

**AIRBORNE MEASUREMENTS OF THE UTLS
AEROSOL CHEMICAL COMPOSITION OVER
GERMANY USING PARTICLE MASS
SPECTROMETRY**

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ABSTRACT

Aerosol particles affect the Earth's radiation budget by interacting with solar and terrestrial radiation but they can also act as cloud or ice nuclei both of which depend on physical characteristics and chemical composition of the particles. In addition to natural aerosols, commercial aircraft is a significant anthropogenic source of aerosol particles in the extratropical upper troposphere and lower stratosphere (UTLS). Yet, the knowledge of UTLS aerosol particles and the contribution of aircraft exhaust on the formation e.g. of cirrus and contrails is limited although these cloud types have a strong impact on radiative forcing. This study focuses on the occurrence of individual particle types in UTLS ambient air as well as cirrus and compares them with phases of aircraft exhaust plumes and contrails. The hybrid mass spectrometer ERICA was deployed for airborne measurements of aerosol chemical composition in a size range of 174 nm and 3.2 μm . A standard aerosol inlet and counterflow virtual impactor were used to sample interstitial particles (56058) and cloud residuals (3408) in the wintertime UTLS region over Northern Germany. The particle analysis is based on fuzzy c-means clustering and complementary measurements of trace gases and cloud properties as well as synoptical analysis and simulations of air mass history.

This study revealed that biomass burning (BB) and carbon-containing particles dominated the winter UTLS region over Northern Germany. Of the cloud residuals, sea spray, mineral dust, and BB were the most abundant. Westerlies largely influenced the particle occurrence: sea spray was attributed to Atlantic air masses and BB particles were assigned to North American wild fires. Meteoric material was detected above and inside the tropopause layer. In addition, laboratory measurements of ammonium sulphate provided a potential source of cation sulphur signals in ambient particle mass spectra. Further, the nitrate-rich particle type detected during the ND-MAX campaign was not attributed to a recombination process of nitrogen oxide precursors. Moreover, a comparison unveiled that contrails can grow on the same particles as cirrus, suggesting the formation of both via the liquid phase as confirmed by the ice water content analysis. The composition of contrails was rather driven by the UTLS aerosol background than by particles of aircraft fuel combustion. However, the lower detection limit of ERICA inhibits the sampling of exhaust-related particles below 174 nm, not allowing for the analysis of an impact on the aerosol population and contribution to contrail formation.

ZUSAMMENFASSUNG

Aerosolpartikel beeinflussen den globalen Strahlungshaushalt durch Wechselwirkung mit Sonnen- und terrestrischer Strahlung. Sie können zudem als Wolkenkondensations- oder Eiskeim fungieren in Abhängigkeit ihrer physikalischen Eigenschaften und chemischen Zusammensetzung. Abgesehen von Aerosolen natürlichen Ursprungs liefert die kommerzielle Luftfahrt einen signifikanten anthropogenen Beitrag zu Aerosolpartikeln in der oberen Troposphäre und unteren Stratosphäre (UTLS). Allerdings ist das Wissen um Aerosolpartikel in der UTLS und der Beitrag von Flugzeugemissionen zur Bildung von Cirren und Kondensstreifen nach wie vor gering, obwohl diese Wolkengattungen einen erheblichen Einfluss auf den Strahlungsantrieb haben. Diese Arbeit betrachtet das Auftreten verschiedener Partikeltypen in der Umgebungsluft der UTLS Region sowie Cirren und vergleicht sie mit dem Vorkommen in Flugzeug-Abluftfahnen und Kondensstreifen. Das hybride Massenspektrometer ERICA wurde für flugzeuggetragene Messungen im Aerosol-Größenbereich von 174 nm bis 3.2 μm eingesetzt. Mithilfe eines Standard-Aerosol- und eines Wolkenresidueneinlasses wurden interstitielle Partikel (56058) und Wolkenresiduen (3408) in der UTLS über Norddeutschland im Winter gemessen. Die Partikel wurden analysiert mithilfe des Sortier-Algorithmus fuzzy c-means sowie Messungen von Spurengasen und zu Wolkeneigenschaften. Außerdem wurden synoptische Beobachtungen und Simulationen zur Luftmassenhistorie herangezogen.

Diese Arbeit konnte zeigen, dass Partikel aus Biomasse-Verbrennung (BV) und kohlenstoffhaltige Partikel die Messungen dominiert haben. Unter den Wolkenresiduen waren zumeist Meersalz, Mineralstaub, und BV-Partikel. Das Auftreten dieser Partikel wurde durch die Westwinde begünstigt, die zu einer Advektion von Meersalz aus dem Atlantik und BV-Partikeln aus nordamerikanischen Waldbränden führte. Meteoritenstaub wurde in der Tropopausenregion und darüber beobachtet. Zudem lieferten Labormessungen mit Ammoniumsulfat eine potentielle Quelle für Sulphur-Signale, die im Kationenspektrum mancher Partikel gemessen wurden. Der während der ND-MAX-Kampagne detektierte nitratreiche Partikeltyp war nicht auf eine Rekombination aus Vorläufersubstanzen von Stickoxiden zurückzuführen. Außerdem offenbarte der Vergleich von Cirren und Kondensstreifen, dass beide Wolkentypen aus denselben Partikeltypen hervorgingen. Eine Analyse des Eiswassergehalts legte die Entstehung über die Flüssigphase nahe. Insgesamt setzten sich die Kondensstreifen aus den Partikeltypen zusammen, die auch in der Umgebungsluft enthalten waren.

Abgasbezogene Typen unterhalb von 174 nm Partikelgröße spielten keine Rolle, konnten aufgrund des Detektionslimits von ERICA aber auch kaum detektiert werden. Der Einfluss der abgasbezogenen Typen auf die Aerosolpopulation und Kondensstreifenbildung war daher nicht analysierbar.

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INTRODUCTION

1.1 CURRENT STATE OF KNOWLEDGE OF EXUTLS AEROSOL COMPOSITION AND CLOUD FORMATION

1.1.1 *Aerosol particle categories*

Atmospheric aerosols consist of solid or liquid particles which are suspended in ambient air. The particles are of variable chemical composition and particle sizes in a range of a few nanometers to tens of micrometers (Seinfeld and Pandis, 2016), which are a result of several sources and formation mechanisms. Primary aerosols are directly released into the atmosphere by the emittent, whereas secondary aerosols form in the atmosphere by the nucleation of new particles or condensation of precursor gases onto already existing particles. Aerosol particles undergo aging processes such as coagulation, condensation, and chemical reactions that alter their size and chemical composition. However, the chemical composition of particles also determines the way the particles are processed (Myhre et al., 2013). For example, a salt particle will rather support the condensation of atmospheric water vapor due to its large hygroscopicity than a hydrophobic black carbon particle and is, thus, exposed to other aging processes during its residence time in the atmosphere. The chemical composition of aerosol particles is highly complex due to a large number of sources. Primary inorganic particles are typically larger than $1\text{ }\mu\text{m}$ and comprise sea spray, mineral dust, or volcanic ash. Besides, plants and biomass burning or combustion processes release pieces of organic materials into the atmosphere. Carbonaceous material is typically smaller than $1\text{ }\mu\text{m}$ and consists of organic carbon and black carbon of which the latter is the main light-absorbing anthropogenic constituent (Boucher et al., 2013). Secondary particles usually form of nitrate, sulphate, and volatile organic compounds (VOCs) via oxidation and subsequent condensation in the atmosphere, which is known as gas-to-particle conversion, or by particle nucleation (Myhre et al., 2013). Natural surface sources contributing to primary aerosol in the atmosphere are numerous: sea spray emissions, dispersion of soil dust and rock debris in deserts, emission of biomass burning smoke, and injection of volcanic material. Additionally, particles containing meteoric material contribute to the aerosol population, especially in the lower stratosphere and above. Anthropogenic aerosol sources include fuel combustion, industrial

processes, roadway and fugitive dust, wind erosion from cropland, construction, and transportation activities under the use of cars, ships, airplanes and other vehicles (Tomasi and Lupi, 2017). The aerosol impact on global climate change is very complex because of the large number of potential aerosol sources and chemical constituents. Further, the aerosol formation and growth processes are manifold, leading to variable physical properties and chemical compositions that, in turn, drive the effect on radiative budget, cloud formation and, thus, climate change.

Aerosols affect the Earth's radiation budget in several ways. A direct interaction with solar radiation is given, as aerosol particles can reflect or scatter the incoming radiation back to the outer space and, thus, lead to a cooling effect. On the other hand, they can absorb solar radiation resulting in a warming effect (Arias et al., 2021). Beside these direct effects of aerosols, semi-direct effects appear as well but cannot compete with direct or indirect aerosol effects described below (Lohmann and Feichter, 2001). The semi-direct effect describes the absorption of solar radiation by pollution aerosol that leads to a warming of the atmosphere. As a result, the static stability of the atmosphere is increased, whereas the convection and cloud formation are suppressed. Further, the heating has the potential to enhance the evaporation of existing clouds and to inhibit the formation of new clouds (Hansen et al., 1997; Lohmann and Feichter, 2001; Myhre et al., 2013).

