

Nitrogen species in the Tropospheric Multiphase System

Contribution to the Barnsdale Expert Meeting on Nitrogen

Hartmut Herrmann, Paolo Barzagli, Gerald Spindler, Erika Brüggemann,
Thomas Gnauk and Andreas Tilgner

*Leibniz-Institut für Troposphärenforschung, Chemistry Dept.
Permoserstraße 15, D-04318 Leipzig, Germany*

Summary

The Barnsdale 2005 meeting focuses on the role of nitrogen species in the atmosphere. Within this short contribution three aspects are treated. The first is that the atmosphere has to be viewed as a multiphase system, i.e. that conversion processes occurring in more than one phase only should be considered. Secondly, nitrogen species, in both reduced or oxidized forms, do establish a considerable fraction of current PM₁₀ load in the Leipzig area as identified in recent field experiments. Thirdly, there have been recent developments in atmospheric aqueous phase mechanism development which are shortly described and referenced.

Introduction

Nitrogen species are an important part of the chemical ensemble of the troposphere [Zellner, 1999; Finlayson-Pitts and Pitts, 2000]. Many of their chemical conversions should be viewed upon as processes where gas phase chemical conversions, transfer to different phases, i.e. dispersed solids, aqueous aerosol particles and haze and cloud droplets and subsequent particle-phase associated chemical conversions are coupled. The main interactions in the multiphase system have already been described early, eg. by W. Jaeschke, [Jaeschke 1986] and are depicted in the subsequent viewgraph.

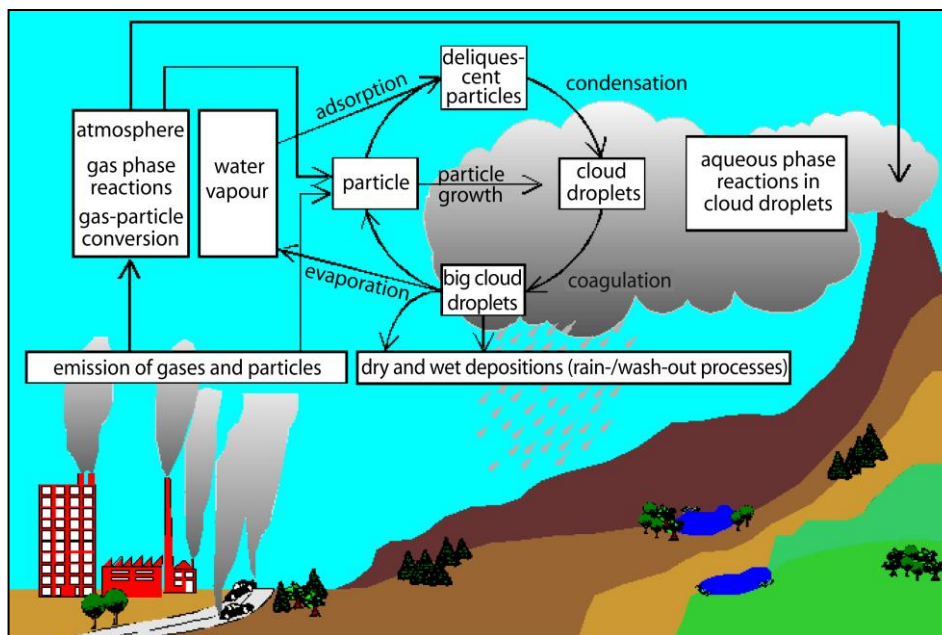


Figure 1. The tropospheric multiphase system, after W. Jaeschke et al. [Jaeschke et al., 1986].

Scientific activities

The IfT chemistry department is studying tropospheric multiphase chemistry in (a) laboratory experiments deploying aqueous phase, gas phase and phase transfer experiments, (b) field

experiments for a better characterisation and understanding of aerosol and cloud chemical composition and processing and, finally, (c) multiphase model development with the CAPRAM (Chemical Aqueous Phase Radical Mechanism) line of chemical mechanisms. More detailed information can be found under www.tropos.de.

Scientific results and highlights

The multiphase system

The system depicted in Figure 1 opens way for a variety of conversions, some of the physical and chemical interactions in the particle phase are depicted in Figure 2, and some of important chemical species are shown in Figure 3.

