrate aerosols are formed. The concentrations and the phase of the aerosols are dependent on the concentrations of the reactants, the relative humidity and the temperature. In this chapter first of all the formation of sulphuric acid and nitric acid in the gas phase will be discussed. Then the aerosol chemistry used in this study will be covered.

3.1 Sulphuric acid formation

Sulphuric acid in the atmosphere is formed by the oxidation of sulphur dioxide. By far the most important oxidator in the gas phase is the hydroxyl radical. The net reaction equation is:



The first step is the reaction of OH with sulphur dioxide. This is also the rate-determining step in the reaction mechanism.



Sulphuric acid has a very low vapour tension as a result of which the concentration of sulphuric acid in the gas phase is very low. The sulphuric acid formed will condense directly or react with a base. Roughly all the oxidised sulphur dioxide will become aerosol sulphate.

Except in the gas phase sulphur dioxide can also be oxidised in clouds. Sulphur dioxide then dissolves in cloud droplets. In the droplet sulphur dioxide reacts with hydrogen peroxide or ozone. Catalysed by metals sulphur dioxide can also be oxidised by oxygen into sulphate (Restad et al, 1998). When air flows through clouds the composition of this air will then be modified. Laj et al (1997) observed that the sulphate content of aerosols increases significantly if they flow through a cloud. However this process has not been included in this study as cloud chemistry is not being studied yet.

3.2 Nitric acid formation

Nitric acid in the atmosphere acts as a sink for NO_x . Nitric acid may be formed from gas-gas reactions and from heterogenous reactions. Figure 3.1 gives a schematic view of the chemistry of nitrogen oxides. This diagram shows that nitric acid is formed and broken down by various reactions. In addition to the reactions shown nitric acid is also formed by reactions of NO_3 with organic hydrocarbons. In this paragraph the gas phase chemistry of nitric acid is covered. The equilibrium between nitric acid and aerosol nitrate and dry and wet deposition is discussed later.

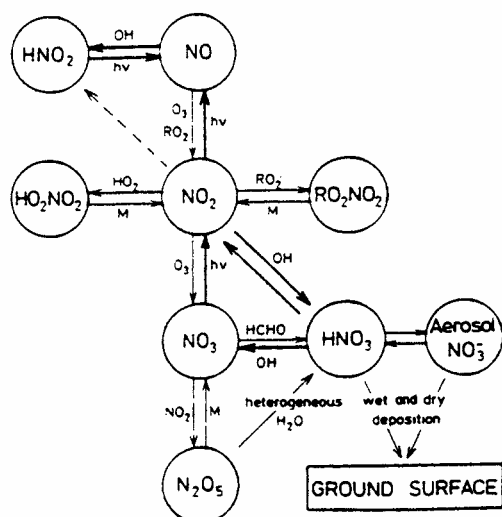


Figure 3.1 Schematic overview of the chemistry of nitrogen oxides
Source: Warneck, 1988

By day the reaction of NO_2 with OH is the most important removal mechanism for NO_x and hence the most important source of nitric acid:



Nitric acid reacts with OH to form water and NO_2 :



Part of the nitric acid formed will be converted by photolysis back into NO_2 and OH :



The photolysis rate in the troposphere is however so small that the majority of the nitric acid is removed by dry and wet deposition (Dentener and Crutzen, 1993). Also the reaction rate of reaction 7 is lower than the removal rate of nitric acid by dry and wet deposition. At night these reactions are not significant because they are dependent on photolysis.

As at night the rapid photolysis of NO_3 also stops, the formation of this radical becomes important. NO_3 is in equilibrium with N_2O_5 . This equilibrium is very temperature-dependent. At low temperatures the equilibrium is on the side of N_2O_5 . NO_3 may react with aldehydes and substituted benzenes (Warneck, 1988). Nitric acid is formed by this. In the CBM-IV mechanism the aldehydes are identified as formaldehyde (FORM) and other aldehydes (ALD). These aldehydes react as follows with NO_3 :



Phenols and cresols (PHEN) react as follows with NO_3 :



The CBM-IV mechanism also includes the substance methyl glyonate, MGLY. Methyl glyonate is a decomposition product of alkanes, acetylene, isoprene and aromatics. Methyl glyonate also reacts with NO_3 to form nitric acid:



In most cases the reactions of NO_3 during the night cannot explain the short atmosphere life time of NO_3 measured (Dentener and Crutzen, 1993). Platt et al. (1984) observed that the shorter life time of NO_3 are correlated with relative humidities higher than 50%. This indicates that reactions of NO_3 or N_2O_5 with water may be important. N_2O_5 can react with water vapour:



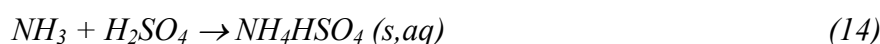
This reaction is however also too slow to explain the short life time of NO_3 . For this reason reactions of N_2O_5 and/or NO_3 on the wet surface of aerosols are probably the cause of this shorter life time. (Dentener and Crutzen, 1993). The reaction of N_2O_5 on wet aerosols supplies 2 equivalents of nitric acid (see reaction 13). To calculate the reaction constants of these heterogenous reactions, the reactive (wet) aerosol surface and the probability with which N_2O_5 and NO_3 react on the surface must be known. To calculate the reactive aerosol surface the size distribution of wet aerosols is necessary. Size distributions of wet and dry aerosols are however rarely distinguished in measurements (Dentener and Crutzen, 1993). As in this study no size distribution of wet aerosols is calculated, this reaction is not included

in this study. Since this reaction is a source of nitric acid this will have to be included in later studies.

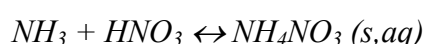
Nitric acid in the atmosphere may react with ammonium hydroxide to form ammonium nitrate. This is an equilibrium reaction. Whether ammonium nitrate is formed, and if so to what extent, depends among other things on the sulphate concentration. The location of the equilibrium is discussed in the following paragraph. Wet and dry deposition are important removal processes for nitric acid and are covered in paragraphs 4.3 and 4.4.

3.3 Aerosol chemistry

In this paragraph the aerosol chemistry used is discussed (Ackermann et al, 1995). The chemistry is a simple version of the chemistry that Ackermann et al. use in MADE (Ackermann, 1998). In this study it is assumed that the aerosol and the gas phase are always in equilibrium. Ackermann et al. do not make this assumption. This system only contains sulphate, bisulphate, nitrate, ammonium and water in the aerosol phase. The size distribution of the aerosol is not taken into account. It is assumed that the sulphuric acid is neutralised by ammonia. This is an irreversible process. The products are ammonium bisulphate or ammonium sulphate depending on the quantity of ammonia (Ackermann et al, 1995).



When excess ammonia is present, the following equilibrium occurs:



The excess ammonia is also called free ammonia, because this is not bound irreversibly to the sulphate. Ammonium nitrate can therefore only be formed when the ratio ammonium/sulphate is greater than two.

The aerosol chemistry can therefore be divided into two schemes, depending on the ammonia concentration. The equilibrium thermodynamics for these two schemes are covered below.

3.3.1 The high ammonium scenario

In the high ammonium scenario the ratio of ammonium/sulphate is greater than two. This means that all the sulphate is bound in $(NH_4)_2SO_4 (s,aq)$. The free ammonia and the nitric acid will form an equilibrium with $NH_4NO_3 (s,aq)$. Ackermann et al. assume that a neutral aerosol, and hence no NH_4HSO_4 , is formed. It

will however be seen that this assumption is not correct. In a neutral solution of ammonium sulphate and nitrate, nitric acid can in fact dissolve. This results in an acid aerosol. This process plays an important part when the concentration of free ammonia and hence the formation of ammonium nitrate, is low. The thermodynamics of this system are described in this paragraph. First the equilibrium between (free) ammonia and nitric acid is discussed. Gaseous ammonia and nitric acid are in equilibrium with ammonium hydroxide and nitric acid in the solution. This equilibrium is described by Henry's law:

$$A_x = H_x * P_x.$$

Here A_x is the activity, H_x Henry's constant and P_x the equilibrium vapour pressure of substance x. The activity of a dissolved substance is thus proportional to its vapour pressure. The size of Henry's constant depends on the solubility of the substance. For dilute solutions the activity is roughly equal to its concentration. In case of (over)saturated aerosols this approximation is not permissible.

Above a liquid aerosol an equilibrium constant is defined for the $\text{HNO}_3/\text{NH}_3/\text{NH}_4\text{NO}_3(\text{aq})$ system. This is given by the product of the equilibrium vapour pressures:

$$K_p^* = P_{\text{NH}_3} * P_{\text{HNO}_3}$$

The vapour pressures of nitric acid and ammonia are given by Henry's law. When the vapour pressures of ammonia and nitric acid are so great that the equilibrium constant is exceeded, ammonium nitrate is formed.

In water nitric acid and ammonia dissociate. Dissociation constants are defined for this:

$$K_a(\text{NH}_4^+) = A_{\text{NH}_3} A_{\text{H}^+} / A_{\text{NH}_4^+}$$

$$K_a(\text{HNO}_3) = A_{\text{NO}_3^-} A_{\text{H}^+} / A_{\text{HNO}_3}$$

For a solution of ammonium nitrate in water

$$A_{\text{NH}_4^+} A_{\text{NO}_3^-} = (\gamma_{\pm} m)^2$$

applies, where γ_{\pm} is the mean activity coefficient and m the molarity. By combining these equations the following relation is found for K_p^* :

$$K_p^* = (\gamma_{\pm} m)^2 K_a(\text{NH}_4^+) / (K_a(\text{HNO}_3) H_{\text{HNO}_3} H_{\text{NH}_3})$$

In this study this distribution constant is approximated by the distribution constant above a saturated solution of ammonium nitrate. If a solution is saturated, the activity product is equal to $(\gamma_{\pm\text{sat}} m_{\text{sat}})^2$, the solubility product.

This gives the following approximation for K_p^* , called K_p here.

$$K_p = (\gamma_{\pm sat} m_{sat})^2 K_a(NH_4^+) / (K_a(HNO_3) H_{HNO_3} H_{NH_3})$$

This distribution constant is among other things dependent on the temperature. Mozurkewich (1993) has deduced this dependence for K_p :

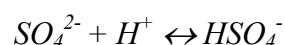
$$\ln(K_p) = 118.87 - 24084/T - 6.025 \ln(T)$$

This dependence is valid between 256 and 305 K. The distribution constant is also dependent on the humidity. This dependence is however ignored in this study. This distribution constant also applies for dry ammonium nitrate aerosols. The solid phase is in equilibrium with a saturated solution of ammonium nitrate, which in turn is in equilibrium with the gas phase. If the water coating around the solid nucleus is taken to be infinitely thin a dry aerosol occurs, in equilibrium with the gas phase.