Aerosol particles are a key player in the formation process of clouds and precipitation. They can act as cloud nuclei (CN) or ice-nucleating particles (INP) to form cloud droplets or ice crystals, respectively. As aerosol particles have a large impact on cloud formation, properties, and lifetime, they also affect the interplay between clouds and radiation, which is known as the aerosol indirect effect. First, an enhanced concentration of aerosol particles may result in a higher cloud reflectivity as the same amount of water is distributed to a higher number of particles that provide a larger surface area to scatter incoming solar radiation. This is known as cloud-albedo-effect or Twomey-effect (Twomey, 1977). Moreover, an increase in particle concentration reduces the probability of an individual cloud droplet to grow to a critical particle size for precipitation. In consequence, the cloud will persist for an enhanced period, and thus lead to enhanced radiative forcing. This is referred to as cloud-lifetime-effect or Albrecht-effect (Albrecht, 1989). The net effect of radiative forcing may be cooling in case that more sunlight is redirected to the space due to the cloud albedo, or warming if outgoing longwave radiation from the Earth is trapped by the cloud. Still, large uncertainties are reported for the several aerosol and cloud effects on global climate change, implying the low level of knowledge about the impact of aerosol particles on global climate (Lee et al., 2023). In

addition, aerosol particles provide surfaces for heterogeneous chemical reactions, e.g. for the depletion of stratospheric ozone (Cadle et al., 1975; Solomon et al., 2015, 2022 and references therein).

1.1.2 *The UTLs region*

Aerosol particles in the upper troposphere and lower stratosphere (UTLS) have been the subject of research for the last 60 years and ongoing. The UTLs region faces the chemical and dynamical properties of both spheres and is characterized by a complex interplay of clouds, radiation, and deep convection as well as large- and small-scale circulation patterns (Randel and Jensen, 2013). A layer of enhanced particle concentration at a level of approximately 20 km was first characterized for its physical properties and chemical composition by Junge et al. (1961). Hamill et al. (1997) described that layer as located from the tropopause until approximately 30 km, mainly consisting of sulphuric acid (Thomas, 2003) but also of meteoric material and other non-sulphur particles (Kremser et al., 2016). The predominance of sulphur material is due to volcanic eruptions that directly inject sulphur dioxide (SO_2) and water vapor (H_2O) into the stratosphere (Hamill et al., 1997; Solomon et al., 2011; Vernier et al., 2011; Kremser et al., 2016). Sulphuric acid (H_2SO_4) is formed in the stratosphere when SO_2 is oxidized and further reacts with H_2O (Sheng et al., 2015). Besides, sulphur compounds of carbonyl sulfide (OCS), carbon disulfide (CS_2), dimethyl sulfide (DMS), and hydrogen sulfide (H_2S) originate from natural and anthropogenic sources at the ground. They are lifted upwards by large convection inside the tropical regions up to the stratosphere where they are oxidized to sulphuric acid. This cross-isentropical entering into the tropical stratosphere appears due to slow radiative ascent or overshooting convection (Kremser et al., 2016). The tropospheric air masses are subsequently distributed polewards within the entire stratosphere as part of the Brewer-Dobson-circulation (Dobson et al., 1926; Brewer, 1949; Dobson and Massey, 1956). In addition to tropical convection and volcanic injections, aerosol particles and precursor gases can reach the extratropical lowermost stratosphere (LMS) via quasi-isentropical mixing from the tropical tropopause layer (Kremser et al., 2016).

Much attention has been given to the Junge layer due to its interplay between the aerosol particles and the incoming solar and outgoing terrestrial radiation. As the eruption of Mt Pinatubo in 1991 was the strongest eruption in the 20th century (McCormick et al., 1995; Thomas et al., 2009), it had a large impact on the chemical composition of the atmosphere (Textor et al., 2004; von Glasow et al., 2009; Poberaj et al., 2011; Aquila et al., 2013) and the radiation budget of the Earth. Besides their potential to absorb upwelling longwave radiation

(Weisenstein et al., 2022), sulphuric acid particles in the stratosphere scatter the incoming solar radiation back to the outer space, resulting in a cooling of the troposphere (Labitzke and McCormick, 1992; McCormick et al., 1995). This concept was discussed for geoengineering in terms of direct stratospheric aerosol injection or gas-phase-injection of species that can form particles in the stratosphere (Shepherd, 2012; Council, 2015; Keith et al., 2014; MacMartin and Kravitz, 2019; Field et al., 2021) but was criticized due to large ambiguity of other climate feedback (Crutzen, 2006). Pope et al. (2012) mentioned the advantages of an application of other particle types of a large refractive index such as mineral dust and its component titanium dioxide (TiO_2). As these particles scatter incoming solar radiation more effectively than H_2SO_4 aerosols, the necessary amount of TiO_2 to inject into the stratosphere would be ~ 3 times less in mass and a factor of ~ 7 less in volume than for H_2SO_4 . Still, the chemical response of the stratosphere remains unclear, and also the impact of highly-refractive material towards outgoing longwave radiation (Pope et al., 2012).

In general, the aerosol population in the stratosphere is of large variability even in volcanically quiescent periods (Solomon et al., 2011). In consequence, enhancements in the stratospheric aerosol concentration cannot only be traced back to anthropogenic emissions (Hofmann et al., 2009; Randel et al., 2010) or minor volcanic eruptions (Vernier et al., 2011; Neely III et al., 2013; Brühl et al., 2015; Mills et al., 2016). However, the impact of the Asian summer monsoon on stratospheric aerosol is matter of current research (Yu et al., 2017; Lelieveld et al., 2018) and is found to support the vertical transport of air masses largely affected by anthropogenic emissions (Höpfner et al., 2020; Appel et al., 2022). Furthermore, intensive wildfires not only emit a huge amount of biomass burning particles into the free troposphere but also support the ascent of these particles into the UTLS region as part of a pyro-convection (Fromm and Servranckx, 2003; Damoah et al., 2006; Ditas et al., 2018; Yu et al., 2019). The impact of stratospheric aerosol particles is much larger as their lifetime is increased compared to tropospheric particles (e.g. Crutzen, 2006).

Aside from their radiative effect, stratospheric particles provide surfaces for heterogeneous chemical reactions. Sulphuric acid particles catalyze the conversion of inert chlorine as part of the anthropogenic emissions of chlorofluorocarbons (CFCs) into reactive chlorine that participates in the cycle of ozone depletion (Molina et al., 1996; Solomon, 1999; Solomon et al., 2022 and references therein). Surfaces are also provided by polar stratospheric clouds that form only within the polar stratosphere during winter season where temperatures drop below the formation threshold of -78°C . They consist of supercooled ternary solutions of sulphuric acid, nitric acid, and water, of nitric acid trihydrate, or ice

particles (Tritscher et al., 2021; Lauster et al., 2022) and largely contribute to the destruction of the stratospheric ozone layer. This leads to a stratospheric ozone hole as observed within the polar vortex of the Arctic and Antarctic (McCormick et al., 1981) and results in harmful ultraviolet radiation reaching the Earth’s surface.

Besides the entrainment of aerosol particles into the stratosphere, precursor gases are introduced, leading to an in situ formation of stratospheric particles. This new particle formation (NPF) has been observed in the tropical tropopause layer (Brock et al., 1995; Borrmann et al., 2010; Weigel et al., 2011) and in the polar middle stratosphere (Wilson et al., 1992; Campbell and Deshler, 2014). Williamson et al. (2021) observed nucleation mode particles in the LMS, which are almost omnipresent within the northern hemisphere. Besides volcanic emissions, possible sources for precursor gases and nucleation mode particles in the stratosphere are emissions from aircraft and rockets (Lee et al., 2010; Lee et al., 2021; Schröder et al., 2000; Brock et al., 2000). Still, the process of NPF in the stratosphere and UTLS is not well understood. Nevertheless, the LMS provides unique boundary conditions for NPF. First, the vapor pressure of H_2SO_4 is reduced in an environment of cold ambient air and promotes the binary nucleation of H_2SO_4 and H_2O (Easter and Peters, 1994). Second, the volatility of organic matter drops in cold air, resulting in a larger contribution of these species to NPF and particle growth (Tröstl et al., 2016; Stolzenburg et al., 2018; Simon et al., 2020). Third, the aerosol particle concentration and the number of sinks for condensable vapors, clusters and nucleation mode particles is limited compared to the boundary layer (BL) (Kerminen et al., 2018). While NPF in the BL is observed in the presence of large concentrations of precursor gases and the simultaneous absence of strong sinks, only the latter might support NPF in the LMS (Williamson et al., 2019). Next, the LMS provides a dry environment leading to less NPF and particle growth by the adsorption of water vapor. Thus, the process of NPF may happen on another time scale and by unconventional nucleation mechanisms (Williamson et al., 2019) that need to be considered. As some of the species detected within the UTLS region are involved in NPF in the BL, they should be paid attention to. For example, iodine and bromide were reported to be present in the UT (Volkamer et al., 2015; Dix et al., 2013) and LMS (Koenig et al., 2020). However, the oxidation of iodine was also linked to NPF in coastal regions (McFiggans et al., 2010; O’Dowd et al., 1999; O’Dowd et al., 2002; Sipilä et al., 2016) and the Arctic BL (Baccarini et al., 2020). In consequence, the particles detected in the UTLS may have undergone NPF processes in that altitude range. However, the chemical mechanisms are still unknown and need further research.

