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Volatility of traffic-related aerosol particles

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Introduction

Emissions from road transport are considered to be a major source of anthropogenic submicrometer particles in the urban environment. Potential effects upon human health are subject of an on-going scientific and public discussion. One aspect, which is sometimes neglected in the PM number discussion, is the different chemical composition and volatility of atmospheric particles. Here, we focus on the differentiation between volatile material and the non-volatile fraction of particles.
In general, the atmospheric aerosol can be divided into two groups with respect to their volatile behaviour. Several materials are volatile below temperatures of 250°C such as sulphate, nitrate, ammonium, and several volatile organic carbon compounds. The second group contains those compounds which are thermally resistant up to 250°C and includes sea salt, crustal material, trace metals, fly ash, and carbonaceous compounds such as soot. The latter one plays the most important role in anthropogenically influenced regions. Therefore, the volatility measurement is suitable to characterize the fraction of non-volatile carbon on the total number of particles.

The measurement systems

In the scope of this study two measurement systems were used to measure the volatility. The first one is the so-called Volatility Tandem Differential Mobility Analyzer (VTDMA). This instrument is capable of measuring number volatility distributions of thermally conditioned particles of selected monodisperse sizes, therefore allowing the identification of number and volume fractions of non-volatile material within aerosol particles in the submicrometer size range.
The VTDMA system consists of three parts. In the first part defined particle diameters of the polydisperse aerosol population in the ambient atmosphere are selected with a Differential Mobility Analyzer (DMA) and counted with a Condensation Particle Counter (CPC, TSI Model 3010). They are subsequently passed on to a conditioning unit in order to be heated to a specific temperature of usually 280°C to volatilize part or all of their material, leaving only non-volatile components at this particular temperature behind. In the last part of the system the resulting number size distribution of the residual aerosol particles as well as of an according reference distribution at ambient 25°C are measured with a second DMA/CPC.
The inverted size distributions were used to calculate several parameters describing the volatility distribution sufficiently. Integration yields the total number concentration, division of the thermal conditioned one by the initial one gives the residual fraction. This fraction may consist of different material. Therefore, the concept of *quasi-non-volatile* and *partially-non-volatile* particle fraction is introduced. Quasi-non-volatile-particles consist almost entirely of non-volatile material. They are characterized by an unaltered diameter after thermal conditioning, reflecting that the particles contained no evaporative material. All other particles contained variable amounts of volatile material before the heating process and are therefore called partially-non-volatile.
Within this study the volatility size distributions will be standardized. Thus they are a relative measure for the volatility of aerosol particles and need to be interpreted in conjunction with the size distribution measurements (SMPS without thermodenuder).

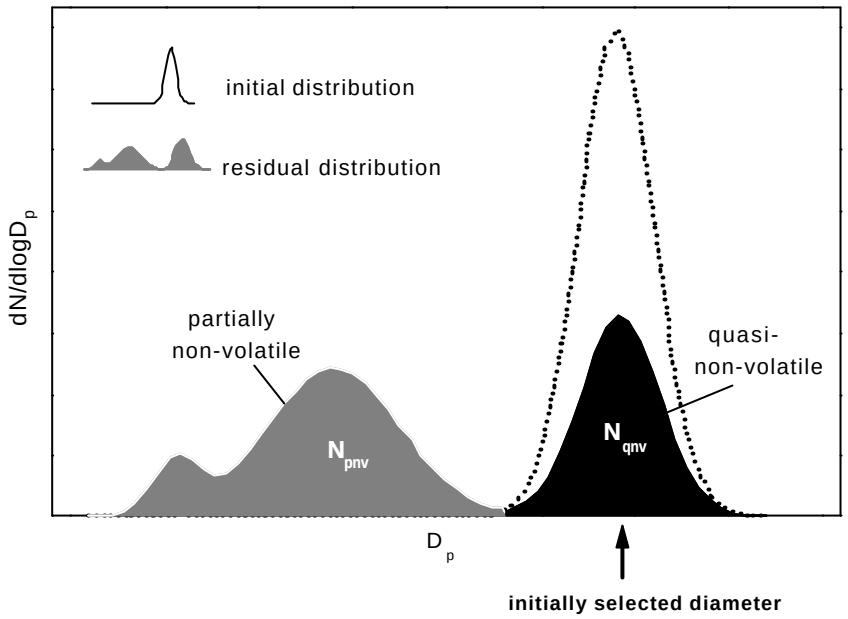

Figure 1: Example of volatility distributions of ambient (dotted) and conditioned (shaded) particles and partitioning of residual particles into quasi-non-volatile and partially-non-volatile particles.