In the above the formation of ammonium nitrate from nitric acid and free ammonia is discussed. Together with the ammonium sulphate this provides a neutral solution of sulphate, nitrate and ammonium. Nitric acid dissolves well in water and will thus also dissolve in the aerosol. The nitric acid solution supplies additional nitrate and protons in the solution:

$$K = K_a(HNO_3) * H_{HNO_3} = A_{NO_3^-} A_{H^+} / P_{HNO_3}$$

This formula shows that nitric acid dissolves less the more acid the aerosol becomes. As the aerosol becomes acid, the buffering action of sulphate also plays a part:



In short, three equilibria play a part in the high ammonia scenario. Namely, the reversible formation of ammonium nitrate, the dissolving of nitric acid and the sulphate-bisulphate equilibrium. It will be found that the dissolution of nitric acid and hence the sulphate-bisulphate equilibrium is important if little free ammonia is present for the formation of ammonium nitrate.

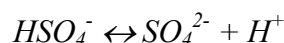
3.3.2 The low ammonium scenario

In the low ammonium scenario not enough ammonia is present to totally neutralise the sulphuric acid. The ammonium/sulphate ratio is less than two. The liquid phase of the aerosols is then acid. The degree to which sulphuric acid is dissociated therefore plays an important part. NH_4HSO_4 (s,aq) and/or $(NH_4)_2SO_4$ (s,aq) will therefore be formed. The ammonia concentration in the gas phase can be ignored. No

ammonium nitrate will be formed as a result of which the HNO_3 concentration in the atmosphere will be higher than for the high ammonium scenario. This effect is intensified because HNO_3 dissolves less as the pH of water falls.

In the low ammonium scenario it is assumed that the aerosols are liquid at all the relative humidities. The effects of deliquescence and hysteresis are therefore ignored. This assumption is argued as follows (Binkowski and Shankar, 1995). If sulphur dioxide is oxidised to sulphuric acid, water vapour will always be present. The sulphuric acid will condense directly, homogenously or on an existing aerosol. Sulphuric acid is hygroscopic and the droplet of sulphuric acid will then very rapidly adjust to the relative humidity. (Remember that sulphuric acid is miscible in all ratios with water). An aqueous solution of sulphuric acid is produced. The ammonia molecules will then bombard the liquid aerosol, after which neutralisation begins.

When all the ammonia is converted into ammonium, the following equilibrium is established:



$$K_a(\text{HSO}_4^-) = (A_{\text{SO}_4^{2-}} * A_{\text{H}^+}) / A_{\text{HSO}_4^-}$$

The quantity of water partly determines how much sulphuric acid can be dissociated. The quantity of water also determines the concentrations of the components and hence the activity of the components. The water content and the activities are calculated in Ackermann's module.

Nitric acid may dissolve in the (aqueous) sulphuric acid solution. The equilibrium condition is given in paragraph 3.3.1. If the initial concentrations and the equilibrium constants are known, the H^+ concentration in the aerosol can be calculated. From the H^+ concentration the concentrations of the separate components of the system then follow.

4. Physical processes

In chapter 2 the aerosol cycle is covered. In this chapter the physical processes that play a part in this cycle are briefly covered. First of all nucleation is covered. Homogenous nucleation and emissions are the sources of particles in the atmosphere. Condensation causes the growth of particles, while because of coagulation smaller particles disappear and bigger aerosols are formed. Finally dry and wet deposition is covered.

4.1 Nucleation

The most important formation process for secondary aerosols in the troposphere is the nucleation of sulphuric acid. When the sulphuric acid concentration becomes greater than the vapour tension of sulphuric acid, sulphuric acid will nucleate homogeneously and hence form a new aerosol or condense on an existing particle. The rate at which sulphuric acid nucleates depends on the formation rate of sulphuric acid and the properties of the aerosols already present. The properties of the particles already present, for example the total surface of the aerosols, determine whether sulphuric acid nucleates homogeneously or condenses. In addition the nucleation rate also depends on the temperature and the water content of the atmosphere.

Wexler et al. (1994) have deduced a critical concentration whereby homogenous nucleation can occur. This critical concentration is the concentration of sulphuric acid, whereby one particle per cm³ per second can be formed. The critical concentration C_{crit} (µg/m³) is given by:

$$C_{crit} = 0.16 \exp(0.1T - 3.5RH - 27.7)$$

RH is the relative humidity and T the absolute temperature. Whether when exceeding the critical concentration a significant quantity of sulphuric acid nucleates, depends on the rate at which sulphuric acid condenses on existing particles. Condensation may be described in a similar way to coagulation (see next paragraph), where one of the particles is a gas molecule instead of an aerosol.

It is important to make a distinction between condensation and homogenous nucleation. In homogenous nucleation new particles are formed in the Aitken mode. In condensation no new particles are formed but the mass of the existing particles is affected. Homogenous nucleation is therefore a source of aerosols, while condensation allows an aerosol to grow in time.

4.2 Coagulation

When two aerosols collide with one another, these aerosols may remain sticking to one another, which is called coagulation. Since under normal atmospheric conditions aerosols have a (thin) water coating, the chance of two particles coagulating after colliding is virtually 1. This means that bigger particles are formed and the number of particles in the atmosphere will fall. In this paragraph the coagulation by Brownian movement in a continuous medium is covered. This theory is taken from Seinfeld (1986).

Say that $dN_1 = f(r_1) dr_1$ and $dN_2 = f(r_2) dr_2$ describe the number of particles in the intervals $r_1 + dr_1$ and $r_2 + dr_2$. The coagulation rate can then be described by the product:

$$K(r_1, r_2) f(r_1) f(r_2) dr_1 dr_2$$

$K(r_1, r_2)$ is called the coagulation function.

For particles for which the radius is much greater than the free path length of air molecules ($\lambda = 6.5 \cdot 10^{-2} \mu\text{m}$), the coagulation function is:

$$K(r_1, r_2) = 4\pi(r_1 + r_2)(D_1 + D_2)$$

where D_i are the diffusion constants of coagulating particles. The diffusion constants are given by the Stokes' and Einstein formula:

$$D_i = kT/6\pi\eta r_i$$

In this formula k is Boltzmann's constant, T the absolute temperature and η the viscosity of air. The coagulation function then becomes:

$$K(r_1, r_2) = kT/3\eta (r_1 + r_2) (1/r_1 + 1/r_2)$$

Since $r \propto v^{1/3}$ the coagulation function can also be expressed in volume units:

$$K(r_1, r_2) = kT/3\eta (v_1^{1/3} + v_2^{1/3}) (1/v_1^{1/3} + 1/v_2^{1/3})$$

The last two equations show that the coagulation between two particles with different radii takes place much faster than coagulation between two particles of the same size.

4.3 Sedimentation

In this paragraph the sedimentation of particles in a continuous medium is discussed. Sedimentation is understood to mean the settlement of particles under grav-

ity. Sedimentation is the most important removal process for large particles in the atmosphere. As the particles become smaller, sedimentation becomes less important as a removal process and dry deposition by Brownian movement becomes more important. Dry deposition is covered in paragraph 4.4. When the Archimedian force is ignored, gravity is in equilibrium with the frictional force. For spherical particles in air:

$$4\pi r^3 \rho_p g / 3 = 6\pi r \eta v_g$$

then applies, with ρ_p the density of the aerosol, g the gravity acceleration and η the viscosity. The sedimentation rate v_g is then given by:

$$v_g = 2r^2 \rho_p g / 9\eta$$

The sedimentation rate thus increases quadratically by the radius of the particle. When the radius of a particle is of the same order of magnitude or is smaller than the free path length in air ($\approx 6.6 \times 10^{-2} \mu\text{m}$), air is no longer a continuous medium. The calculated sedimentation rate must then be corrected by multiplying this by the Cunningham correction factor (see Annex D).

4.4 Dry deposition

Dry deposition is the removal of substances from the atmosphere on the earth's surface, for example by taking up by plants or adhesion to the surface.

The dry deposition flux F of a component is determined by the deposition rate v_d and the concentration C of this component in the atmosphere:

$$F = C * v_d$$

The deposition rate (in m/s) depends on the atmospheric stability and the component considered. For gases the chemical and physical properties determine the rate of deposition. In the case of aerosols the particle size is the rate-determining factor. It is therefore important to distinguish between the deposition of gases and particles.

4.4.1 Dry deposition of gases

The dry deposition of gases is described as if it were an electric current through a series of resistances. The deposition rate is given by the equation (Seinfeld, 1986):

$$v_d = \frac{1}{r_a + r_b + r_c}$$

The equation includes three resistances, which are discussed below. r_a is the atmospheric resistance and is determined by the turbulent transport from a reference height z_{ref} to the height z_0 , where the wind speed is zero. This resistance is therefore dependent on the meteorological conditions. The atmospheric resistance is independent of substance properties. r_a is given by:

$$r_a = \frac{u}{u_*^2}$$

In this equation u is the wind speed at z_{ref} and u_* the shear stress resistance. From the definition it appears that r_a is dependent on the reference height.

The second resistance r_b is the resistance resulting from the viscous sub-layer. Before a substance can be deposited the substance must first diffuse through this layer. The diffusion through this thin layer (0.1-1 mm) may determine the rate (Seinfeld, 1986). In the New National Model (NNM, 1998) r_b is calculated in accordance with

$$r_b = \frac{2}{ku_*} \left(\frac{Sc}{Pr} \right)^{2/3} \quad \text{where} \quad Sc = \frac{\nu}{D}$$

with k the Von Karman constant, ν the kinematic viscosity of air and D the diffusion constant. Sc and Pr are the Schmidt and Prandtl numbers. The Schmidt number is inversely proportional to the diffusion rate. The smaller the Schmidt number the easier a gas diffuses through the boundary layer. Table 4.1 gives the Sc numbers for a few gases (NNM, 1998). For these gases the Prandtl number is 0.72. The degree of adsorption or solution of a component on the surface determines how much of the component is removed after diffusion by the viscous boundary layer. The corresponding resistance r_c is the surface resistance. This resistance depends among other things on the substance, the surface (dry/wet) and the time of day. Table 4.1 gives mean r_c values for the summer season, 1 April to 30 September.