In contrast to the LMS, the UT is in favor of NPF as temperatures are low and the supersaturation with respect to water is large (Lee et al., 2004; Weigelt et al., 2009). Especially, the tropical tropopause layer is the preferred region to form aerosol particles and to supply the stratosphere and the Junge layer with new particles in the absence of volcanic eruptions (Brock et al., 1995; Borrmann et al., 2010; Weigel et al., 2011). Same as for the stratosphere, the pre-existing aerosol surface area is small as aerosol particles are scavenged by the convective clouds. Further, the production of radicals and ions is enhanced because of an increased actinic flux and galactic cosmic ray intensity compared to the BL (Kazil and Lovejoy, 2004). NPF in the free troposphere is proposed to be driven by ion-induced binary nucleation, ternary nucleation of ammonia, sulphuric acid, and water (e.g. Coffman and Hegg, 1995; Weber et al., 1996; Kirkby et al., 2011; Dunne et al., 2016) or nucleation of ammonia and nitric acid (Wang et al., 2020). Wang et al. (2022) demonstrated a synergistic NPF process of nitric acid, sulphuric acid, and ammonia for upper tropospheric conditions. Still, the simultaneous detection of concentration of ultrafine particles and key nucleating species is rare and only reported in a few cases (Weber et al., 1996; Clarke et al., 1998; Mauldin III et al., 2003; Weber et al., 2003). Another large source of UTLS particles are biogenic VOCs such as isoprene (Palmer et al., 2022). The condensed oxidation products of these organic species are referred to as secondary organic aerosol (SOA). An analysis of the UTLS chemical composition in the tropics unveiled a large fraction of organic particles within a particle size range of 250 nm to 2 μ m (Froyd et al., 2009, 2010; Murphy et al., 2006). These measurements agree with reports about Amazonian aerosol populations dominated by organic material up to the UT (Andreae et al., 2018; Schulz et al., 2018).

As mentioned, the chemical composition of UTLS aerosol is matter of current research. A large number of measurements focused on the tropical regions due to the large convective cumulonimbus towers that transport aerosol particles and precursor gases from the troposphere high up into the stratosphere. Still, the chemical composition in the extratropics remains unclear. This thesis provides an overview of the particles detected within the UTLS region in midlatitudes during winter season.

1.1.3 *Cirrus clouds*

Cirrus clouds are optically thin clouds, which consist of ice particles and cover about 30% of the midlatitude upper troposphere (Wylie and Menzel, 1999). Their effect on global climate can be cooling as they increase the albedo of the Earth with respect to incoming solar shortwave radiation but they also reveal

a warming potential due to absorption of outgoing longwave radiation. While tropical cirrus clouds have a strong warming effect, mid-latitude cirrus have a cooling tendency (Cox, 1971). In contrast, Krämer et al. (2020) described the warming and cooling effect of cirrus depending on the cirrus formation process. Further, the effect is the same across all latitudes. The net effect of the contribution of cirrus depends on their chemical composition, physical parameters such as size, shape, and surface roughness as well as parameters of the Earth's surface and atmosphere (Liou, 1986; Tang et al., 2017). Still, the influence of cirrus clouds on climate sensitivity is of large uncertainty (Boucher et al., 2013; Stevens and Bony, 2013).

The impact on cirrus clouds is driven by a large number of parameters. For example, the midlatitudes are characterized by strong meridional gradients, contrasts between land and ocean, and by natural and anthropogenic aerosol sources that influence the formation process and life cycle of cirrus. Further, cirrus clouds are affected by the meteorology underlying various weather systems (Voigt et al., 2017). Still, there is lack of information about the processes that govern the formation of cirrus and so they are crudely represented in weather forecasts (Bauer et al., 2015). Moreover, the UTLS region that cirrus clouds belong to is difficult to access (Voigt et al., 2017). The accuracy of measurements is limited as jet aircraft are fast-flying at high altitudes and do not capture the evolution of cirrus clouds. The cloud properties change continuously with time but airborne measurements only provide snapshots. Evidently, cirrus clouds are difficult to investigate from the formation to the dissipation process as they are only recorded along the flight track (Krämer et al., 2016). In addition to natural processes, cirrus clouds can be affected by the dense air traffic at these altitudes (IPCC, 1999; Lee et al., 2021). In contrast to in situ detection of cirrus, remote sensing techniques allow for continuous measurements regarding the evolution of cirrus clouds. These techniques include ground- and satellite-based sensors such as infrared or lidar systems which scan the cirrus properties by the emission of radiation in a predefined range and the detection of the backscattered fraction (e.g. Sassen et al., 2008; Stubenrauch et al., 2008; Palchetti et al., 2016).

Naturally, most cirrus clouds form when air masses ascend on mesoscale or large-scale. The uplift is often linked to frontal systems, ridges, jet streams, lee waves, or convection (Gayet et al., 2012; Krämer et al., 2009; Lawson et al., 2006; Muhlbauer et al., 2014; Stith et al., 2014; Jackson et al., 2015; Heymsfield et al., 2017). Warm conveyor belts transport within a few days water vapor into the UT, where the air masses reach supersaturation with respect to water and ice as well as freezing temperatures. During the ascent, the air cools down and reaches a relative humidity above 100%, at which droplets can form. Subsequently, the droplets can freeze in the presence of an INP and an environment below 0°C.

At higher altitude levels, cirrus clouds may also form without the liquid phase, meaning that ice crystals nucleate directly from the vapor phase. Homogeneous freezing, i.e. the freezing without an ice nucleus (e.g. Kärcher and Lohmann, 2002), was suggested to be the dominant pathway for the formation of cirrus clouds (Kärcher and Ström, 2003). However, the detection of heterogeneous ice nuclei in several cirrus samples implied that also heterogeneous freezing has a considerable contribution on cirrus formation (Cziczo et al., 2013). The input of an ice nuclei may promote the heterogeneous freezing at temperatures below 0°C and, thus, in a temperature range that is far above the onset of homogeneous freezing at -38°C (Vali et al., 2015). Depending on their formation process, cirrus clouds unveil variable physical properties and, thus, may have a negative or positive feedback on radiative forcing (Krämer et al., 2020).

In order to characterize cirrus clouds, measurements are focused on ice water content (IWC), ice crystal number and size, as well as relative humidity including supersaturation with respect to ice. Additionally, the number and chemical composition of INPs is of major interest to study the impact of individual particle types on the formation of cirrus clouds. The investigation of ice water content in cirrus clouds unveiled the existence of two different types of cirrus. *In situ-origin cirrus* describes the uplevel cirrus clouds that form directly from the gas phase below the threshold of homogeneous freezing of -38°C or of heterogeneous freezing, depending on the properties of the INPs. In contrast, the second type forms of liquid droplets that freeze heterogeneously or homogeneously during the uplift of the cirrus from an altitude level far below. Ergo, this cirrus type formed via the liquid phase and is referred to as *liquid-origin cirrus* (Krämer et al., 2016). Both types are separatable due to different ranges of IWC. The liquid-origin type reveals an IWC range of 10^{-3} to 1 g m^{-3} , whereas the content of in situ-origin cirrus ranges between 10^{-7} to 10^{-2} g m^{-3} due to a strong limitation of water vapor in the UT compared to altitudes below. Apart from the IWC, both cirrus types also differ in ice crystal size and thickness, represented by the number concentration of ice crystals (Luebke et al., 2016). In situ-origin cirrus are typically thinner, i.e. they have a lower vertical extension compared to thick cirrus, and tend to slightly warm the atmosphere. On the other hand, thick cirrus predominates at lower altitudes and have a strong cooling effect on the global radiation budget (Krämer et al., 2020).