The second system consists of two SMPS (TSI Inc.) and a Thermodenuder (TD). Where the first SMPS measures ambient number size distribution and the second SMPS was placed behind a newly constructed TD, held at four different temperatures (80, 130, 180, and 280°C). The TD removes volatile compounds of aerosol particles by thermal desorption. It consists of two units, a heating and a cooling section. In the first part of the instrument, aerosol particles are heated to a certain temperature (maximum ~ 300 °C) where all volatile material is evaporated. The subsequent cooling tube is filled with active carbon for the adsorption of evaporated gas phase compounds.

Results

From August 17 to August 22, 2000 measurements were carried out at a parking area close to the German highway A4 in the north of Aachen. In addition to VTDMA and Thermodenuder/SMPS, several trace gas concentrations (O_3, NO_x, NO, CO) as well as meteorological parameters were also recorded with the Ford Mobile Laboratory.

The results were probably significantly influenced by meteorological conditions, particularly wind direction and speed, due to the different dispersion of the vehicle exhaust. In the scope of this study, data of three measurement days from that site will be presented and compared.

At first, typical VTDMA-results taken on Friday, August 18 will be shown here. Four diameters (30, 50, 80, and 150 nm) were selected to measure the fraction of evaporated number and mass at 280°C. Figure 2 shows the number size distributions measured with and without thermal conditioning for the four diameters. The 30nm particles are almost completely evaporated at 280°C. At 50 and 80 nm a significant fraction remains which is only slightly shifted to smaller diameters. At 150 nm the highest fraction of quasi-non-volatile material occurs. The number of the partially-non-volatile particles is obviously also increasing with increasing initially diameter.

Figure 3 shows the evolution of number of the total non-volatile fraction and also the partially-non-volatile fraction of the selected size fractions. Additionally, the total number concentration during the day is plotted as the black line. The lowest fraction of non-volatile particles occurs always in the 30nm fraction while the highest values were measured for 80 and 150nm particles. There is no clear correlation between the total number concentration and the non-volatile fraction recognizable.

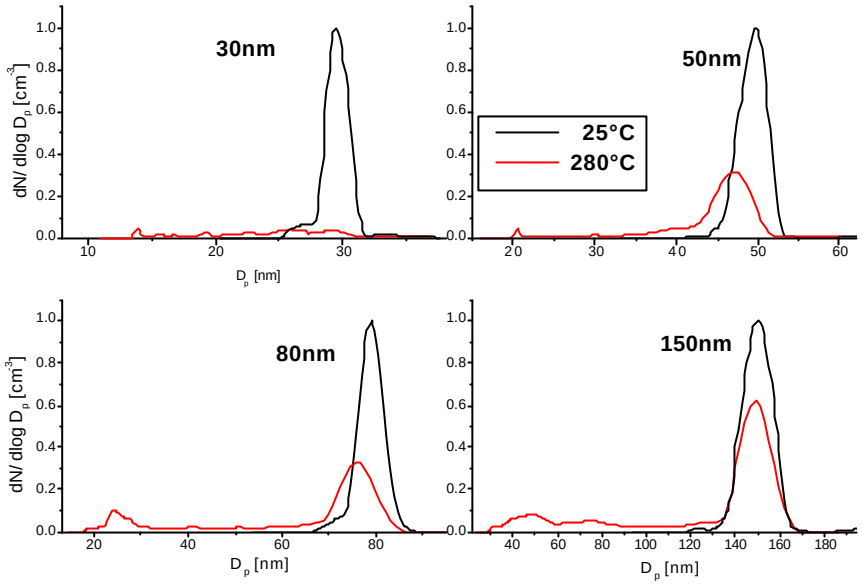

Figure 2: Mean volatility number distributions (normalized), each averaged over seven single measurements taken during Friday, August 18.