Table 4.1 *Sc-values and mean summer Rc-values*
Sources: NNM, 1998, HS = Hey and Schneider 1991

GAS	SC	R _c (NNM)		R _c (HS)	
		day	night	day	night
SO ₂	1,25	45	10	54	67
NO ₂	1,07	230	870	150	300
NH ₃	0,68	28	15	30	30
HNO ₃					
NO	0,86	2000	2000	2000	2000

4.4.2 Dry deposition of aerosols

The deposition of aerosols may also be described in a similar way to Ohm's law. Compared with the deposition of gases two aspects are important. Firstly the surface resistance for aerosols is zero, as a particle that has reached the surface is regarded as deposited. Secondly aerosols have a downward starting rate, the sedimentation rate. When these aspects are taken into consideration, the equation for the total dry deposition rate (Binkowski and Shankar, 1995; Seinfeld, 1986) becomes:

$$v_d = (r_a + r_b + r_d r_d v_g)^{-1} + v_g$$

In this equation the resistance as a result of the viscous sub-layer is called r_d to distinguish this from the same resistance for gases. The (Brownian) diffusion of small particles through the viscous sub-layer looks very similar to that for gases. However, the bigger the particles the more important sedimentation and impaction become. In NNM (1998) the following definition of impaction is given: due to inertia as a result of its mass a particle is sometimes no longer able to follow a deflecting air stream and may then reach the earth's surface. The resistance of the viscous sub-layer is then given by (Binkowski and Shankar, 1995):

$$r_d = \left[\left(Sc^{-2/3} + 10^{-3/St} \right) \left(1 + 0.24 \frac{w_*^2}{u_*^2} \right) u_* \right]^{-1} \quad \text{where} \quad St = \frac{u_*^2 v_g}{g \nu}$$

St is the Stokes' number and is a measure of impaction. w_* is the convective velocity scale of the mixed layer. Wesely et al. (1985) approximate the factor with the Schmidt and Stokes' numbers of 0.002. This parametrisation of Wesely is thus independent of the particle size and gives a mean deposition rate.

Schaap (1999) give in appendix D the calculation of the deposition rate for a polydisperse aerosol with a log-normal size distribution. By deducing an equation for the Brownian movement and the sedimentation rate from the polydisperse aerosol, using the above theory the equation for the deposition rate is deduced.

In addition to dry deposition, particles are also removed from the atmosphere by wet deposition. This process will be discussed in the next paragraph.

4.5 Wet deposition

Wet deposition takes place in and under clouds. Aerosols that can get into a cloud droplet by nucleation will rain out at a given moment. In addition particles in and under the cloud are washed out by rain (Wash-out). Greenfield has described these processes. He calculated the fraction of particles with a different diameter removed as a function of time and the precipitation intensity (see Figure 4.1). Particles from the accumulation mode are found not to be washed or rained out well. This

Greenfield gap causes the maximum in the aerosol spectrum. Below the wash-out of particles (and gases) is briefly covered. Rain-out of particles is not discussed, because this process is not considered in LOTOS yet.

The wash-out process is described in this study by (De Leeuw et al., 1988):

$$\frac{dC_m}{dt} = -\Lambda C_m$$

where Λ is the scavenging coefficient. The size of the scavenging coefficient depends on the droplet size spectrum and the precipitation intensity (I). For particles the particle size is also important and for gases the solubility is important. For poorly soluble gases such as NO and NO₂ the wash-out can be ignored. The dependence on the particle size is ignored. Table 4.2 gives the scavenging coefficients used for HNO₃, NH₃, H₂O₂ and aerosol sulphate as a function of the precipitation intensity.

Table 4.2 Scavenging coefficients as a function of precipitation intensity I (m/s) Source: de Leeuw et al, 1988

Component	Λ
HNO ₃	$1,81 * I^{0,68}$
NH ₃	$2,64 * I^{0,68}$
H ₂ O ₂	$2,45 * I^{0,68}$
Sulfaat (aërosol)	$7,62 * I^{0,89}$

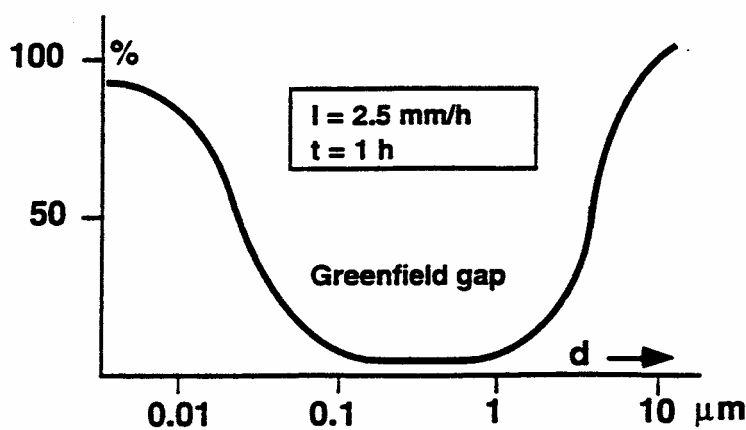


Figure 4.1 The fraction of removed aerosols as a function of diameter, time and precipitation intensity

5. Box model study

In this chapter the box model developed in this study is discussed. The purpose of the model is to clarify the aerosol chemistry using a few sensitivity analyses/experiments. The basis for the box model is the chemical mechanism of the LOTOS model. LOTOS is the abbreviation for Long Term Ozone Simulation. The mechanism has been extended for aerosol chemistry. The extended mechanism was tested using the reported contributions to the EUROTRAC Chemical Mechanism Working Group comparison (Poppe et al., 1996).

In this study a simple version of the aerosol chemistry module of MADE (Ackermann et al., 1995, 1998) was used. This module has been revised. The revisions to the module are discussed below. This module was used to investigate how the nitrate content of an aerosol is affected by the temperature and relative humidity. The aerosol chemistry module is then coupled to the chemical mechanism. With a scenario from the EUROTRAC comparison the effect of the aerosol chemistry on the gas phase chemistry was investigated.

5.1 Model description and results

5.1.1 Gas phase reaction mechanism

The chemical mechanism as used by TNO is a Carbon Bond IV mechanism. The reaction diagram is derived from the original CBM-IV mechanism, which was first used in the RTM-III model. To be able to incorporate aerosols into LOTOS it was found to be necessary to add a few substances and reactions to this chemical mechanism.

First of all nitric acid was added. The formation reactions of nitric acid (reaction 6,9,10,11,13) were included in the LOTOS mechanism, but only as a loss term for the reactants. The nitric acid production was thus made explicit. Reactions 7 and 8, the photodissociation of nitric acid and the reaction of nitric acid with OH, were added. These reactions were discussed at length in paragraph 3.2. In addition to nitric acid it was also necessary to add ammonia. No chemical conversions of ammonia are included in the reaction mechanism, as these are not important compared with dry and wet deposition of ammonia.

Hydrogen peroxide was added because of its possible effect on the concentrations of OH and HO₂ radicals. Test results showed that the modelled HO₂ concentration was too high. The reaction of HO₂ with XO₂ was found to be missing. This reaction was added.

Isoprene was included in the reaction mechanism as this substance is necessary to be able to compare the box model with one of the scenarios in the EUROTRAC comparison. It is also known that isoprene is a precursor for organic aerosols (Kavouras et al., 1998).

The relevant reactions with corresponding reaction constants are included in the diagram of the chemical mechanism used in Annex A.

The chemical mechanism was tested using the reported contributions to the EUROTRAC Chemical Mechanism Working Group comparison (Poppe et al., 1996). For this the box model was set up in accordance with the guidelines for this comparison. Since in this comparison only the chemical mechanisms are compared, the meteorological parameters chosen were constant. Deposition is not considered. The prescribed photolysis frequencies were included in the chemical mechanism. As a result parameters other than the chemical mechanism have no effect on the results. The results of the box model are then not realistic, but only intended as a comparison. A detailed description of the guidelines for this comparison is included in Annex B.

The chemical mechanisms in the EUROTRAC comparison are compared with one another by applying these to five scenarios. The chemical mechanism developed was tested by comparing this with three of these scenarios, namely LAND, BIO and PLUME1. The PLUME1 scenario is called the PLUME scenario in this report. The prescribed emissions of VOCs in the PLUME scenario are divided over the CBM-IV species.

Annex C includes the results of the LAND, BIO and PLUME scenario. The results of these scenarios fall within the range of the reported results. No discrepancies are found. From this it is concluded that the extensive chemical mechanism gives acceptable results compared with other mechanisms and that it is suitable for use in LOTOS.

5.1.2 The aerosol module

To gain an understanding of aerosol chemistry two experiments were carried out with Ackermann's aerosol chemistry module. First at constant temperature ($T = 288 \text{ K}$) and different ammonium/sulphate ratios the nitrate content was determined. In this experiment the total sulphate content is $7.5 \mu\text{m}/\text{m}^3$ and the total HNO_3 concentration $6.5 \mu\text{g}/\text{m}^3$. The ratio was varied by varying the total ammonia concentration. This experiment was repeated with different humidities.

Figure 5.1 gives the result of this experiment for two relative humidities, namely 60 and 80%. When the results are compared it is found that the nitrate content at $\text{RH} = 60\%$ is zero in the low ammonium scenario (to ratio = 1.95), while for $\text{RH} = 80\%$ a significant nitrate content is calculated. The reason for this is that at $\text{RH} = 60\%$ the sulphate concentration in the liquid aerosol is too high, as a result of which the module is not able to calculate a nitrate content. The input values of the nitrate content and the nitric acid concentration are then given as output. In this case the input value of nitrate was zero.

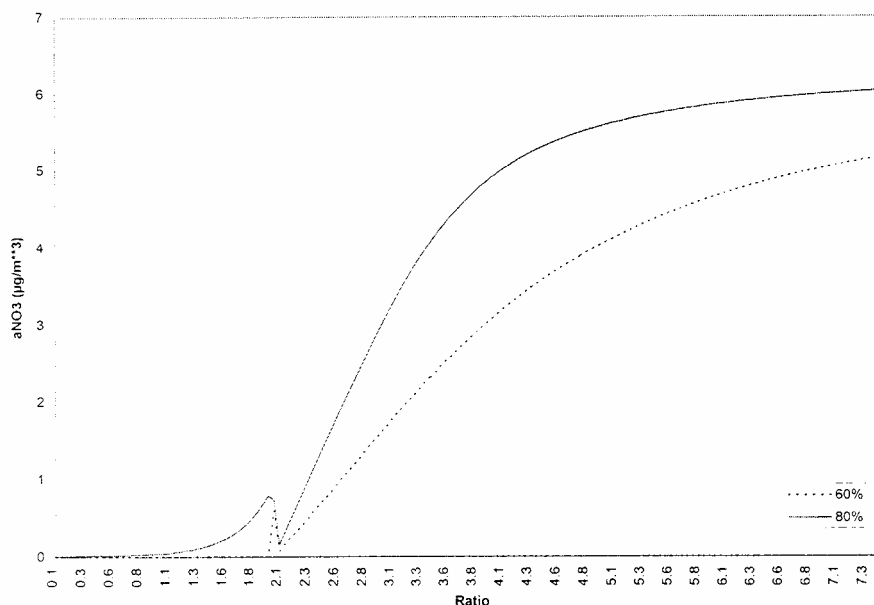


Figure 5.1 Aerosol-nitrate content as a function of the ammonium/sulfate ratio at an RH of 60 and 80% and at 288 K

With a relative humidity of 80% the nitrate content shows a discontinuity on the transition from the low to the high ammonium scenario. The nitrate content is virtually zero for the ratio 2.05, while the final value in the low ammonium scenario is around $0.75 \mu\text{g}/\text{m}^3$. Since for the ratio 2.2 and below virtually no ammonium hydroxide is present in the gas phase, no ammonium nitrate can be produced.