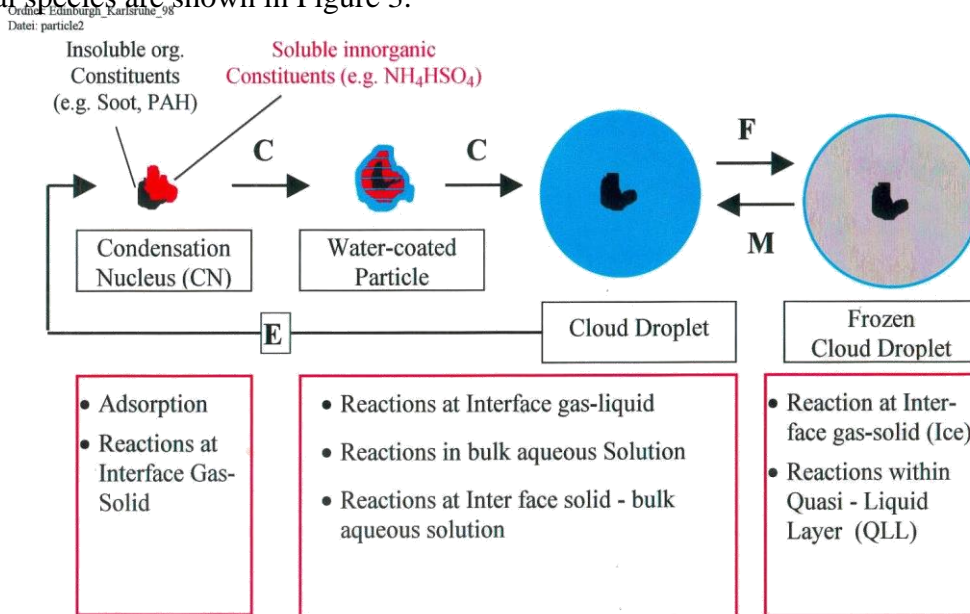


Figure 2. An individual particle being physically modified.

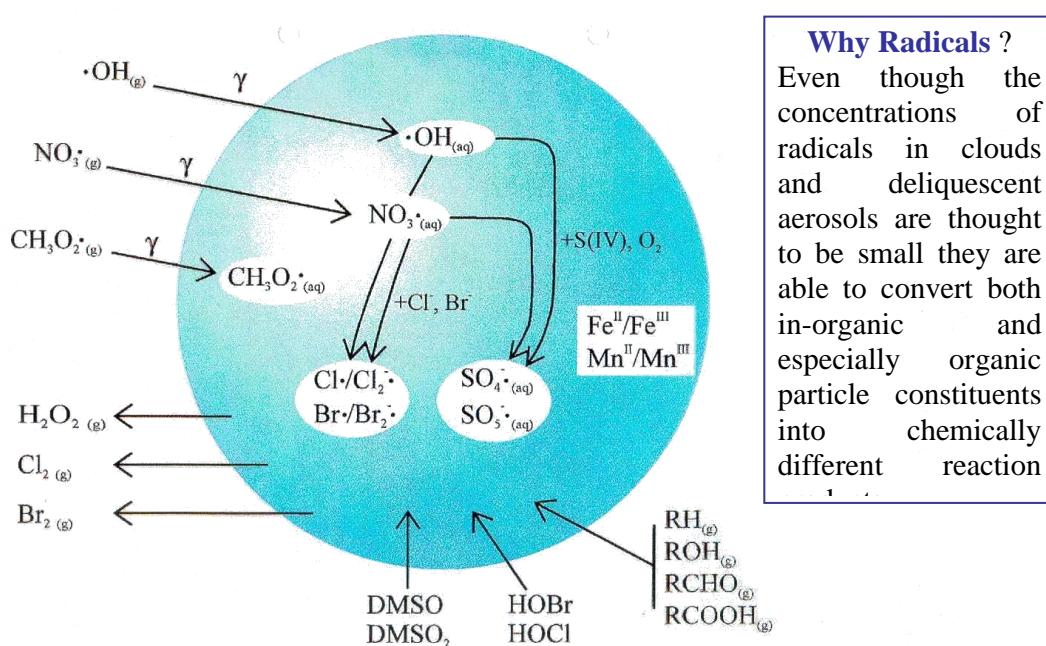


Figure 3. A schematic of selected aspects of tropospheric aqueous phase radical chemistry.

Multiphase conversions appear to be of huge interest with regard to the following sub-systems related to N-chemistry: (i) HONO formation, (ii) formation of (multifunctional) organic nitrates, (ii) photochemistry of nitrate and nitrite and the production of NO and NO₂ in aqueous solution and from ice and others.

Reduced and oxidized nitrogen particle constituents

The following graphs show recent results from PM₁₀ characterisation measurements at the IfT research station Melpitz. In Figure 4 the definition of easterly (continental) and westerly (maritime) sectors is shown, whereas Figure 5 shows the results from chemical analysis.