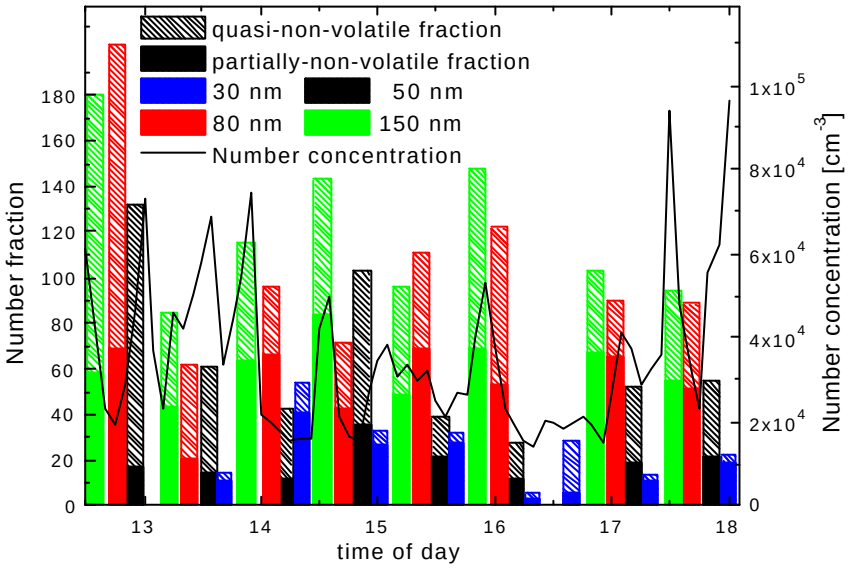

Figure 3: Evolution of the non-volatile and the partially-non-volatile number fraction of selected particle sizes as well as the total number concentration during the day (August, 18).

In Figure 4 NO_x and the particle concentration show a similar behaviour, both are mainly influenced by traffic emissions at this site (cf. also Fig. 5). The temperature of the thermodenuder was changed during the day to perform measurements at 80, 130, 180, and 280°C. Above 80°C there is always a significant difference between the number concentration with and without TD.

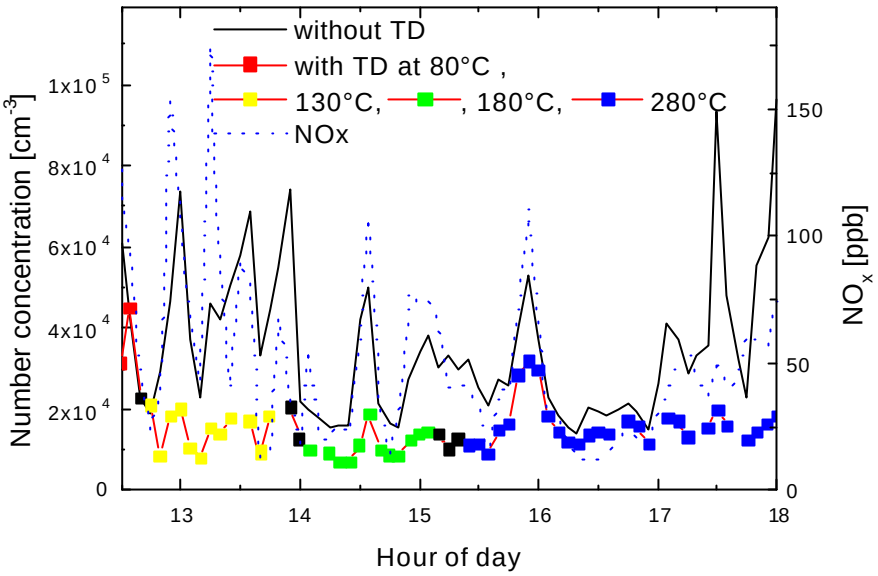

Figure 4: Evolution of the total number concentration with and without passing the thermodenuder at different temperatures as well as the NO_x-concentration (August 18).

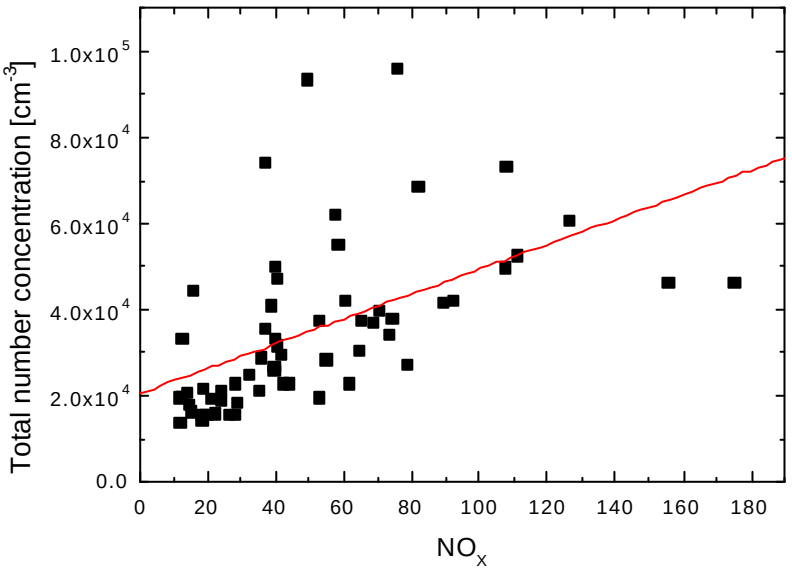

Figure 5: Relation between total number concentration and NO_x-concentration on August 18.