The aerosol nitrate in the low ammonium scenario therefore comes from the dissolution of nitric acid in the water phase of the aerosol. As nitric acid dissolves better when the water phase is less acid, this process will also be important in the high ammonium scenario. If the ratio is 2.05 a significant quantity of nitric acid will therefore have to dissolve in the neutral ammonium sulphate solution. This results in an acid aerosol in the high ammonium scenario. The cause of the discontinuity is therefore the assumption that the aerosol is neutral in the high ammonium scenario. The aerosol module was revised, so that this also calculates the dissolved nitric acid in the high ammonium scenario. This also considers the equilibrium between sulphate and bisulphate. With this module two sensitivity analyses were carried out. The experiment described above was repeated. The experiment was also carried out by varying the temperature at a relative humidity of 80%. The results of these experiments are given in Figure 5.2 and 5.3. Figure 5.2 shows the nitrate content as a function of the ammonium/sulphate ratio and the relative humidity. The figure shows that the nitrate content in wet aerosols increases with the relative humidity. This is logical since the wet aerosols contain more water at higher relative humidities.

The dry aerosol at $RH = 20\%$ clearly behaves differently from the wet aerosols. Until the ratio between the total ammonium and sulphate becomes approx. 2.7, no ammonium nitrate is formed. In the low ammonium scenario no aerosol nitrate can occur as there is no water phase in which nitric acid can dissolve. In the high ammonium scenario no ammonium nitrate is formed as the distribution constant of ammonium nitrate is not exceeded. The ammonia concentration is so low that:

$$(NH_3) * (HNO_3) < K_p$$

When ammonium nitrate is present, it appears that the nitrate content is greater in relation to the wet aerosols. This can be explained by the fact that the activities of ammonia, gaseous nitric acid and solid ammonium nitrate are equal to 1, while the activities of the ions in the water phase of an aerosol are (much) less than 1. As a result the distribution constant for ammonium nitrate in solution is effectively increased, as a result of which the equilibrium lies more towards the gas phase.

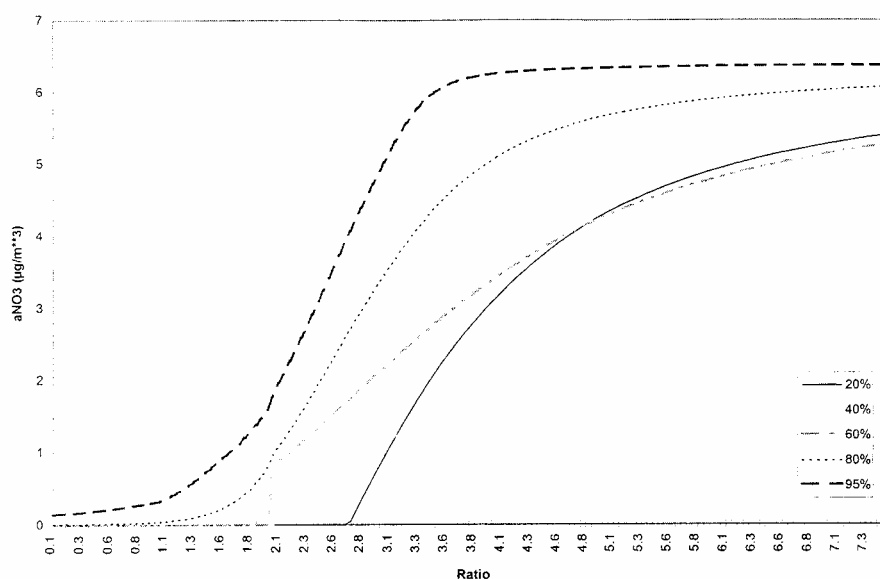


Figure 5.2 Aerosol nitrate content as a function of the ammonium/sulfate ratio and of the relative humidity at 288 K

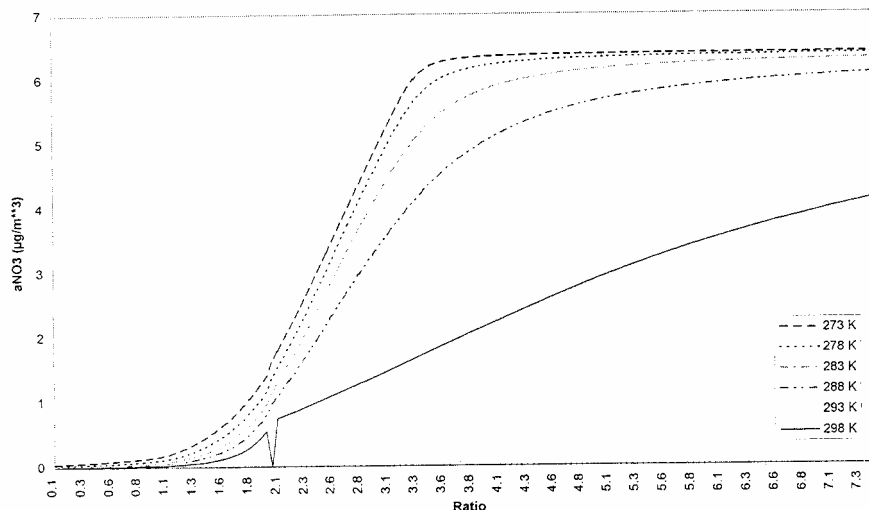


Figure 5.3 Aerosol nitrate content as a function of the ammonium/sulfate ratio and of the temperature at RH is 80%

When the nitrate contents before and after adjustment of the aerosol module are compared with one another, it is found that the discontinuity is removed. When a lot of free ammonia is present (ratio $\gg 2$), the adjustment does not result in an increased nitrate content. The solution of nitric acid is then an important process when little free ammonia is present.

Figure 5.3 gives the nitrate content as a function of the temperature for wet aerosols. The discontinuity at 298 K and ratio = 2 is caused by the fact that no solution was found for the nitrate content.

As anticipated, it is found that the nitrate content increases considerably when the temperature falls. The vapour pressure of a (liquid) substance after all increases as the temperature falls. This dependence is generally valid for volatile substances. The fact that the aerosol concentrations increase considerably as the temperature falls is one of the causes for the winter smog phenomenon.

This paragraph demonstrates that the aerosol module did not consistently model the nitrate content in the aerosols. By considering the dissolution of nitric acid in the high ammonium scenario this inconsistency was eliminated. This process is found to be important when little free ammonia is present, as a result of which the discontinuity at the transition between the scenarios is eliminated. The nitrate content in wet aerosols increases as the relative humidity rises. Dry aerosols contain relatively more nitrate than wet aerosols. In addition the ammonium nitrate content in the aerosol falls as the temperature rises.

5.1.3 Gas phase and aerosol chemistry

In the aerosol chemistry module the thermodynamic equilibrium is calculated between the gas phase and the aerosol phase. This equilibrium affects the gasphase chemistry. To study this effect, the module is coupled with the box model. By using the PLUME scenario of the EUROTRAC comparison only the chemistry is considered. After calculating the concentrations of the substances in the gas phase, the equilibrium state between the gas phase and the aerosols is calculated. The equilibrium is assumed to establish itself directly. The gaseous sulphate formed by the oxidation of SO_2 is assumed to be gaseous sulphuric acid.

First of all the PLUME2 scenario is run. The PLUME2 scenario unlike the PLUME scenario does have an initial concentration of SO_2 , namely 5 ppb. For this the aerosol module is not called upon. Then the aerosol module is called upon. Here the initial concentration of ammonia was 7.5 ppb. At $t = 72$ h the transition from the high to the low ammonia scenario takes place. This is the PLUME3 scenario. The relative humidity in the PLUMEx scenarios is 59.1% at a constant temperature of 288K. Figure 5.4a shows the resulting concentration curves for ozone. As a comparison the concentration curve of ozone is included in the PLUME scenario. The figure shows that the ozone concentration rises $< 1\%$ as a result of the increased initial concentration for SO_2 . The increased SO_2 concentration results in a lower OH concentration and a higher HO_2 concentration, which is known to result in a small increase in the ozone concentration. When the aerosol concentrations are calculated the ozone concentration falls. Concentrations of substances such as NO_x and VOC hardly change. With respect to the PLUME2 scenario in the PLUME3 scenario nitric acid is fixed as aerosol nitrate (see Figure 5.4 b). By day less nitric acid is converted into NO_2 , as a result of which less ozone is formed. When nitrate is released in the form of nitric acid this will be the other way round. Potentially these aerosols may then affect the gas phase chemistry by acting as a sink or source for nitric acid. This experiment shows that the effect is small. Taking aerosols into account the ozone concentration falls after 120 hours by approx. 2% with respect to the PLUME scenario.

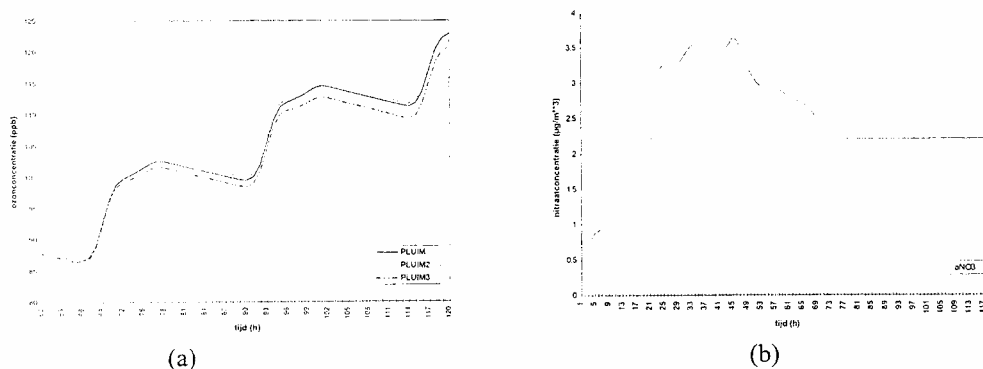


Figure 5.4 a) Ozone-concentration. b) Aerosol nitrate content in Plume 3

Figure 5.4 b shows the aerosol nitrate content as a function of time. Up to $t = 72$ the high ammonium scenario applies. For the first thirty hours the nitrate content increases in proportion to the nitric acid concentration, after which the nitrate content stabilises. This stabilisation and the following fall in the nitrate content are caused by the fixing of ammonium in ammonium sulphate. The nitrate content falls most by day, as by day the sulphate production is greatest. As a result less ammonia is available to form ammonium nitrate. In the low ammonium scenario a constant nitrate content is given. This is caused by too high a sulphate concentration (see Figure 5.2, $RH = 60\%$). Since the aerosol becomes more and more acid as the ammonium/sulphate ratio falls, the nitrate content would have to fall further.