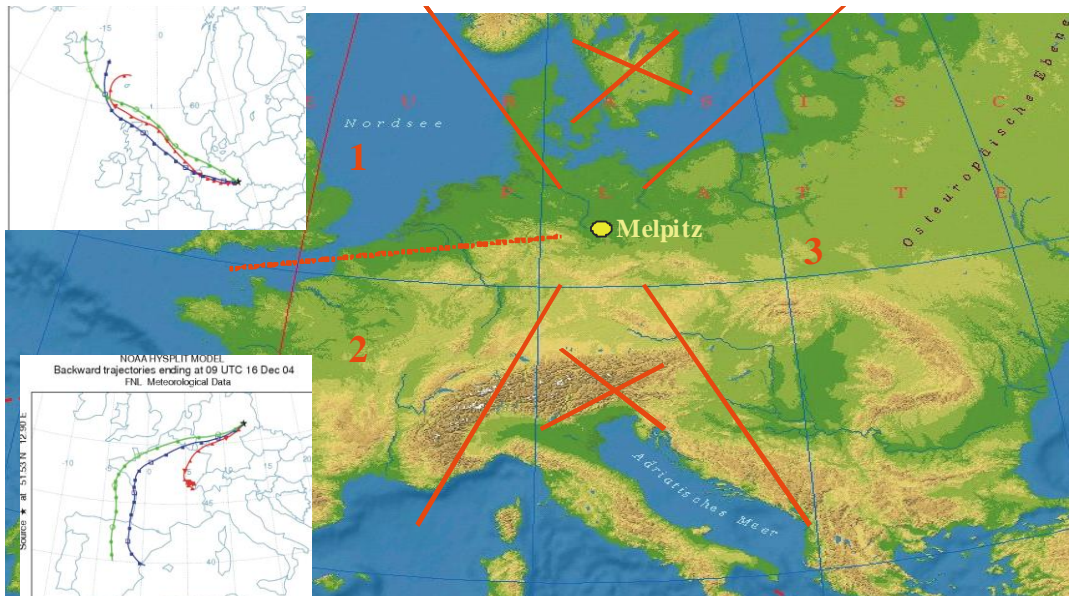


Figure 4. Sector definition for Melpitz PM₁₀ characterisation.

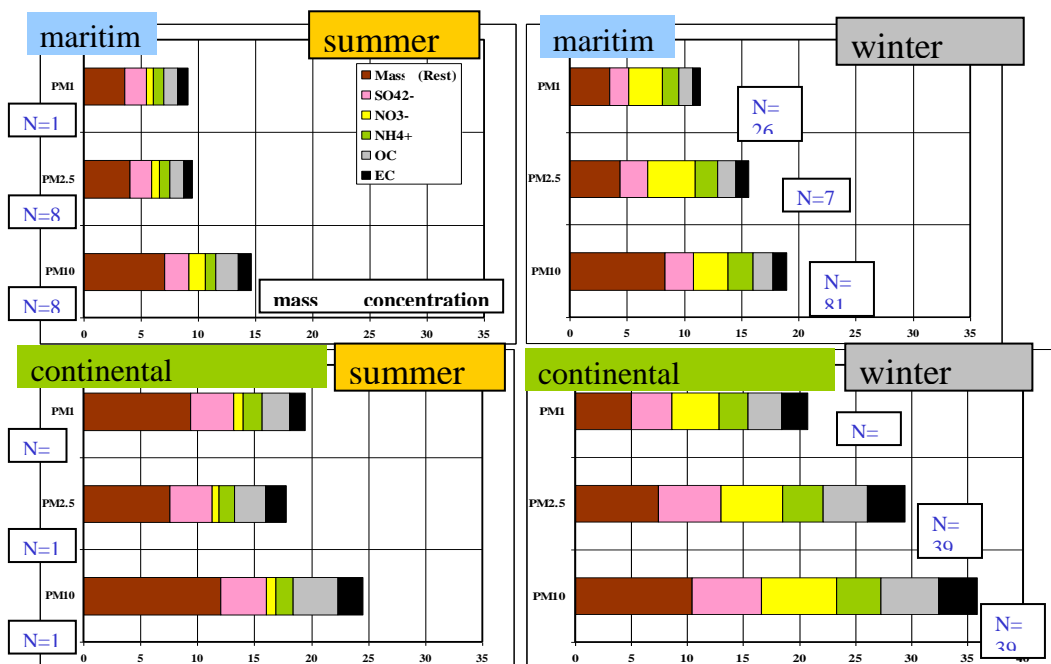


Figure 5. Average seasonal results of sector-resolved PM₁₀ analysis [Spindler et al., XXXX]

In a long-time study, differences in the PM load from these different sectors can be much different. Apparently, under winter conditions with, transport from the east leads to a higher PM₁₀ load compared to westerly back trajectories. It should be noted that both reduced nitrogen in the form of ammonium as well as oxidized nitrogen in the form of nitrate form an important fraction of PM₁₀, especially in winter.