In all seasons and throughout the extratropics, the cirrus formation is dominated by mineral dust. In the northern hemisphere, this particle type is predominant in 75 to 93% of all cirrus clouds (Cziczo et al., 2013; Twohy, 2015; Kanji et al., 2017; Froyd et al., 2022). In consequence, airborne mineral dust aerosols are of large importance when facing the atmospheric radiative balance and global climate (Knippertz, 2014). As the world's deserts emit 1000 to 4000 Tg of dust

aerosol per year, it is one of the most abundant aerosol types in the world. However, just a very small fraction of these dust particles reaches the UT and is available for the formation of cirrus clouds (Pruppacher and Klett, 2010). In addition to mineral dust, anthropogenic metals largely contribute to cirrus formation (Cziczo et al., 2004; Cziczo et al., 2013; Cziczo and Froyd, 2014). Another important player are sea spray particles that make up to 25% of ice residuals in cirrus clouds, especially in maritime regions (Cziczo et al., 2013). They are present in the entire atmosphere but especially in the marine BL, from which they are transported upwards via deep convection inside cumulonimbus clouds and detrained from their anvils (Vignati et al., 2010; Murphy et al., 2019; Patnaude et al., 2024). Released into the UT, sea spray aerosols are involved in subsequent cirrus formation, independent from their aging process within the marine boundary layer (Patnaude et al., 2024).

Ammonium sulphate (AS) has the potential to nucleate ice particles in cirrus clouds homogeneously as well as heterogeneously and, thus, may have a significant impact on the formation of cirrus clouds (Abbatt et al., 2006; Baustian et al., 2010; Wise et al., 2010; Wagner et al., 2020; Beer et al., 2022). Liquid AS particles were observed to undergo homogeneous ice nucleation at a supersaturation with respect to ice of 1.55 and a temperature of -51°C (Bertram et al., 2000), whereas solid-state AS can already induce heterogeneous freezing at a supersaturation of 1.20 below about -52°C (Gao et al., 2006), implying the heterogeneous mechanism as the preferred one. Nevertheless, little is known about the predominant way of contribution of AS to cirrus clouds. Since AS is mostly observed in a mixed state including organic material, its potential to act as an INP also depends on the organic mass fraction and the particle morphology that is affected by subsequent aging processes (Bertozzi et al., 2021).

The contribution of organic material is of large uncertainty even though it is widely abundant in the UT (Froyd et al., 2010; Schill et al., 2020; Schwarz et al., 2017; Hodzic et al., 2020) and was also reported as a dominant ice residual within cirrus contrails (Petzold et al., 1998). The impact of SOAs on cirrus formation is limited as only a minor fraction freezes heterogeneously (Wolf et al., 2020), whereas the majority of SOAs is assumed to nucleate via homogeneous freezing. Black carbon particles are ineffective INPs but their contribution to ice nucleation may be enhanced for sizes above 100 nm when they contain surface pores, or after prior cloud processing (Mahrt et al., 2018; Mahrt et al., 2020). Despite their low abundance of 1 in 10^3 to 10^5 aerosol particles, INPs govern the cirrus cloud formation.

We still lack sufficient in-situ airborne measurements to understand the influence of aerosol chemical composition on cirrus cloud formation. Therefore, the

chemical composition of cirrus clouds was also considered within this thesis as a reference for the chemical properties of aircraft-induced condensation trails.

1.1.4 *Aircraft impact on UTLS*

The impact of airplanes on the UTLS is manifold, encompassing the aerosol particulate matter and greenhouse gases including water vapor, among which condensation trails (contrails) are formed. Not only the emitted carbon dioxide (CO_2) enhances the anthropogenic greenhouse effect, but also the contrails contribute to global climate forcing. Calculations exhibited that the net radiative forcing induced by global aviation is mainly caused by non- CO_2 contributors, led by aircraft contrails (Lee et al., 2021). In detail, aircraft largely contribute to the Earth’s radiation budget as they emit several combustion products (see Fig. 1.1). First, per kilogram fuel burned, the aircraft emit 3.16 kg of CO_2 . Second, 1.23 kg of water is emitted for every kilogram fuel burned, increasing the amount of H_2O available for condensation and, thus, formation of contrails. Additionally, water vapor reduces the atmospheric window which the thermal infrared radiation passes through, also resulting in a warming feedback. Further gas-phase species include nitrogen oxides and oxidized sulphur compounds. Moreover, the aircraft turbines release particulate matter as part of the fuel combustion, containing large quantities of ultra-fine soot particles as well as organic and sulphate particles (Lee et al., 2021; Moore et al., 2017; Kleine et al., 2018) that catalyze the formation of contrails. Among the non-volatile particles of elemental carbon, ultra-fine metal pieces are released that are traced back to kerosene, engine lubrication oil, or engine wear. These compounds also support the ice nucleation and, thus, the formation of ice clouds such as cirrus and contrails (Agrawal et al., 2008; Abegglen et al., 2016). In contrast to long-lived emissions of CO_2 , contrail cirrus only remain in the troposphere for a few hours. Hence, the avoidance of contrail formation would have an immediate cooling effect (Vázquez-Navarro et al., 2015). Efforts to reduce them include weather-dependent flight routing in order to avoid areas of favorable conditions, and variations of cruise altitudes (Teoh et al., 2020; Grewe et al., 2017). However, some of these mitigation strategies create additional costs due to increased fuel combustion, longer flights, or reduced airspace capacity. As a consequence, the use of several alternative fuel types is currently discussed (e.g. Voigt et al., 2021).

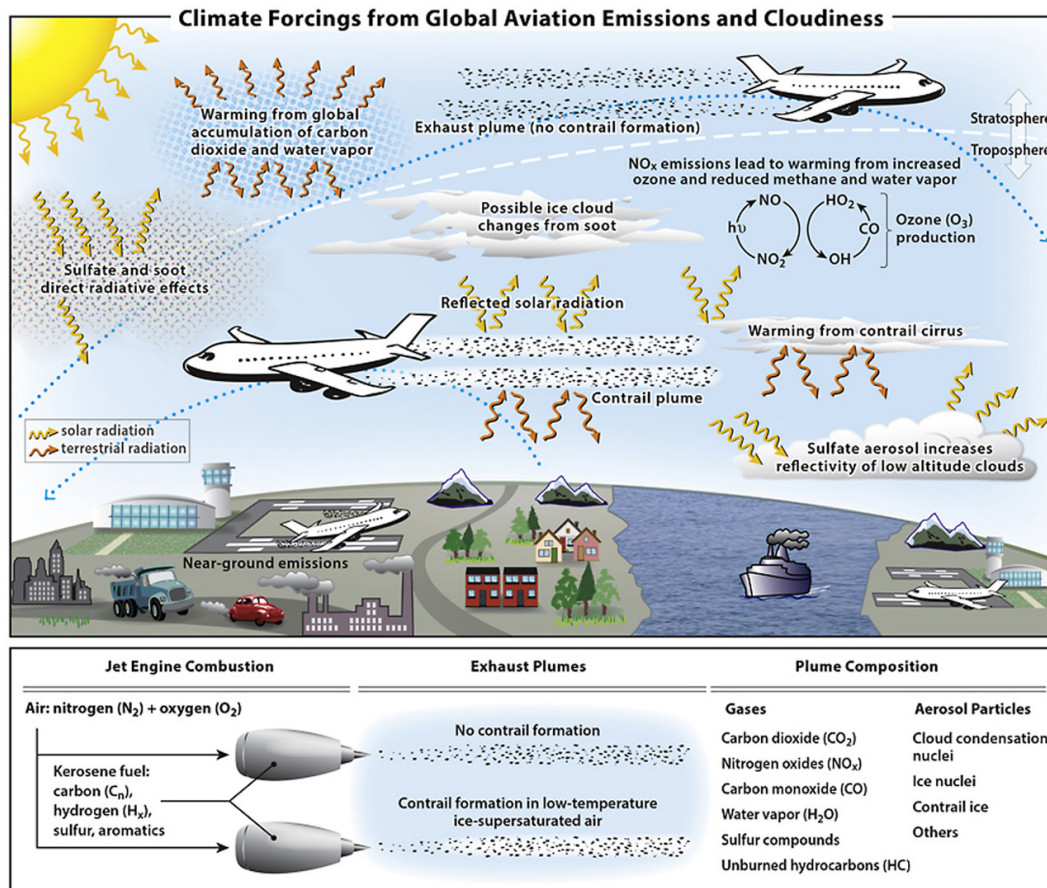


Figure 1.1: Schematic overview of the processes by which aviation emissions and increased cirrus cloudiness affect the climate system. Net positive radiative forcing (warming) contributions arise from CO_2 , water vapor, NO_x , and soot emissions, and from contrail cirrus (consisting of linear contrails and the cirrus cloudiness arising from them). Negative radiative forcing (cooling) contributions arise from sulfate aerosol production. Net warming from NO_x emissions is a sum over warming (short-term ozone increase) and cooling (decreases in methane and stratospheric water vapor, and a long-term decrease in ozone) terms. Net warming from contrail cirrus is a sum over the day/night cycle. These contributions involve a large number of chemical, microphysical, transport, and radiative processes in the global atmosphere. Reprinted from Atmospheric Environment, 244, D.S. Lee, D.W. Fahey, A. Skowron, M.R. Allen, U. Burkhardt, Q. Chen, S.J. Doherty, S. Freeman, P.M. Forster, J. Fuglestad, A. Gettelman, R.R. De León, L.L. Lim, M.T. Lund, R.J. Millar, B. Owen, J.E. Penner, G. Pitari, M.J. Prather, R. Sausen, L.J. Wilcox, The contribution of global aviation to anthropogenic climate forcing for 2000 to 2018, 117834, Copyright (2021), with permission from Elsevier. (The license is provided by Elsevier and the Copyright Clearance Center; License Number 5794070458008.)