Comparison of three measurement days

The results of three different measurement days at the highway will be compared now. The ambient conditions varied slightly, e.g., meteorological parameters as well as the composition of the traffic. The ambient temperature was rather similar (18-21°C), only the relative humidity was higher on Saturday and the wind speed was significantly higher (< 1.5 m/s) than on Friday (< 0.3 m/s) and Sunday (< 0.4 m/s). The wind came directly from the highway on all three days. The mean NO_x-concentration during the measurement period was on Friday 63 ppb, on Saturday 82 ppb, and on Sunday 23 ppb, reflecting the different influence of traffic conditions on the measurement site. Traffic density calculations resulting from several traffic counts on the investigated days yield typical values of 2000 – 3000 passenger cars/

hour on workdays as well as during the weekend, but the number of trucks and busses is significantly reduced during the weekend (~ 60 h^{-1}) compared to workdays (~ 600 h^{-1}).

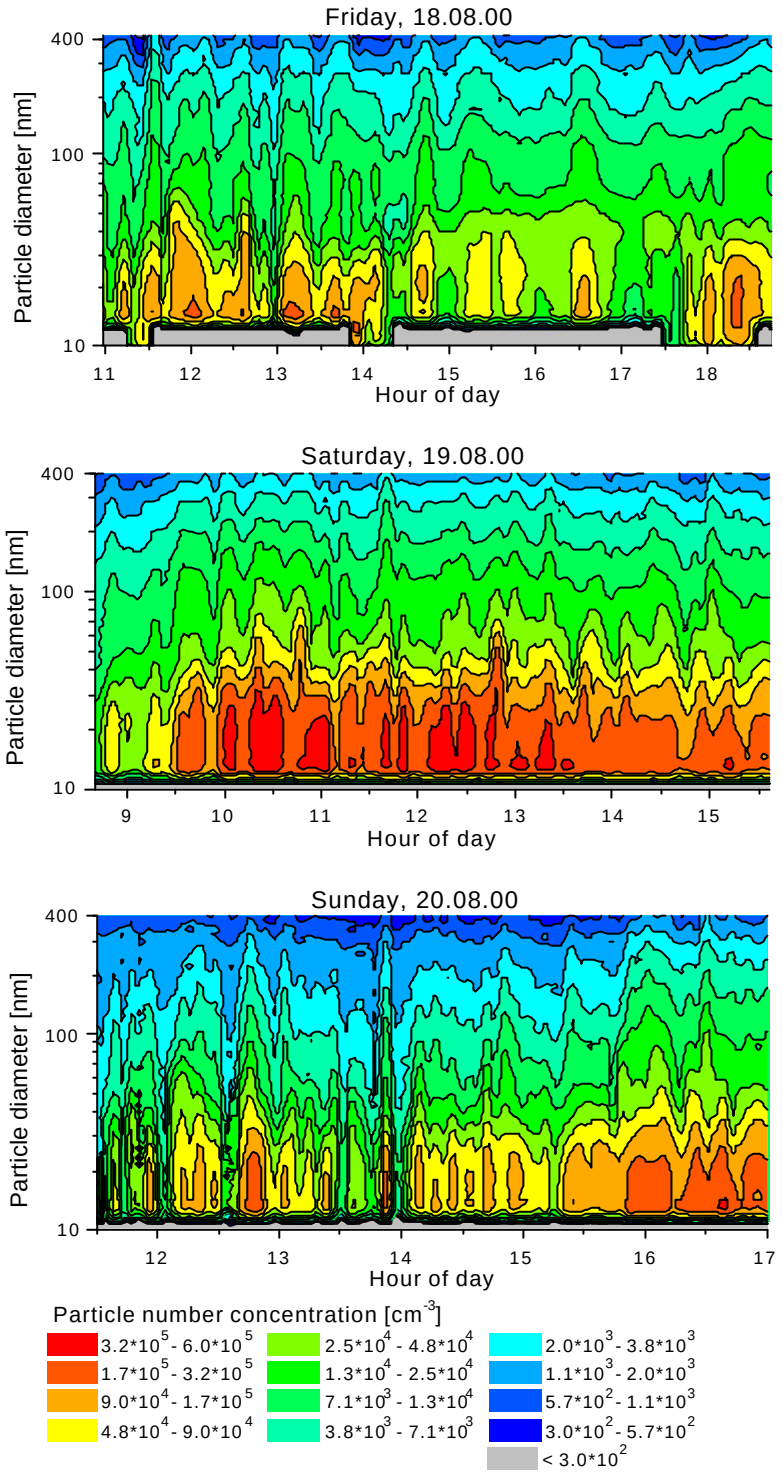

Figure 6: Evolution of number size distributions on August 18, 19, and 20, 2000.