As an illustration in Figure 5.5 the nitrate content is shown for relative humidities of 70 and 71%. These values are obtained by increasing the relative humidity only in the aerosol module. At 71% the nitrate content is calculated in the low ammonium scenario. At 70% the input value is retained. At $RH = 71\%$ the sulphate concentration only becomes too great to calculate a nitrate content at $t = 105$. At $t = 95$ the calculated nitrate content is a factor of 2 lower than the value at 70%, while this content should be a little bit higher. The graph shows that at lower humidities a great error in the nitrate content may occur, when the transition from the high to the low ammonium scenario occurs or has occurred. As long as the sulphate concentration in the low ammonium scenario remains too high to calculate the nitrate content, changes in the composition of the air or meteorological conditions have no effect on the nitrate concentrations calculated. As a result an under- or overestimate of the nitrate concentrations may occur, depending on the history of an air packet.

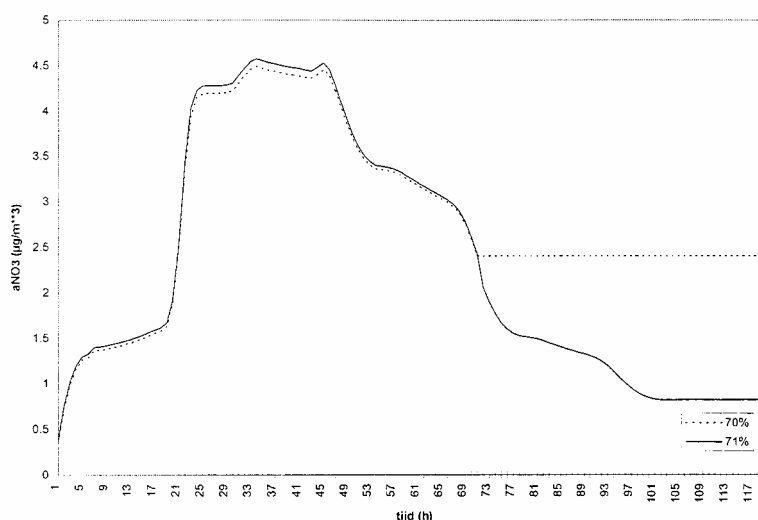


Figure 5.5 Nitrate content for the PLUME3-scenario at $RH = 70\%$ and 71%

It can be concluded from the results of these experiments that the formation of ammonium nitrate and ammonium sulphate aerosols have a slight effect on the gas

phase chemistry. It should be noted here that no physical processes are involved in this equation. Aerosols behave physically differently to gases, as a result of which the composition of the atmosphere is affected. In addition the effect of the aerosol load on photolysis is not taken into account. When the sulphate concentration in the aerosol becomes too high to calculate a nitrate content in the low ammonium scenario, errors may occur in the resulting nitrate content. Depending on the history of an air packet the nitrate content is over- or underestimated.

6. Aerosols in LOTOS

In this chapter the incorporation of aerosols into LOTOS is discussed. With the model aerosol concentrations are calculated for August 1997. LOTOS is a photochemical dispersion model. The model was developed to simulate the ozone concentrations over Europe. The model uses a Eulerian grid that divides Europe into 70 by 70 cells of 0.5 degrees of latitude by 1 degree of longitude. In the vertical, three layers are distinguished up to a height of approx. 2 km. The bottom layer represents the mixed layer. This chapter only discusses the changes in the model that are necessary to incorporate aerosols.

The chemical mechanism developed and the aerosol module are included in LOTOS. The mechanism differs in one point from the mechanism described in chapter 5. Isoprene is not included in LOTOS. The deposition of SO₂ and aerosols are calculated using the Wesely parametrisation (Wesely, 1989 and 1985). The deposition of particles is modelled independently of the particle size, the model is already designed to do that. When the deposition is modelled depending on the particle size, it is necessary to describe all the other processes as size-dependent too. This has not been done yet in this first version. For wet deposition the scavenging coefficients from paragraph 4.4 were used. The scavenging coefficients of all aerosol components were set the same as those for sulphate.

6.1 Simulated aerosol concentrations for August, 1997

In this study the aerosol concentrations are simulated for August 1997. The emissions in this period were assumed to be the same as in the corresponding period in 1994. For a few measuring stations in the Netherlands hourly PM₁₀ measured values and daily average concentrations of sulphate, nitrate and ammonium are available. These measured data from the National Air Quality Metering Network (LML) were made available by RIVM (RIVM, 1996). No measured values were available for the rest of Europe at the moment of writing this report.

Figure 6.1 shows the calculated sulphate and nitrate distributions over Europe for 21 August, 12:00 h. This Figure clearly shows ammonium nitrate is important in areas with high ammonia emissions, such as the Netherlands and the Po plain in Italy. The sulphate aerosol shows high concentrations in central Europe, where the SO₂ emissions are very high.

Comparison of known sulphate, nitrate and ammonium concentrations over the whole of Europe with measured values is not possible, as no measured values are available yet. For this reason this comparison is only carried out for the Netherlands.

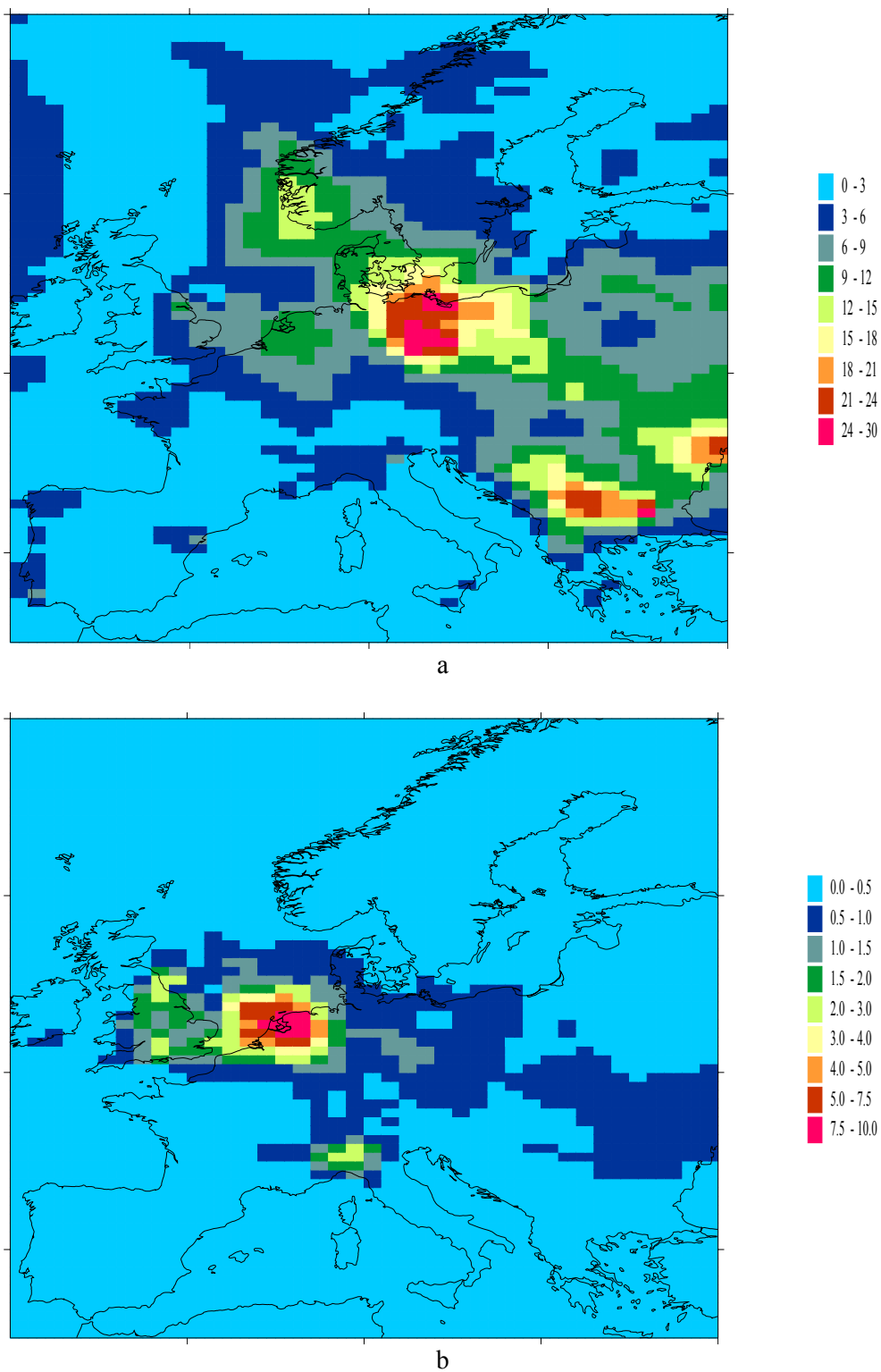


Figure 6.1 Distribution of sulphate (a) and nitrate (b) in $\mu\text{g}/\text{m}^3$ over Europe as calculated by the LOTOS-model for 12.00, August 21, 1997