Current tropospheric multiphase chemistry mechanisms

Modelling studies have previously indicated that the interaction of trace gases with the liquid phase of clouds modifies also the chemistry in the gas phase [e.g. Crutzen and Lelieveld, 1991; Kreidenweis *et al.*, 2003]. Due to the complexities resulting from the interplay of physical and chemical cloud processes, many models focus either on the complex multiphase chemistry in only a few aggregated drops size classes [Herrmann *et al.*, 2000; Djouad *et al.*, 2003], or on the details of microphysics by assuming strongly simplified chemical mechanisms [Fahey and Pandis, 2001]. The recent development of more sophisticated cloud models that incorporate more comprehensive chemical mechanisms now makes it possible to study the interaction between microphysical and multiphase chemical processes in greater detail [e.g. Wolke *et al.*, 2005]. For further details and referencing an overview has been recently published on aqueous phase processes aspects relevant to the tropospheric chemistry [Herrmann, 2003].

Further, recent developments in laboratory and modelling studies indicate that aqueous phase chemical processes, which are not only restricted to cloud chemical conversions but also include deliquescent particle chemistry, might have profound effects in atmospheric chemistry. Such effects comprise establishing aqueous phase parts in the oxidation of volatile organic compounds (VOCs) of both biogenic and anthropogenic origin, release of reaction products both inorganic and organic to the gas phase and, mass production for the aerosol phase. However, only few studies have attempted to characterise the conversions of organic compounds within the tropospheric aqueous phase [Herrmann *et al.*, 2005; Ervens *et al.*, 2004; Ervens *et al.*, 2003; Warneck, 2003].

The latest version of the CAPRAM series is represented by CAPRAM 3.0, where particular emphasis is given to the aqueous phase chemistry of organic compounds (Figure 6).

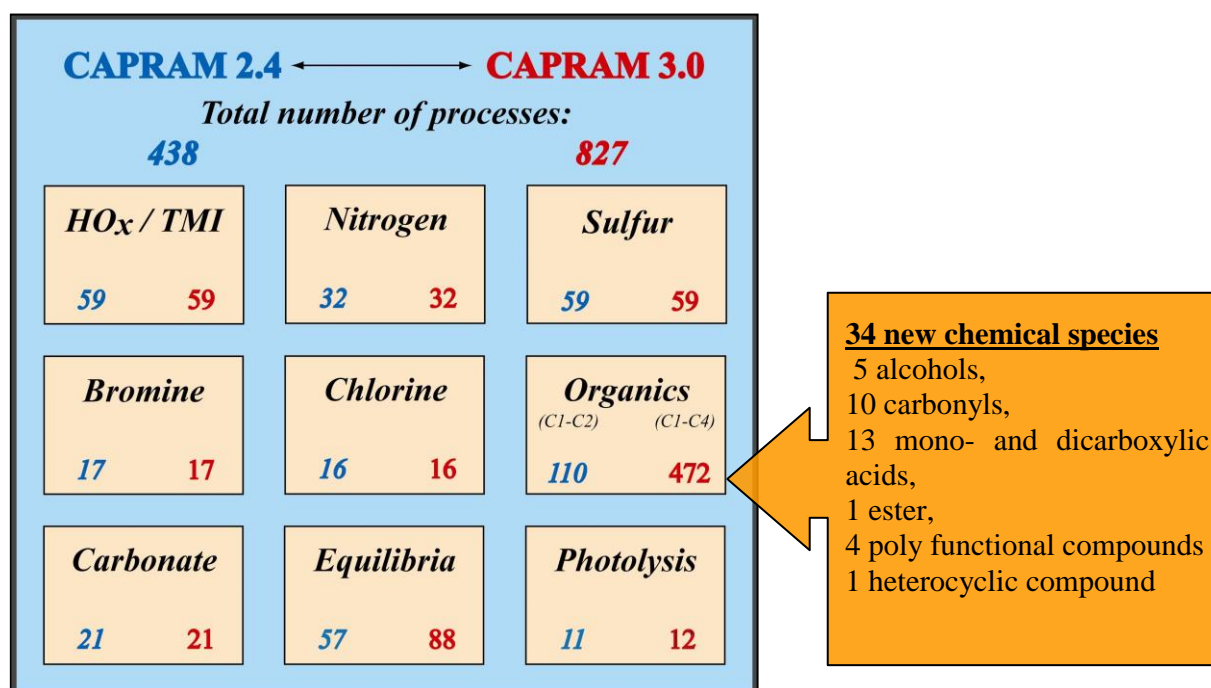
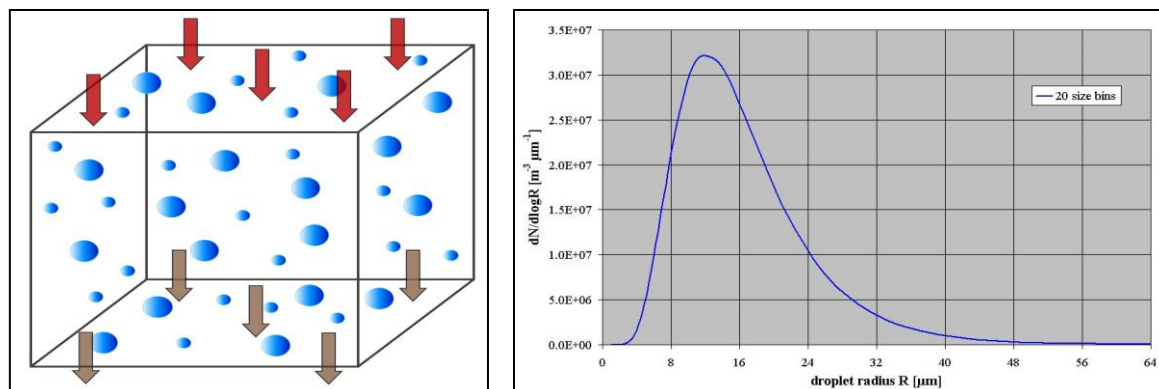