Figure 6 shows the evolution of the number size distribution on the three days, the highest number concentration occurs between 10 and 30 nm, and the maximal measured on Saturday exceed those of the other days. Thus, the pollution level at the measurement site is mainly determined by meteorological conditions connected with the transport of the traffic emissions.

Figure 7 contains the mean size distributions of the three measurement days at the A4 taken without and with thermodenuder. The shape of the curves without thermodenuder is very similar, but the maximum value of Saturday exceeds those of Friday and Sunday significantly. These black curves have a maximum between 10 and 20 nm, the curves consist obviously of two dominating modes: one in the ultrafine range

(10 – 20 nm) and one in the accumulation mode range recognizable as a shoulder around 100 nm. After the heating process, the number concentration in the smaller mode in significantly reduced. However, also the number concentration above 100 nm is significantly reduced, reflecting the presence of some volatile material in this size range whether the particles are completely volatile or partially-non-volatile.

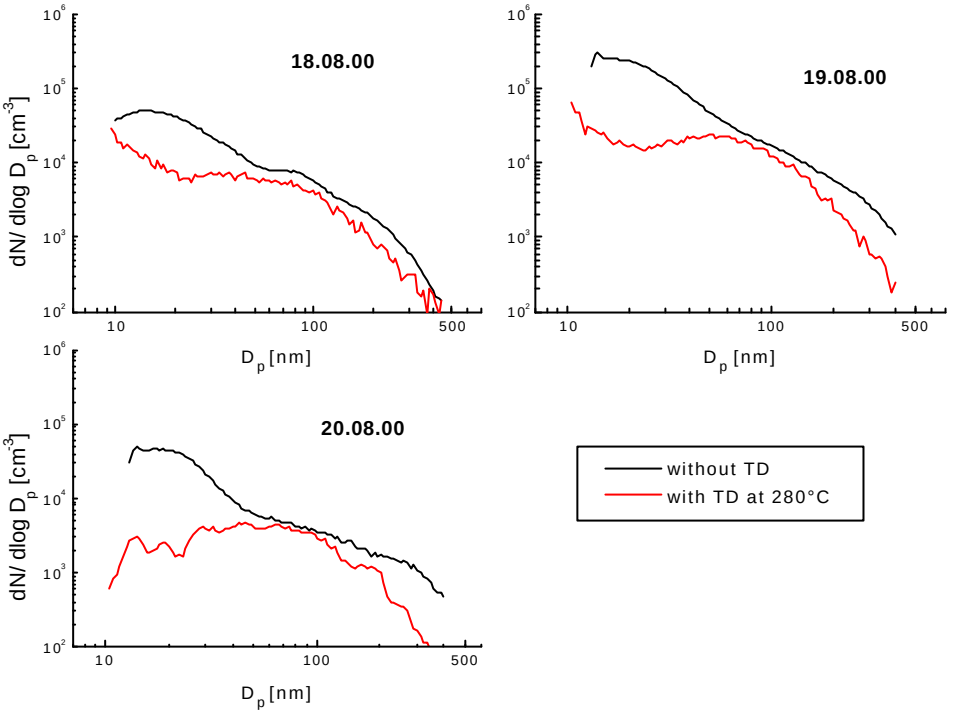

Figure 7: Mean number size distributions with and without thermodenuder on August 18, 19, and 20.