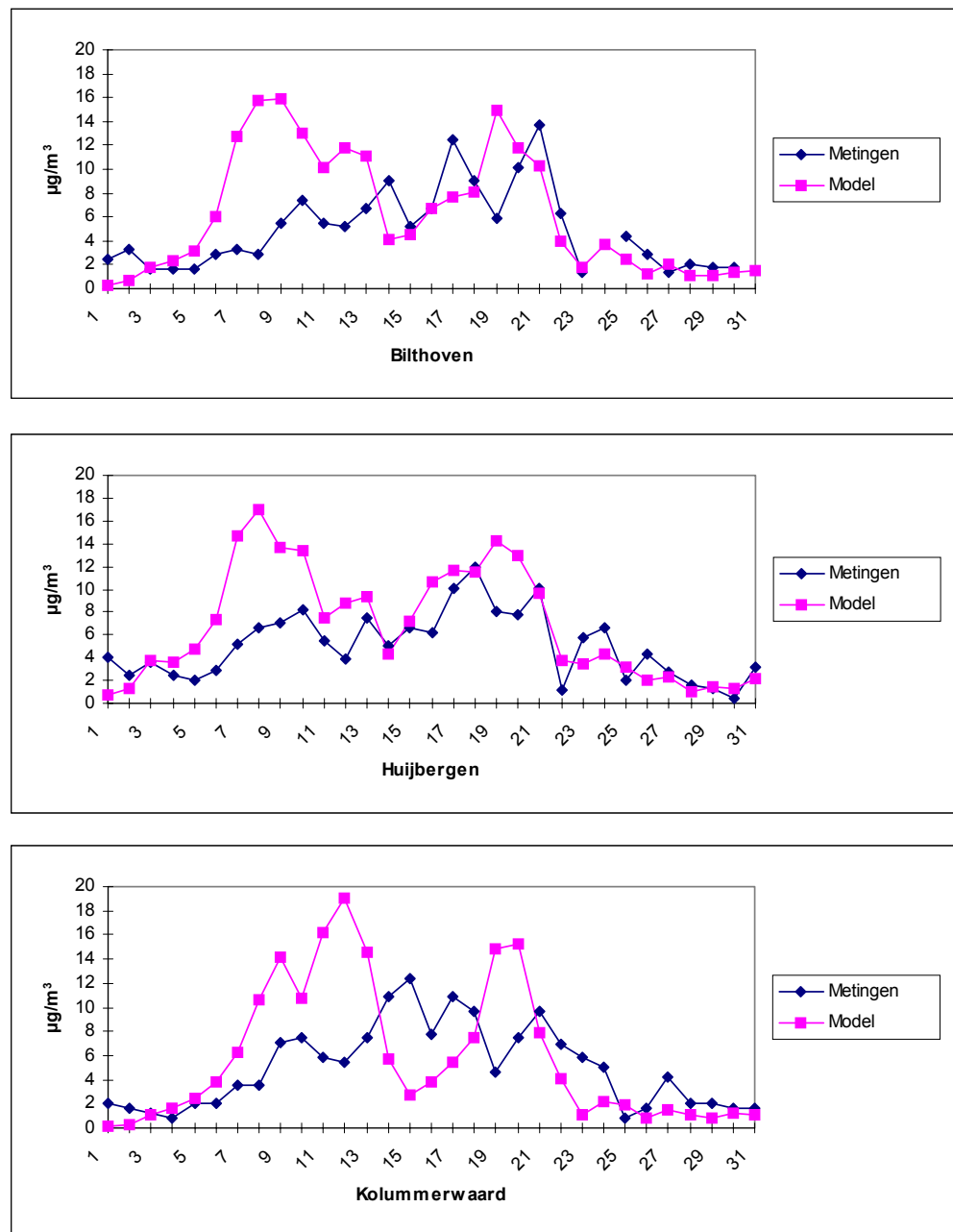


Figure 6.2 Measured and calculated daily averaged sulphate concentrations at 6 Dutch stations in August 1997

Figure 6.2 sets out for six measuring stations in the Netherlands the measured daily average sulphate concentrations. In the same Figure the calculated daily average sulphate concentrations are shown for the corresponding grid cells of LOTOS. The calculated values are mixed layer averages. Except for Kolummerwaard and Vre-depeel the simulated concentration curve over time corresponds reasonably well with the measured curve.

The sulphate concentrations in the first hot period from 5 to 11 August are greatly overestimated by the model. This overestimate is made at all the stations. There is

an inflow of air from the East, as a result of which the air inflow has high sulphate concentrations. During the second hot period from 16 to 20 August there is an inflow of warm air from the South. During this period the sulphate concentration is slightly overestimated.

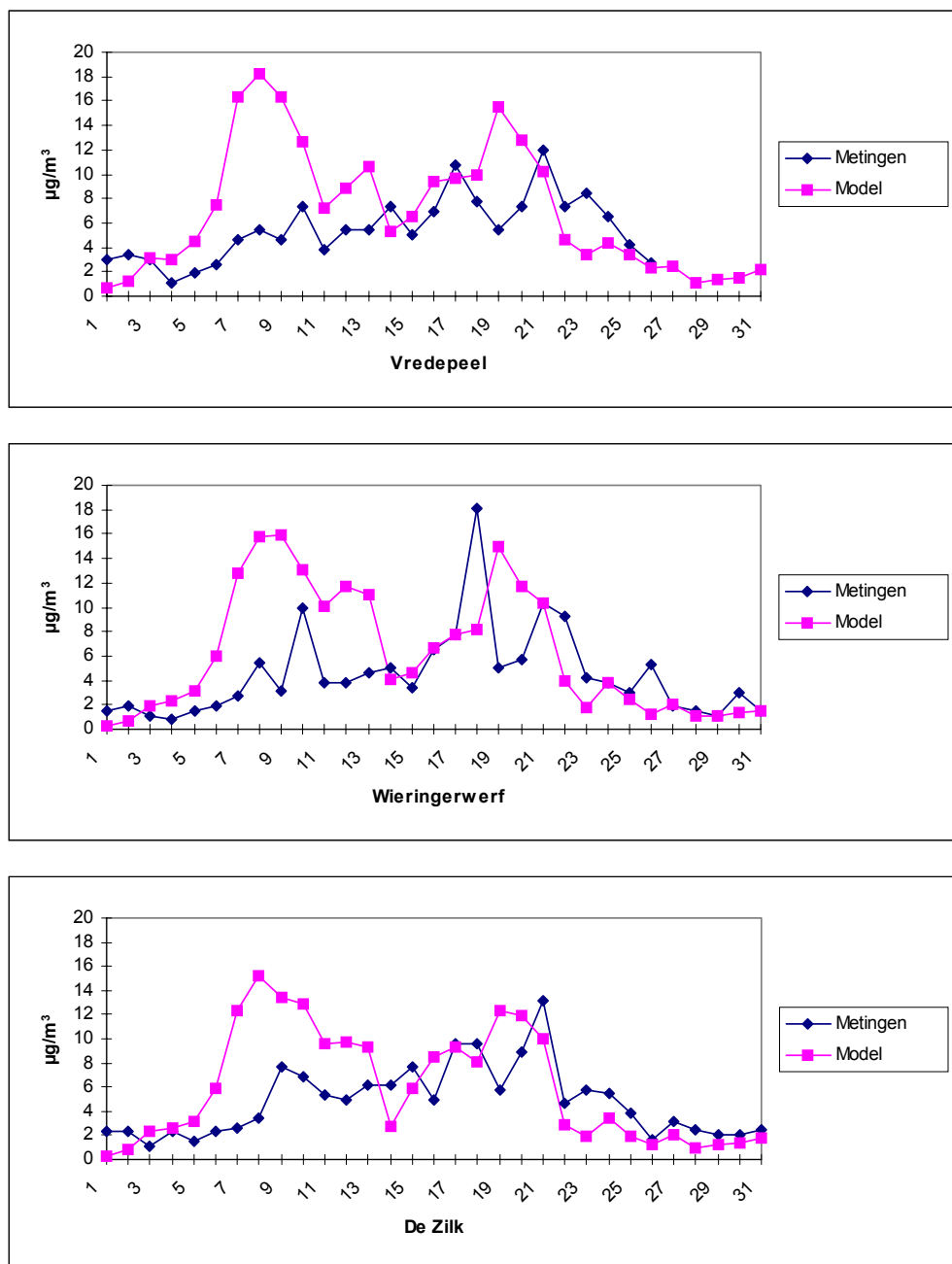


Figure 6.2 (continuation)

The considerable overestimate during the first hot period is therefore associated with an easterly flow. Emission data show that the emissions of sulphur dioxide in Germany between 1994 and 1997 fell by around 30% (ETC_AC, 1999). The cause

of the overestimate of sulphate is then probably partly the overestimate of the SO₂ emissions in Germany.

For the same stations Figure 6.3 sets out the measured and calculated daily average nitrate contents in August 1997. It is immediately obvious that the nitrate concentrations are overestimated in the model. After 7 August the course of the concentration is reasonably well simulated. The measured maxima correspond to the calculated maxima. It is also noticeable that the concentration curve for nitrate unlike that for sulphate in Kolummerwaard corresponds reasonably well with the measurements. For 7 August the model results show increased daily average concentrations, while no increased concentrations of nitrate are measured.

The calculated and measured daily average ammonium concentrations are given in Figure 6.4. The modelled concentrations are the (molar) sum of the sulphate (2x) and nitrate concentrations. This is clearly shown by the graphs. The calculated ammonium concentrations are for example increased in the first week. This was also the case for nitrate.

The discrepancies between the calculated concentrations and the measured values may be determined by several factors. Firstly the measurements show the minimum concentration because losses may occur due to evaporation of ammonium nitrate during the measurement itself (Ten Brink et al., 1997).

Secondly it is difficult to compare the measured values with the calculated values. Is the measurement point reasonably representative for a grid cell of 60 by 60 km? Local effects may greatly affect the measurements, as a result of which the representativeness of a measurement decreases. It could be important that the calculated concentrations are mixed layer averages, while the measurements are carried out close to the ground. For gases, depositing substances have a concentration gradient with the height. The concentration on the surface is low and increases with the height until the mixed layer average concentration is reached. The faster a gas is deposited the steeper the gradient is. Because of this gradient a lower concentration is measured close to the ground than is present for a mixed layer average. Aerosols do not have a high deposition rate. It is not anticipated that the gradient for aerosols will be great. Because of constant sedimentation of aerosols the gradient will fall further. For sulphate the measured concentration will probably not be much lower than the modelled concentration.

In the case of ammonium nitrate the equilibrium with ammonia and nitric acid also plays a part in predicting the concentration at measurement height. Ammonia and nitric acid are rapidly depositing gases, as a result of which these show a considerable concentration gradient with the height. Since the concentration of nitric acid and ammonia in the gas phase decreases when ammonium nitrate is deposited, ammonium nitrate will evaporate to get into equilibrium with the gas phase. Because of a higher temperature on the surface this process is increased and the concentration of ammonium nitrate falls further. This process would partly explain the discrepancy between calculated and measured nitrate concentrations. Measurements above the Speulderbos seem to confirm this hypothesis (Van Oss et al., 1998).

Thirdly the modelling of ammonia and nitric acid can cause discrepancies. In the model the concentration of ammonia is overestimated, which leads directly to an overestimate of the ammonium nitrate. The sensitivity for ammonia modelling was investigated and is covered in paragraph 6.3.

Fourthly rough assumptions were made in the aerosol chemistry. An example is the assumption that the distribution constant is always the same as that for a saturated aerosol. Also the modelled aerosol only consists of a limited number of components. In actual fact an aerosol will never meet this condition.