1.1.5 Contrails

Condensation trails or contrails are thin line-shaped ice clouds that form by mixing of aircraft exhaust constituents with ambient air at cruise altitude. The formation of contrails is induced by the simultaneous release of water vapor and soot particles into an environment of very low temperatures that is quickly supersaturated with respect to water. These ambient properties are typically provided at flight levels above 8 km and temperatures below -40°C . The supersaturation is reached by the mixture of hot aircraft engine exhaust with ambient air in the wake vortex (Bräuer et al., 2021a). As the water vapor is released by the aircraft turbines, it rapidly condenses onto the soot particles and other particles of atmospheric background aerosol, resulting in small water droplets (Voigt et al., 2021). At these large supersaturations, water vapor condenses preferably onto larger soot particles, but is generally adsorbed by any particle type (Wong and Miake-Lye, 2010; Kleine et al., 2018). Once the droplets are formed, they immediately grow in size and tend to freeze as more ambient air is mixed into the engine exhaust plume (Heymsfield et al., 2010; Kärcher, 2018; Bräuer et al., 2021a).

The formation of contrails depends on the atmospheric conditions and the properties of the aircraft exhaust. In short, relative humidities of more than 100% are necessary to induce the formation of cloud droplets and this is controlled by the local temperature and pressure beside the available amount of H_2O . These conditions were physically described by Schmidt (1941) and Appleman (1953) and are quantified by the so-called Schmidt-Appleman-temperature (T_{SA}), which states that for temperatures below a certain threshold contrails can form. As soon as the droplets exist, they freeze instantly to ice crystals by homogeneous freezing and are no longer dependent on supersaturation with respect to water. Due to the low efficiency of soot to act as INPs, the majority of soot-containing ice crystals is not formed by heterogeneous freezing. The supersaturation with respect to ice is lower than that of water, meaning that ice crystals will grow at the cost of water droplets, which is better known as Wegener-Bergeron-Findeisen- (WBF-) process (Storelvmo and Tan, 2015 and references therein). In general, contrails form in the moist regions of the UT that also trigger the formation of cirrus clouds. These places are in the warm conveyor belts where also cirrus appears, and sometimes in warm moist layers even before the surface warm front and front-related cirrus arrive. Apart from the warm fronts, contrails are also observed in turbulent regions ahead of the surface cold front (Kästner et al., 1999; Irvine et al., 2012). Moreover, contrails preferably form and persist in ice-supersaturated regions (ISSR) that may be found in anticyclonic flow (Kästner et al., 1999; Immler et al., 2008) or in the presence of gravity waves (Spichtinger et al., 2005). Located within an ISSR,

a contrail can grow and spread resulting in a large contrail cirrus cover on a regional scale (Minnis et al., 2013; Vázquez-Navarro et al., 2015). These areas are also referred to as contrail outbreak regions (Schumann, 2005; Carleton et al., 2008).

Contrails have a significant impact on global climate change. They alter the Earth’s radiation budget in a similar way as cirrus clouds do, mainly by scattering incoming solar radiation, depositing solar energy, and by absorbing outgoing longwave radiation (Burkhardt and Kärcher, 2011; Boucher et al., 2013). Their net radiative forcing mainly depends on the ratio of scattered solar direct radiation and trapped terrestrial radiation. Strongly warming contrails were majorly observed over the US and North Atlantic, whereas cooling contrails rather appeared over Southeast Asia, North Asia, Europe, and the eastern North Atlantic (Teoh et al., 2023). The global effective radiative forcing (ERF) of contrails ranges between 17 and 98 mW m⁻², thus the mean net effect of 57 mW m⁻² is warming (Lee et al., 2021). Because of their occurrence induced by global aviation, it is important to inspect the contrail contribution as part of the aviation’s impact on global climate change. Of the net ERF from aviation of 101 mW m⁻², contrail cirrus is the major contributor with 57.4 mW m⁻², followed by the share of CO₂ and NO_x of 34.3 and 17.5 mW m⁻², respectively (Brasseur et al., 2016; Burkhardt and Kärcher, 2011; Kärcher, 2016; Kärcher, 2018; Lee et al., 2021). Cirrus contrails may have a large fingerprint on regional anthropogenic climate forcing, especially in corridors that show a high frequency of air traffic such as Europe or the United States. There, the ERF is above 500 mW m⁻² in spite of a rather low impact on global scale. The effect of international aviation on global anthropogenic climate forcing is of 3.5% (Lee et al., 2021). A large increase in ERF of 64% has been observed for the period of 2005 to 2018 due to an intensifying global air traffic within the last two decades. Ergo, future climate projections suggest a 3-4 fold enhancement of global surface warming by the year 2050 (Chen and Gettelman, 2016; Bock and Burkhardt, 2019).

Although the air space area over East Asia is congested with air traffic and its growth rate is predicted to increase, the expectations of contrail formation and associated ERF are of large difference. Bock and Burkhardt (2019) and Teoh et al. (2023) did not expect the region of East China, Korea, and Japan to be in favor of contrail formation and associated large ERF. Aircraft fly at lower altitudes and the ice-supersaturated coverage areas are limited by the Hadley Circulation, providing inappropriate conditions for contrail formation over East Asia. In contrast, Chen and Gettelman (2016) performed simulations that imply the most significant increase in contrail cirrus radiative forcing over East Asia, in accordance with increased aircraft fuel consumption in that region. However,

the positive ERF is partly compensated by negative forcing due to aviation emissions of particulate matter. In consequence, the ERF is of large uncertainty and strongly depends on the occurrence of suitable conditions for contrail formation. For example, the air traffic is also expected to increase in Southeast Asia and India which provide a high frequency of ice supersaturation and, thus, a high probability of contrail formation and consecutive ERF (Lamquin et al., 2012; Bock and Burkhardt, 2019).

The climate-relevant impact of contrails largely depends on their physical and chemical properties. A reduction of ice particle numbers results in less warming of the atmosphere due to less energy deposition (Burkhardt et al., 2018). As the huge number of soot particles induces a large number of ice crystals, the idea is to reduce the emission number of soot particles by changing the jet fuel composition (Kärcher, 2018). Indeed, the usage of biofuels caused a drop in soot emissions and smaller ice crystal numbers within contrails (Moore et al., 2017). Further, a direct link between the low aromatic content of sustainable aircraft fuel and the reduced number concentration of soot particles in contrails was unveiled by Voigt et al. (2021) and Märkl et al. (2024). Apart from ice crystal concentrations, the contrail optical depth and extinction coefficients were reduced for the application of biofuel blends (Bräuer et al., 2021b). However, the chemical composition of contrails still remains unclear. The dataset of airborne measurements with the ERICA instrument within the ND-MAX campaign 2018 is analyzed within this framework and provides insight to the composition of contrails.

1.2 OBJECTIVES AND STRUCTURE OF THE THESIS

As illustrated within the previous sections, a broad knowledge has already been established about aerosol particles in the UTLS region. However, UTLS research mainly focused on the tropical UT and the input of aerosols into the stratosphere via the tropical tropopause layer. Little attention has been given to the extratropical situation along the UT and LMS. This thesis aims to provide a better understanding of the situation within the midlatitudes, especially in northern hemisphere winter season. Further, the impact of anthropogenic emissions released in the BL and aircraft-induced particulate matter on the background aerosol concentration are analyzed. Along with the detection of particle source regions and the vertical atmospheric profile, the influence of local weather pattern and global circulation pattern is examined. In a second step, the contribution of the detected particles towards cirrus and contrail formation is assessed providing insight to the formation process of both ice-cloud types.

In summary, the following questions are addressed in this study on the basis of in-situ aircraft-borne measurements:

- What particle types contribute to the upper tropospheric aerosol?
- Where do these particle types come from?
- What is the atmospheric background particle population consisting of?
- Which particle types can be attributed to aircraft exhaust?
- Which types are suitable for cirrus and contrail formation?
- Which cirrus formation processes take place in the UTLS region?