Figure 6. Number of processes included in CAPRAM 2.4 [Ervens *et al.*, 2003] and CAPRAM 3.0 [Herrmann *et al.*, 2005].

Simulations carried out in a zero-dimensional box model (Figure 7) showed, among others effects, strong influence on radical budget when a detailed chemistry of higher organics (up to C4) has been considered [Herrmann *et al.*, 2005].



- Emissions: $10^5 - 10^7 \text{ cm}^{-2} \text{ s}^{-1}$
 - Depositions: $10^{-7} - 10^{-5} \text{ s}^{-1}$
 - $\Sigma \text{LWC} = 0.3 \text{ g}_{\text{aq}} \text{ m}^{-3} \text{ air}$
 - $T = 288 \text{ K}$, $p = 1013.25 \text{ hPa}$
 - variable number of size bins [$1 \mu\text{m} < r_{\text{drop}} < 64 \mu\text{m}$] 20 bins used
 - different atmospheric scenarios (marine, remote, urban)
 - Gas phase mechanism: RACM (Stockwell *et al.*, 1997)
 - Uptake: following the approach by Schwartz (1986)
- constant microphysical
conditions for chemical
process studies

Figure 7. Experimental conditions applied in the 0-dimensional box model.

In the case of the nitrate radical, it has been shown that in simulations with both mechanisms CAPRAM 2.4 [Ervens *et al.*, 2003] and CAPRAM 3.0 are leading to similar nitrate radical (NO_3) levels at the beginning. At later simulation times it becomes evident that in the presence of extended organic chemistry the NO_3 concentration significantly decreases (30% after 96 hrs) compared to CAPRAM 2.4. In the medium polluted scenario the observed differences in the concentration level of nitrate radical are attributed to the sink reactions with substituted carboxylic acids and their anions, which represent an alternative oxidation pathway for higher organics under nighttime conditions. Moreover, the aqueous phase conversion of NO_3 radicals through its reactions with organic compounds might have an indirect influence on the pH due to the formation of HNO_3 .

Furthermore, the oxidation pathway of nitrogen-containing heterocyclic compounds has been introduced for the first time in an aqueous phase tropospheric model [Herrmann *et al.*, 2005]. On the basis of a recent aqueous phase study [Friesen *et al.*, 1999] and results on NMP gas phase oxidation obtained in the MOST project (<http://most.univ-lyon1.fr>) a reaction mechanism for the oxidation of N-methylpyrrolidin-2-one (NMP) is included.

Future Outlook

Nitrogen chemistry will be a very lively and interesting field in tropospheric multiphase chemistry studies for the future. HONO, organic nitrates, polyfunctional organic nitrates, nitrated aromatics such as nitrophenols, N-heterocycles and, last but not least, multiphase NO_3 and NO_2 chemistry are constituting subjects of the highest interest.

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