All the physical processes that an aerosol undergoes depend on the size of the aerosol. This study does not take into account the size distribution of the aerosols. This is the fifth important cause of uncertainties in the calculated concentrations of sulphate, ammonium and nitrate.

6.2 Sensitivity for ammonia modelling

Ammonia has a life time of a few hours in the atmosphere. This short life time is caused by rapid deposition and neutralisation of acids. Emissions of ammonia mainly come from stock-farming. These emissions take place on the surface. Because of the great spatial variability of ammonia sources and the short life time of ammonia it is anticipated that the NH_3 concentration will show great horizontal gradients (Dentener and Crutzen, 1995).

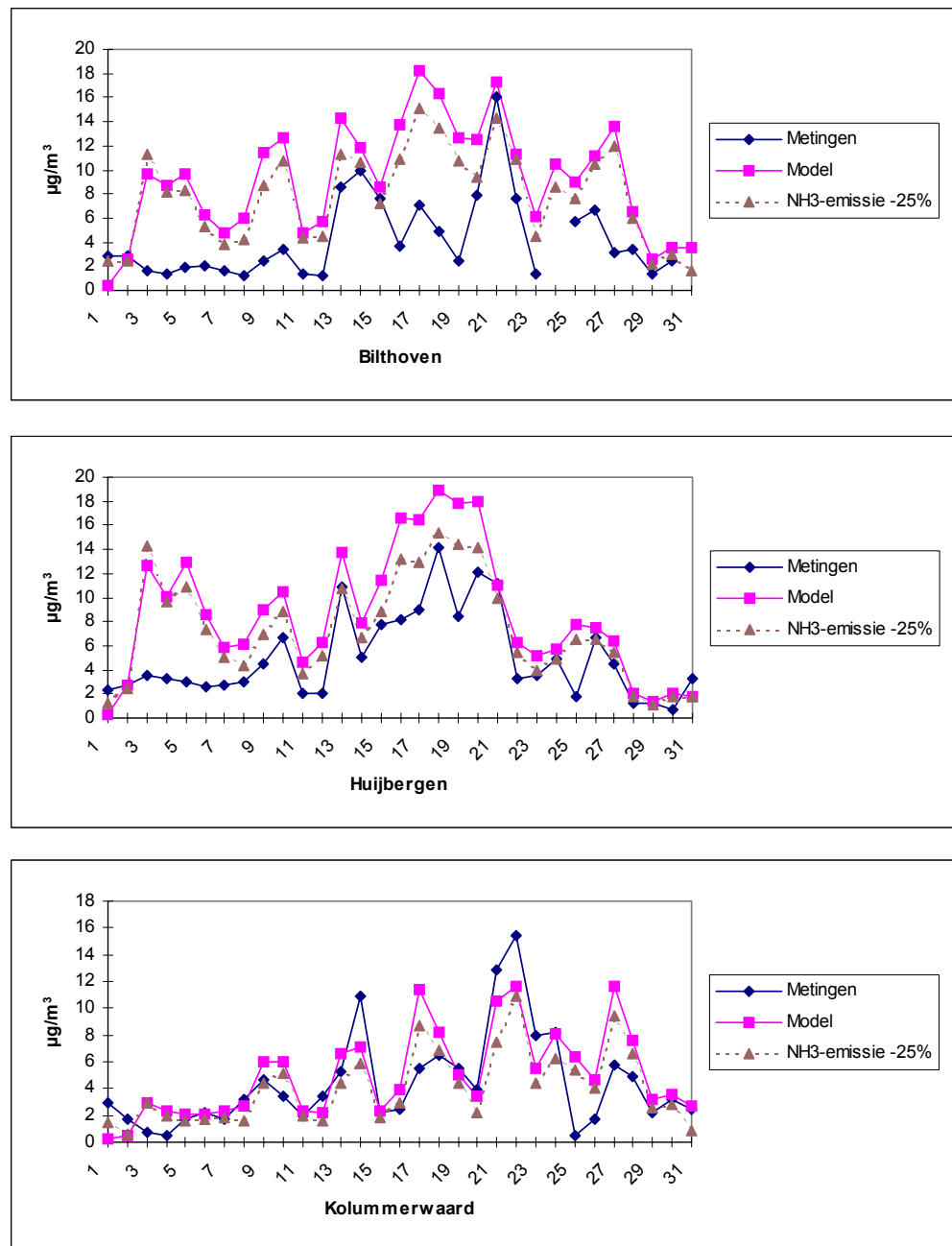


Figure 6.3 Measured and calculated daily averaged nitrate-concentrations for 6 measuring stations in August 1997

In addition the ammonia concentration falls (considerably) with the height (Warneck, 1988). Locally these factors may result in very high deposition fluxes. In LOTOS NH_3 is modelled on a large scale and with a mixed layer average. The vertical gradient in the mixed layer cannot be represented. Together with the fact that on a local scale great variations in the NH_3 concentration may occur it is probable that the deposition of NH_3 in LOTOS is underestimated. Dentener and Crutzen

(1995) and EMEP (1998) take into account these sub-grid phenomena by removing respectively 25% and 19% of the ammonia emissions directly from the system. With LOTOS the sensitivity of the aerosol concentrations to these sub-grid phenomena is investigated. For this the ammonia emission is reduced by 25% to correct for underestimated deposition.

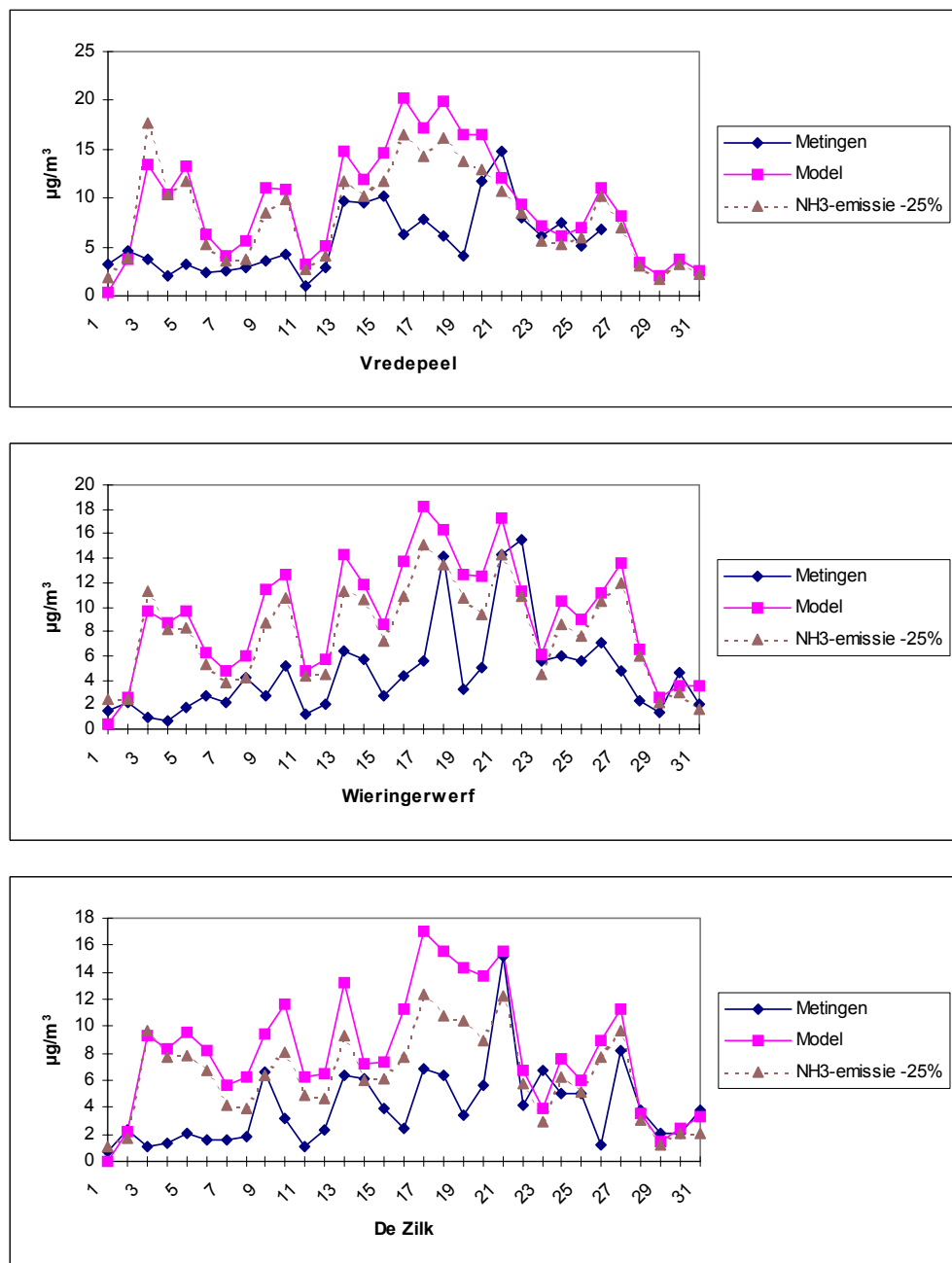


Figure 6.3 (continuation)

The results of this experiment are shown in Figures 6.3 and 6.4. The sulphate concentration is hardly affected by the emission reduction of NH_3 . As anticipated the nitrate concentrations fall as the ammonia concentration is reduced. The sulphate/ammonia ratio after all falls. When the emission of ammonia is reduced by a quarter the nitrate concentration falls upto $\pm 30\%$. The effect is greatest during periods of fine weather. The curve of the concentrations over time does however remain the same. Ammonia modelling could be the greatest source of the overestimate of nitrate and ammonium. Since the concentration curves remain the same with an emission reduction for ammonia the improvement of these curves must take place in other areas.