To the author's knowledge, this is the first study to analyze the chemical composition of aircraft contrails based on single-particle mass spectrometry data that cover a wide range of particle types including refractive material. Thus, these data uniquely provide an exclusive view on the individual particle types that control the UTLS aerosol population and its impact on high-level cirrus clouds and contrails.

The thesis is structured as follows: Chapter 2 provides an overview of the main instrument ERICA including its working principle and information provided about the detected aerosol particles. Besides, the data processing and analysis is introduced. Along with the presentation of the sampling inlets of interstitial aerosol particles and cloud residuals, the principles of the complementary instruments are described. Furthermore, the classification of individual events is illustrated in the context of the atmospheric regime and the events of interest such as exhaust, background, cirrus, and contrail. This includes the consulted input parameters and the criteria upon which the events were defined. Similarly, the potential source regions of aerosols are shown and the analysis of backward trajectories is explained. In chapter 3, the flight campaign ND-MAX and a meteorological overview are given. Chapter 4 presents the findings of the airborne measurements conducted in winter 2018 including the chemical composition of UTLS aerosol particles and their contribution to cirrus and contrail formation. In addition, laboratory measurements of AS and chemical compounds such as FeSO_4 and SnCl_2 are analyzed to trace back NO_x -related signals in the absence of NO_x compounds. Further, measurements of AS with CuO and CuCl_2 are conducted to examine the origin of cation sulphur signals detected within the campaign. A summary of the key results of this study is combined with an outlook on future measurements in chapter 5.

METHODS

This thesis focuses on the chemical analysis and characterization of midlatitude UTLS aerosol particles and cloud particle residuals. For the determination of the aerosol particle chemical composition, an instrument was deployed that is based on aerosol mass spectrometry. The ERc Instrument for Chemical composition of Aerosol particles (ERICA) was installed on the *Flying Laboratory* NASA McDonnell Douglas DC-8 jetliner besides several other instruments for complementary measurements of various trace gases, water vapor as well as aerosol particle concentrations and distributions. The following sections briefly introduce the working principle of ERICA and the processing of recorded data. In addition, the two sampling inlets for interstitial aerosol particles and cloud particle residuals are presented. Further, a small overview is provided about the aerosol- and trace gas instrumentation aboard the NASA DC-8. The application of complementary data for the definition of events of interest is shown afterwards. Finally, the Chemical Lagrangian Model of the Stratosphere (CLaMS) is described within the introduction of air mass analysis.

2.1 HYBRID MASS SPECTROMETER ERICA

2.1.1 *Principle and setup of ERICA*

ERICA (Molleker et al., 2020; Hünig, 2021; Hünig et al., 2022; Dragoneas et al., 2022) is a hybrid mass spectrometer consisting of two different types of mass spectrometers, called ERICA-LAMS and ERICA-AMS, which share one vacuum chamber. It was designed to conduct airborne measurements of the chemical composition of aerosol particles and to combine the advantages of both measurement techniques in a single instrument.

The ERICA-LAMS (ERICA Laser Ablation Mass Spectrometer) is based on the laser desorption and ionization technique (LDI) where aerosol particles in a size-diameter range of approximately 174 nm to 3.2 μm are vaporized and ionized by a triggered and pulsed ablation laser (Hünig, 2021). The generated cations and anions are then released and accelerated into a bipolar time-of-flight mass spectrometer (B-ToF-MS; Sinha, 1984; McKeown et al., 1991; Murphy

and Thomson, 1995; Hinz et al., 1996; Zelenyuk and Imre, 2005; Brands et al., 2011).

The ERICA-AMS (ERICA Aerosol Mass Spectrometer, abbreviation adopted from the AMS provided by Aerodyne Inc., Billerica, MA, USA) operates on the thermal flash vaporization and electron impact ionization technique, where particles impact on a heated surface, become flash vaporized and ionized by an electron beam (Davis, 1973; Jayne et al., 2000; Jimenez et al., 2003; Allan et al., 2004; Drewnick et al., 2005; Canagaratna et al., 2007). The detectable size-diameter range spans from 80 nm to 2 μ m (Hünig, 2021).

The ERICA setup has been described and characterized in detail in Hünig (2021) and Hünig et al. (2022). An overview of the major components and the working principle is also provided here. As the setup in Fig. 2.1 reveals, the aerosol particles are entering the instrument via the inlet system, which consists of a constant pressure inlet system (CPI) (Molleker et al., 2020) and an aerodynamic lens. The CPI is set up as a pinch device that compresses an in-house made silicone O-ring of 0.5 mm in diameter down to 0.1 mm depending on the ambient pressure. Since the mass flow rate through a critical orifice is proportional to the cross section area and the upstream pressure, the cross section area must be adaptable for variable atmospheric pressure regimes from 1000 to 50 hPa in order to maintain a constant mass flow of ambient air into ERICA. At the entrance of the vacuum chamber, an aerodynamic lens is positioned to provide the sampled ambient air to the mass spectrometer. The aerodynamic lens (Liu et al., 1995a,b) consists of six apertures of decreasing diameter (from 5 mm to 2.9 mm; Peck et al., 2016) and focuses the particle flux into a narrow beam.

The particles are accelerated into the vacuum chamber where they pass two consecutive detection lasers (150 mW UV-laser diodes of 405 nm wavelength each) before they reach the ablation spot. For each of the detection units (DU), the scattered light of the particle is redirected to the photomultiplier tubes (PMTs) by an ellipsoidal reflector in order to be detected and to derive the aerodynamic size of the particle (see also Sect. 2.1.3). The flight time between both detection units is measured to calculate the timestamp of ablation and to trigger the ablation laser, which is a frequency quadrupled Nd:YAG laser (wavelength of 266 nm, 6 ns pulse duration, and 44 mJ pulse energy), as soon as the particle reaches the ablation spot. The ablation process includes the desorption of the particle and the simultaneous ionization of the vapor of generated molecules and atoms that are accelerated then into the B-ToF-MS (Tofwerk AG, Thun, Switzerland). By recording the flight time of ions to the multi-channel detector plates (MCP, model MCP 40/12/10/8 D 46:1, Photonis USA Inc., Sturbridge, MA, USA) and an assumption of the number of charges per ion, the atomic masses and chemical components can be concluded.

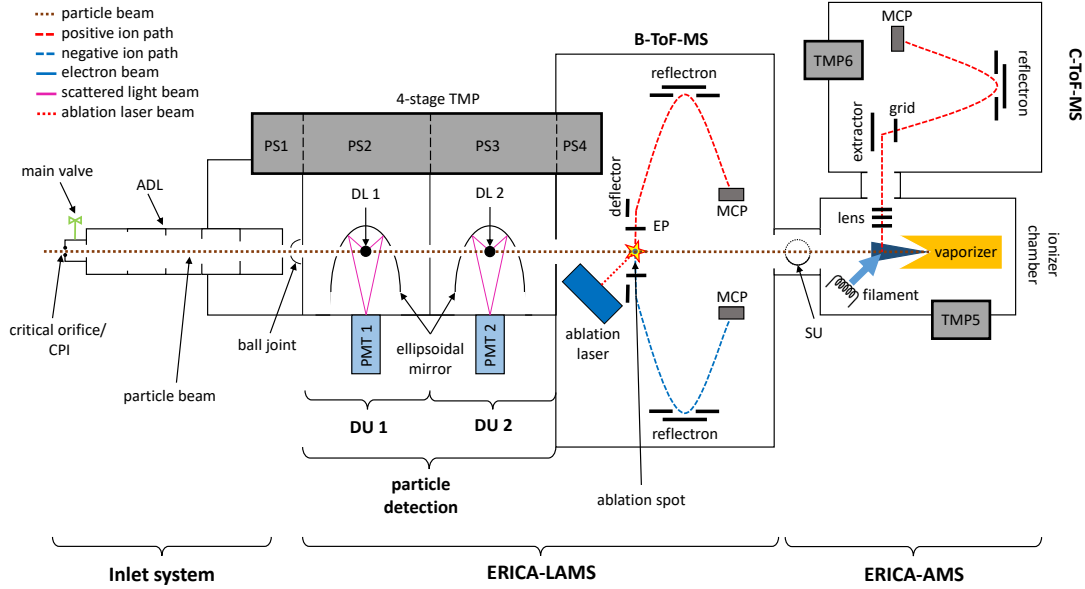


Figure 2.1: Schematic overview of the ERICA setup. Acronyms are defined as follows: ADL = Aerodynamic Lens, CPI = Constant Pressure Inlet, DL = Detection Laser, DU = Detection Unit, EP = Extraction Plate, MCP = Multi-Channel Plate, PMT = PhotoMultiplier Tube, PS = Pumping Stage, SU = Shutter Unit, TMP = Turbo Molecular Pump. Figure adapted with permission from Hünig et al. (2022). The sample inlet received a graphical update and marks the critical orifice/ CPI. Labels were partly adapted (LD = Laser Diode to DL = Detection Laser; PDU = Particle Detection Unit to DU = Detection Unit) and a label of the ionizer chamber was added. (Licensed under CC BY 4.0)

However, due to the limited firing frequency of the UV laser, the majority of the particles is not ablated and continues its way into the AMS section, where it gets flash vaporized when the particles impact on a molybdenum heater body of 600 °C. In a second step, the cloud of vaporized particles is ionized to positive ions by an electron beam originating from a heated tungsten filament via thermionic emission (Kellner et al., 2004). The cations are guided through an electrostatic lens stack and extracted periodically into the compact time-of-flight mass spectrometer (C-ToF-MS; Hünig et al., 2022).