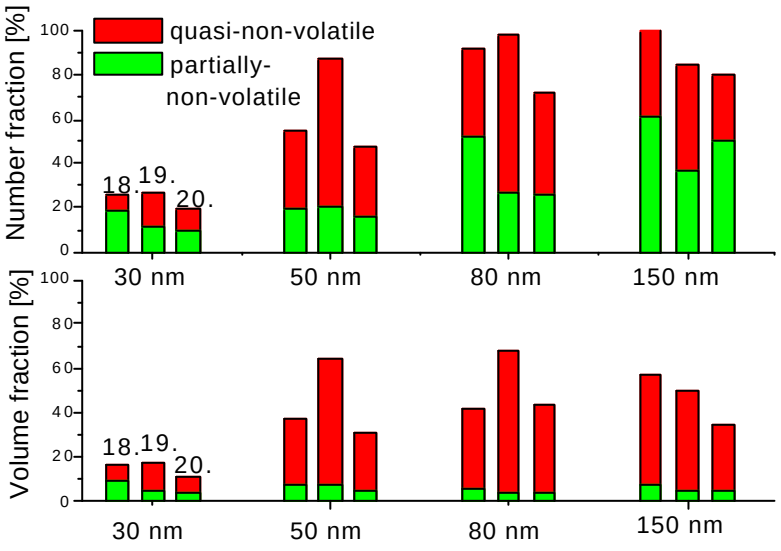

Figure 8: Comparison of the volatile fractions of number and volume between August 18, 19, and 20.

Figure 8 shows the averaged values of the non-volatile fractions, as well as the proportion of partially-non-volatile particles for the three measurement days investigated in this study. The non-volatile fractions vary significantly. The fraction of non-volatile material measured on August 20 is generally lower compared with the other days. The non-volatile number concentration has the lowest value at 30 nm during all days.

Figure 9 shows the dependence of the thermodenuder ratio (with/without TD) on the total particle concentration while only measurements with a TD temperature above 80°C were used.

On Friday and Sunday the same clear trend is recognizable from the data: an increase in the total number concentration without thermodenuder leads to a decrease in the TD-ratio. Thus, it may be concluded that the additional particles (obviously caused by car traffic) are more volatile than the background particle being always present. On August 19 as a relatively high polluted day the number concentrations were above 50000 cm^{-3} during the measurement period, thus there is no influence of background particles detectable at all, the observed particles are completely dominated by car traffic emissions.

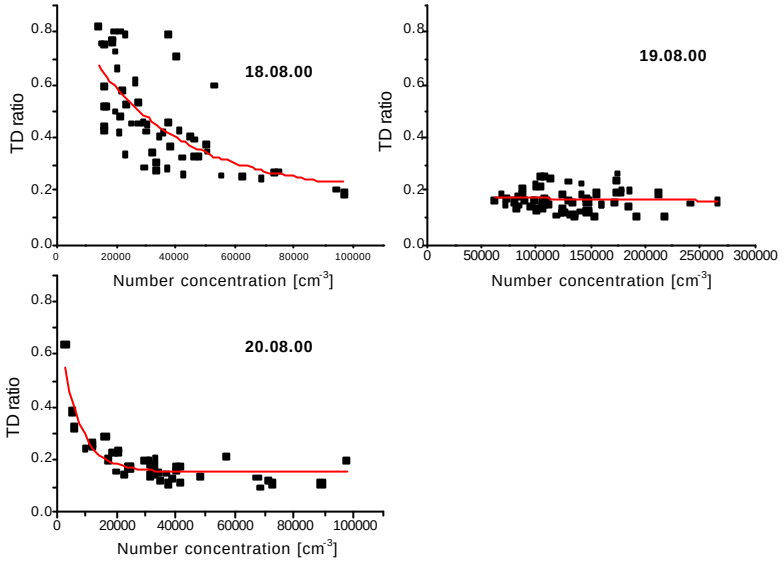

Figure 9: Dependence between the thermodenuder ratio (number concentration with thermodenuder >80°C/ without thermodenuder) and the total number concentration.

Conclusions

In this study was shown that the particle concentration as well as the NO_x-concentration at a certain measurement site are strongly influenced by meteorological conditions in addition to the pollution source.
The highest fraction of volatile material was found in the ultrafine region: at 30 nm only 20 – 30% of the particle number was remaining after the heating process. For the 80nm-particles 70 – 90% were non-volatile at 280°C. This is a result of the higher proportion of soot in this size range which is not volatile at the selected temperatures. The majority of 30nm-particles obviously does not consist of soot.
Furthermore it was shown that with increasing number concentration (traffic influence) the proportion of non-volatile particles decreases. Therefore it can be concluded that most of the traffic related particles in the atmosphere are volatile and thus, do not consist of soot.