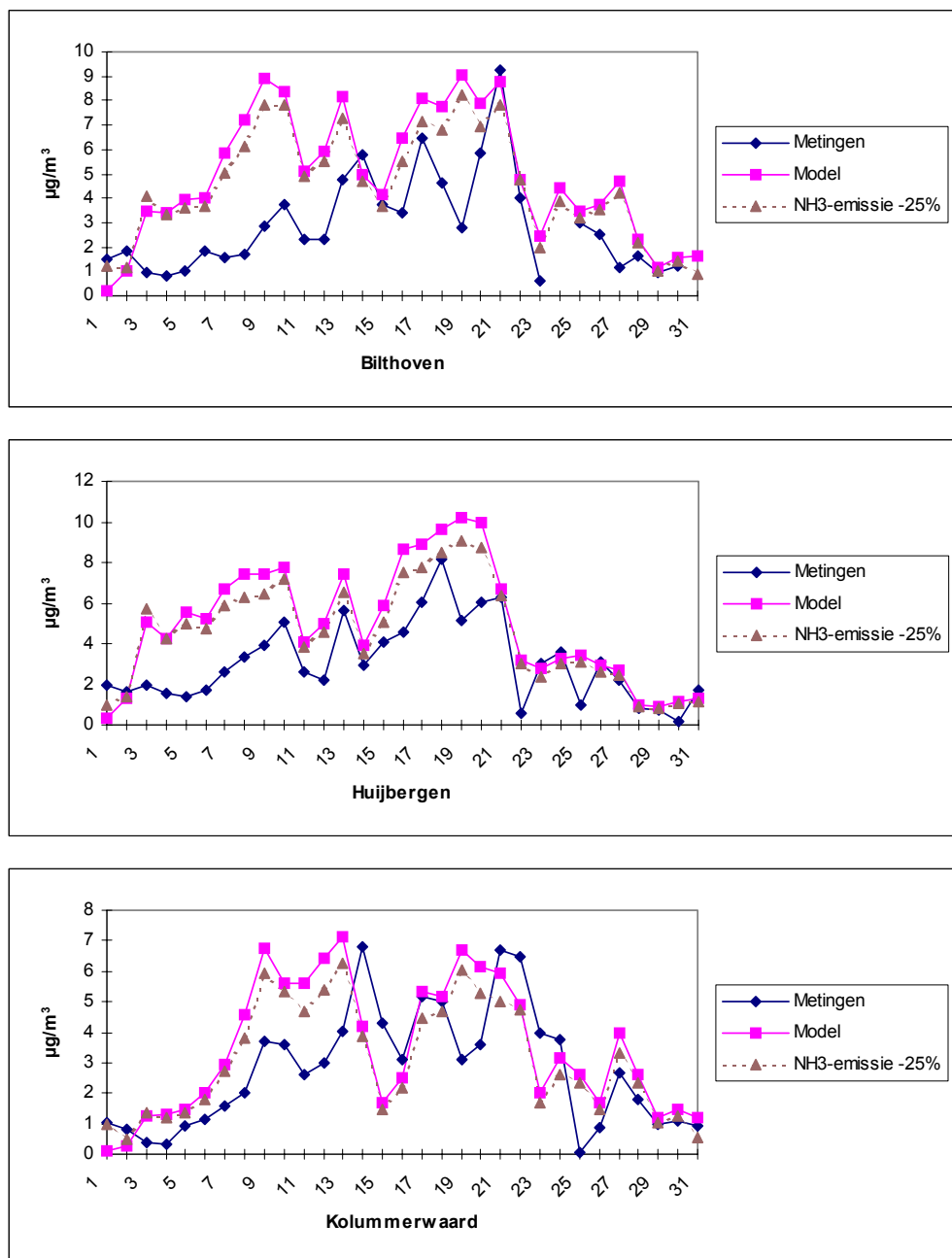


Figure 6.4 Measured and calculated daily averaged ammonium-concentrations for 6 measuring stations for August 1997

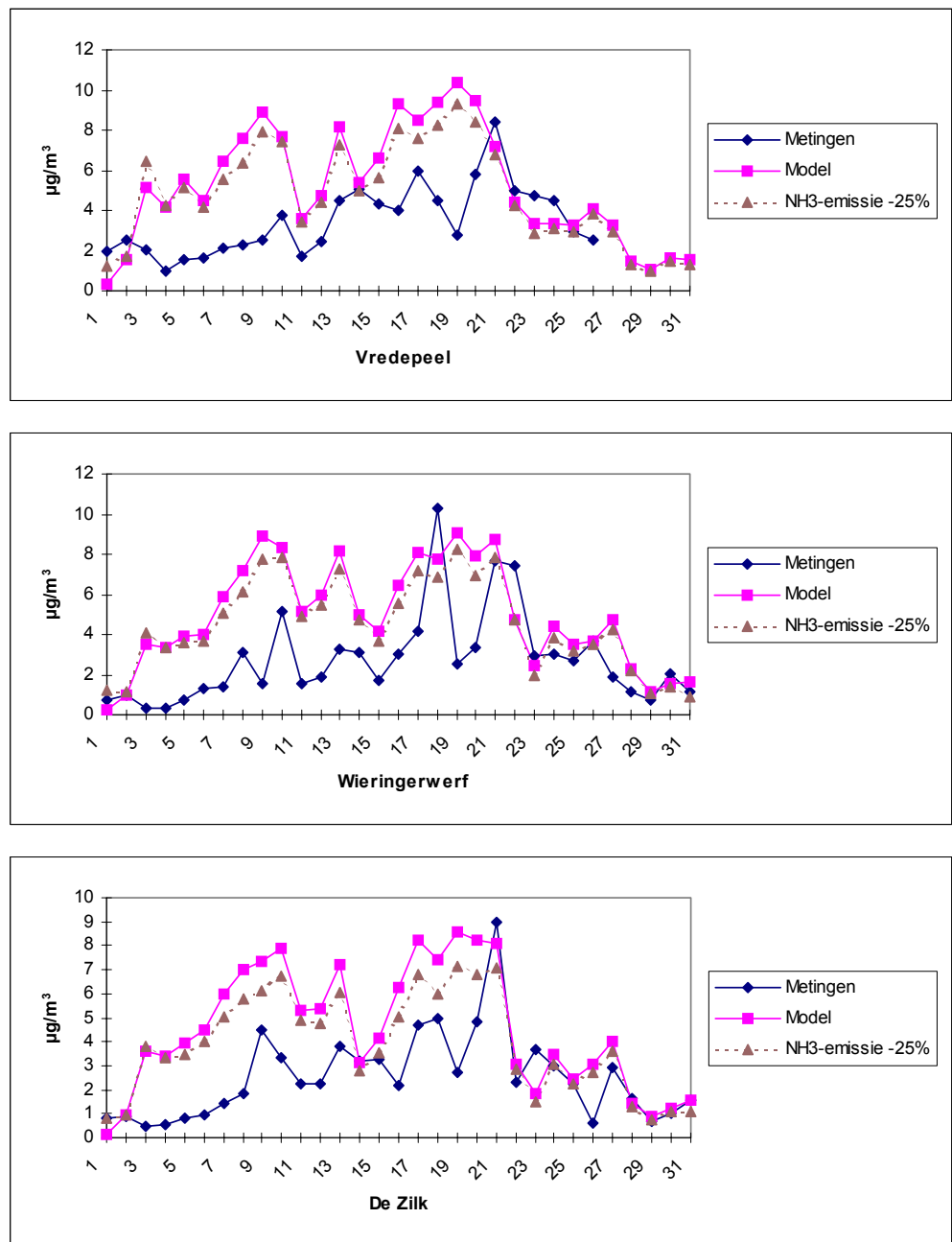


Figure 6.4 (continuation)

7. Conclusions and recommendations

In this study a first step has been taken to model aerosols in LOTOS. For this purpose first the gas phase reaction mechanism is made suitable for the implementation of ammonium sulphate and ammonium nitrate. The new mechanism was tested using the reported contributions to the EUROTRAC Chemical Mechanism Working Group comparison (Poppe et al., 1996). The results of the extended mechanism corresponded well with the reported contributions. From this it was concluded that the mechanism performs well compared with other mechanisms and is suitable for use in LOTOS.

The aerosol module describes the equilibrium between gaseous nitric acid and ammonia, (bi)sulphate, nitrate and ammonium. The module calculates the aerosol composition for two schemes. In the high ammonium scenario the equilibrium between gaseous nitric acid and nitric acid in solution was added to this module. This process is important if little free ammonia is present to form ammonium nitrate. As a result the calculation of the nitrate content in the schemes is consistent with one another and the transition between the schemes is no longer discontinuous.

The effect of the aerosol chemistry considered on ozone formation was investigated by considering aerosols in a scenario of the EUROTRAC comparison. This shows that the consideration of aerosols has little effect on the ozone formation. This can be explained by the fact that the dissociation of nitric acid to form NO_2 takes place slowly. The fixing of nitric acid in nitrate therefore has little effect on the NO_2 concentration. It should be noted here that no physical processes, such as deposition and the effect of the aerosol load on the photolysis frequencies are taken into consideration.

With LOTOS the sulphate, nitrate and ammonium concentrations in August 1997 were modelled. The calculated daily average sulphate concentrations show compared with the measured values a reasonable course over time. The model overestimates the sulphate concentrations considerably when air flows from the East. Probably this overestimate is caused by an overestimate of SO_2 emissions in Germany.

The average nitrate and ammonium concentrations are too high, even though the measured concentrations are probably a lower limit. The concentration of ammonium nitrate is very sensitive to the ammonia concentration. The overestimate of the ammonium nitrate contents is then probably partly attributable to the present ammonia modelling.

The discrepancies between the calculated concentrations and the measured values may also have other causes. Firstly one measurement point is not representative of a whole LOTOS cell. Local conditions may greatly affect measurements. Secondly the concentration close to the ground is not the same as that in the mixed layer. In particular the ammonium nitrate concentrations close to the ground could be lower than the mixed layer average concentrations. In addition assumptions in the aerosol chemistry may cause errors. Finally no account is taken of the size distribution of

aerosols, as a result of which errors occur in the description of the behaviour of aerosols.

Modelling aerosol concentrations over Europe with LOTOS can be improved on a number of points. To model aerosols well it is necessary for the precursors of these aerosols to be modelled well. In particular the modelling of ammonia must be improved. For this a certain percentage of the ammonia emission can be removed directly from the system. In addition by extending the number of layers in the vertical, the vertical gradient of ammonia can be better described.

The physical behaviour of aerosols is described in LOTOS independently of the size. To refine the modelling of aerosols it will be necessary to introduce a size distribution, sectional or modal. As a result it becomes possible to model the physical processes better, depending on the diameter. As a source and sink for aerosols the interaction between particles and clouds must be covered. In LOTOS the vertical domain will have to be increased for this.

In order to compare the calculated aerosol concentrations with measured concentrations better, the concentrations will have to be calculated at measurement level. In addition more information must become available on the representativeness of measurements and the reliability of the aerosol nitrate measurements.

In this study only ammonium sulphate and ammonium nitrate aerosols are modelled. In the future it will be necessary to extend the number of components with other organic aerosols, black smoke and primary aerosols.

Finally the whole modelling of ammonium nitrate is based on thermodynamics.

Without a good description of this chemistry it is not possible to model ammonium nitrate properly. It is also necessary to constantly improve the aerosol module and to test it with new insights.

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9. Authentication

Name and address of the principal:

(based on the master thesis,
Univ. Utrecht of M. Schaap, July 1999)

Names and functions of the cooperators:

M. Schaap

Names and establishments to which part of the research was put out to contract:

-

Date upon which, or period in which, the research took place:

-

Signature:

Approved by:

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project leader

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