The description of the ERICA-AMS is given due to reasons of completeness. However, in the framework of this thesis only data of the ERICA-LAMS have been analyzed. Both mass spectrometer types were successfully deployed for measurements of UTLS aerosol in previous airborne research campaigns such as StratoClim (Molleker et al., 2020; Dragoneas et al., 2022; Hünig et al., 2022), and subsequent campaigns of ACCLIP (Eppers et al., 2024) and PHILEAS (Köllner et al., 2024). Within this framework, however, refractory material was

suggested to support cirrus and contrail formation. As these particle types are not covered by the ERICA-AMS, aerosols were analyzed by single-particle mass spectrometry. In detail, the data analysis focused on the individual particle types that acted as potential CN or INP. The data of ERICA-AMS will be subject of a further study.

2.1.2 *Limitation of ERICA-LAMS*

In contrast to the ERICA-AMS, the quantification of aerosol mass concentration in ERICA-LAMS is nearly impossible due to a large variability of ion signal intensities as a result of alterable laser characteristics, different particle properties, equivocal atomic masses, and nonlinearities inherent in the ablation process itself. First of all, the particle beam divergence, the Gaussian shape of the laser beam profile, and a spatially inhomogeneous laser beam profile lead to variable laser intensities impacting on the detected particle (Wenzel and Prather, 2004; Brands, 2009; Clemen et al., 2020). Second, the ionization efficiency depends on the particle chemical composition (e.g. Bhave et al., 2002). Third, the particle ablation and fragmentation changes with variable laser intensities as well as wavelengths, and depends on particle size, structure and composition (e.g. Bhave et al., 2002; Cai et al., 2006; Sultana et al., 2017). Next, ion signals from major compounds may be small compared to those from less concentrated constituents (Gross et al., 2000; Reilly et al., 2000; Hatch et al., 2014). This is referred to as matrix effect. Finally, the high ionization energy results in the fragmentation of molecules and ions, and thus, complicates the identification of individual organic species (Sullivan and Prather, 2005; Murphy, 2007). Still, the elemental composition of the ablated particle may be obtained to a limited degree. In conclusion, the quantification of most particulate compounds is not gainable. Nevertheless, the single-particle method allows for the investigation of internally mixed particles and partial identification of organic fragments (Sullivan and Prather, 2005; Murphy, 2007; Köllner, 2020). Moreover, refractory material including elemental carbon (EC), metals, and minerals can be detected, allowing for a wide range of organic and inorganic species to be studied. Based on aerosol composition derived from ERICA or complementary measurements of other particle counters, certain particle compounds may be inferred from the mass spectra (see Sect. 4.1; Froyd et al., 2019; Köllner, 2020).

2.1.3 *Particle size information*

The particle size is a quantity that can be derived via the measurement of the particle velocity. This is based on the fact that particles of different sizes are

exposed to inequal accelerations when they are introduced into the vacuum chamber (Jayne et al., 2000; Brands et al., 2011). The particle velocity v_p is determined by the measurement of the travel time $t_{p,tof}$ of a single particle between DU1 and DU2 as described in Sect. 2.1.1. Knowing the flight distance between both DUs ($d_{DU} = 66.5$ mm; Hünig, 2021) and the travel time in terms of clock cycles (*upcounts*), the particle velocity v_p is given for ERICA by:

$$v_p = \frac{d_{DU}}{t_{p,tof}} = \frac{0.0665 \text{ m} \cdot 25 \text{ MHz}}{\text{upcounts} \cdot 40 \cdot 10^{-9} \text{ s}} \quad (2.1)$$

The flight time is measured using an internal clock system with a counter value (*upcount*) that is based on the processor frequency of 25 MHz. Consequently, one *upcount* corresponds to 40 ns.

In detail, the particle velocity is also a function of the density and shape, both of which are highly variable among atmospheric aerosol particles. Thus, an equivalent size has to be introduced that is valid for all kinds of aerosol particles covering the particle density and morphology. When referencing the particle of interest to a spherical particle of the same velocity, and a density of 1 g cm^{-3} , this equivalent particle size is referred to as *aerodynamic diameter* d_a . When considering the free-molecular regime, which is a good approximation for the ERICA vacuum chamber, the equivalent size is called *vacuum-aerodynamic diameter* d_{va} (DeCarlo et al., 2004).

Calibration measurements with reference particles of known density, shape, and size are necessary in order to gain a relation between the measured particle velocity v_p and the particle size d_{va} of interest. Such measurements were conducted in 2017 using monodisperse, spherical PSL particles of various sizes. The results are also valid for the set of measurements reported during ND-MAX in winter 2018 since the setup of ERICA remained in the same configuration and alignment. The underlying analysis was later published by Hünig (2021). A mathematical relation between d_{va} and v_p was derived by Klimach (2012) and is given as:

$$d_{va}(v_p) = \frac{k}{\ln\left(\frac{v_g - v_0}{v_g - v_p}\right)} \quad (2.2)$$

with the particle's starting velocity at the end of the aerodynamic lens (v_0), the velocity of the gas (v_g) and a constant k .

Hünig et al. (2022) conducted a size calibration for the ERICA optical system using PSL particles of 15 different NIST (American National Institute of

Standards and Technology) size standards ranging from $d_{nom} = 80 \text{ nm}$ to $5 \mu\text{m}$. After mapping each particle size to a certain upcount value, a polynomial fit of second order (Eq. 2.3) was used to create a calibration curve in order to link the vacuum-aerodynamic diameter d_{va} to the particle flight time inside the vacuum chamber. The corresponding relationship is:

$$d_{va}(t_{p,tof}) = K_0 + K_1 \cdot t_{p,tof} + K_2 \cdot t_{p,tof}^2 \quad (2.3)$$

with the parameters

$$K_0 = (101.44 \pm 55.4) \text{ nm}$$

$$K_1 = (-1.44 \pm 0.16) \text{ nm } \mu\text{s}^{-1}$$

$$K_2 = 0.0040388 \pm 0.000101) \text{ nm } \mu\text{s}^{-2}.$$

For calibration measurements, a differential mobility analyzer (DMA) was used that provided a monodisperse aerosol population by selecting aerosol particles according to their electrical mobility. The electrical mobility of a particle depends on its size, shape, density and the number of electrical charges it is carrying. A relationship between the vacuum-aerodynamic diameter d_{va} and the *mobility diameter* d_{mob} can be found in the literature (e.g. Jayne et al., 2000; DeCarlo et al., 2004) and is provided in Eq. 2.4:

$$d_{va} = \frac{\rho_p}{\rho_0} \cdot S_p \cdot d_{mob} \quad (2.4)$$

with the particle density ρ_p , the unit density ρ_0 of 1 g cm^{-3} and the so-called Jayne shape factor of the particle S_p .

2.1.4 Performance of ERICA-LAMS during ND-MAX

The performance of ERICA-LAMS is described by the detection efficiency, ablation efficiency, and collection efficiency, which are quickly introduced below.

Detection efficiency

The detection efficiency DE describes the capability of the optical detection system of ERICA to detect aerosol particles in a defined particle size range and is defined by the number concentration of successfully detected particles (N_{coinc}) per number concentration obtained with a reference instrument (N_{ref}):

$$DE = \frac{N_{coinc}}{N_{ref}} \quad (2.5)$$

The detection of particles is affected by losses in the CPI and the aerodynamic lens. In order to quantify these losses, the transmission efficiency (TE) of the inlet system can be measured. The aerodynamic lens implemented in ERICA is a Liu-type (IPL-013 manufactured by Aerodyne Inc.) that has been characterized in detail (Liu et al., 1995a,b) and later improved by Peck et al. (2016) and Xu et al. (2017) to extend the size range of particles that can be transmitted. For the updated lens system, a 50% transmission efficiency lower diameter (d_{50}) of approximately 120 nm was recorded using a lens pressure of 4.53 mbar which equals the ERICA lens pressure (Peck et al., 2016; Xu et al., 2017). Hünig (2021) inferred a value of 1.024 for TE using a mathematical approach described in Klimach (2012) that he adapted by adding a scaling factor TE in order to account for possible losses in the lens. The equation in Klimach (2012) describes the particle detection depending on the particle beam characteristics and laser beam characteristics, respectively. Thus, the curve of the detection efficiency will be a convolution curve of both, the particle beam profile and the laser beam intensity profile (Klimach, 2012; Hünig, 2021).

The particle beam is mainly characterized by the broadening cross section towards the detection stages. These properties were evaluated by Hünig (2021) in detail. For several particle types and particle sizes, the aerodynamic lens was tilted and the detection efficiency was measured. The laser beam profile was assumed as a rectangular function with an effective laser width (as radius) estimated from Mie scattering (Bohren and Huffman, 1998). The effective laser width describes the section of the laser beam at which the scattered light of the particle can be detected, and is inferred from the detected light signals of the particle and the laser beam intensity. In conclusion, the detection efficiency accounts for all potential particle losses along the streamline into the detection stage.

Hünig (2021) reported measurements for the ERICA setup after the Stratoclim campaign that were also valid for the configuration during ND-MAX. The calibration measurements were conducted using PSL particles and ammonium nitrate particles to determine the maximum possible detection efficiency for several settings of the aerodynamic lens. The d_{50} values were obtained by interpolation of the size curves detected for the PSL particles at 184 nm at DU1 and 174 nm at DU2 as lower limits, respectively. The upper limit was only detected for DU1 at 3173 nm. During this set of measurements, a detection efficiency of up to 100% for PSL particles and up to 90% for ammonium nitrate

particles was obtained. However, these values refer to an optimal lens position that has been determined for each particle size and with respect to the particles detected at the individual DUs. Clemen et al. (2020) reported a detection efficiency up to 100% for a size range of 350 to 1500 nm for a fixed lens position of the ALABAMA (Aircraft-based Laser Ablation Aerosol MAss spectrometer) inlet system. Similarly to the ERICA inlet system, the aerodynamic lens system of ALABAMA consists of a CPI and an aerodynamic lens to introduce and focus the particles into a narrow beam before entering the vacuum chamber. Despite the similar inlet design of ERICA and ALABAMA, the values are not comparable since Hünig (2021) decided for a variable lens position to determine the maximum DE .

The detection efficiency during ND-MAX was calculated by the number concentration of coincidences detected with the ERICA optical system and the laser aerosol spectrometer (Model 3340 by TSI Instruments Ltd, Shoreview, MN, USA, see Sect. 2.4.2). As the LAS size range of detection extended from 90 to 7500 nm but ERICA only covered a range of 174 to 3173 nm, a selected number of LAS size bins was considered. In detail, the LAS size bins taken into account covered a range of 176 to 3209 nm. The DE of ERICA was 0.37 for the lens settings $x_1 = 10.48$ mm and $y_1 = 10.59$ mm applied during research flight (RF) 1 and 2. Afterwards, the lens settings were adapted to $x_2 = 10.22$ mm and $y_2 = 10.59$ mm in order to improve the detection efficiency of the ERICA-AMS. However, the adaption of the settings led to a lower detection efficiency of ERICA-LAMS of 0.33.

Hit rate

The ablation efficiency is the proportion of successfully ablated and ionized particles (C_{hits}) in the number of successfully triggered laser shots (C_{shots}) and is often referred to as hit rate (HR). Sometimes, the number of coincidences is used as reference instead of the shot number disregarding the limitation of the ablation laser.

$$HR = \frac{C_{hits}}{C_{shots}} \quad (2.6)$$

The number of shots is mainly affected by two parameters. First, the particle velocity must be determined correctly in order to trigger the ablation laser just when the particle reaches the ablation spot. Second, the laser must be ready to shoot (Brands et al., 2011).

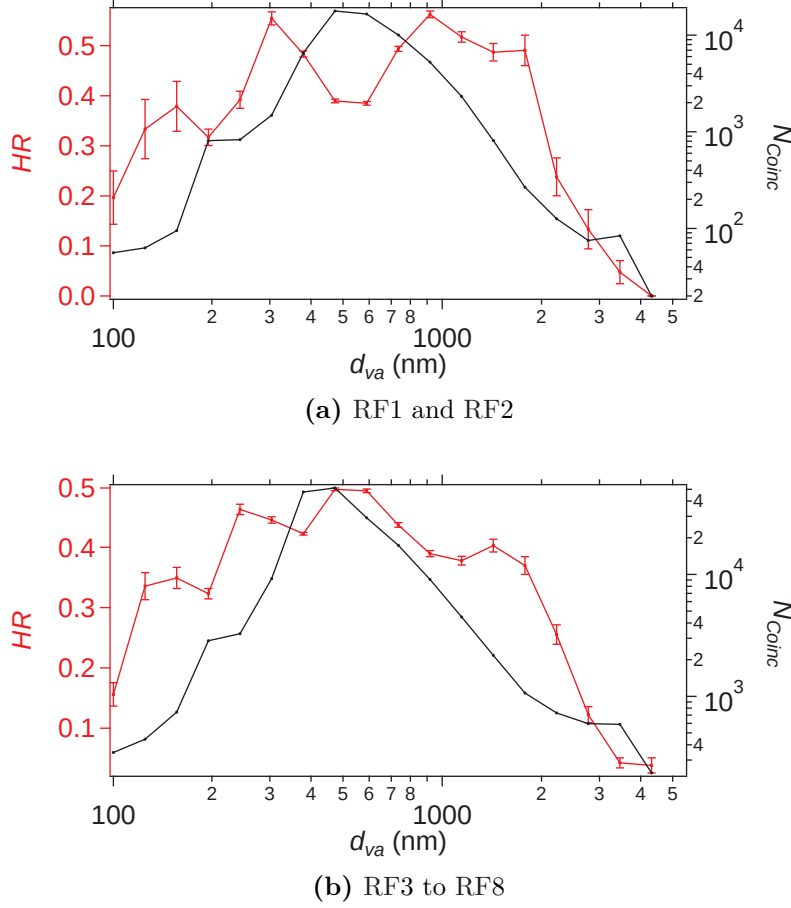


Figure 2.2: Size-resolved hit rate (red) and coincidence (black) of ERICA during ND-MAX for two aerodynamic lens positions of $x_1=10.48$ mm, $y_1=10.59$ mm (RF1+RF2, a) and $x_2=10.22$ mm, $y_2=10.59$ mm (RF3-RF8, b). The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

As the laser repetition rate is set to 120 ms, 8 to 9 particles per second are ablatable in maximum, which is a limiting factor. Moreover, the hit rate depends on the physical and chemical properties of the particles such as particle size (e.g. Kane et al., 2001; Brands et al., 2011), shape (e.g. Moffet and Prather, 2009), composition (e.g. Thomson et al., 1997; Kane et al., 2001; Brands et al., 2011), and electrical charge (Su et al., 2004). Besides, the ablation laser intensity determines the particle types that are detectable (Thomson et al., 1997; Kane et al., 2001; Brands et al., 2011).

The hit rate of ERICA-LAMS was calculated for 20 logarithmic size bins in a range of 90 to 4800 nm for the dataset of ND-MAX (Fig. 2.2). For the first lens position that was applied during RF1 and RF2, two maxima of 55% and 56% were detected for particle sizes of 304 and 918 nm, respectively. For the

adapted lens position that was chosen during RF3 to RF8, a lower hit rate of 49% was found for a size range of 473 to 590 nm. These values agree with measurements of ambient air recorded by Hünig (2021) showing a maximum of 52%. In contrast, the maximum he found was detected at approximately 230 nm. For comparison, Köllner (2020) reported an average of the ALABAMA hit rate of 10%, whereas the A-ATOFMS reached $\sim 30\%$ for a size range of 75 and 250 nm, and the LAAPTOF hit $\sim 58\%$ at a particle size of 300 nm (Su et al., 2004; Gemayel et al., 2016). Thus, the hit rates of ERICA-LAMS detected within the series of measurements during ND-MAX were comparable to those of equivalent single-particle mass spectrometer instruments.

When comparing the size-resolved hit rate for both lens settings, the slope characteristics of both curves below 300 nm and above 1000 nm were similar and attributable to the instrumental setup. For small-sized particles, the number of generated ions was probably low and resulted in less intensive ion signals that might not segregate from background noise. The detection of large-sized particles was impacted by the particle beam divergence and a wide effective laser beam width that resulted in increasing deviations between the calculated and the real particle flight time (Hünig, 2021).

Collection efficiency

The collection efficiency CE accounts for all losses along the particle beam towards the ablation spot, and thus, is a combination of the efficiencies described above. Consequently, it is defined as the number of successfully ablated and ionized particles per number of particles that enter the inlet system of ERICA. Eq. 2.7 provides the definition of CE .

$$CE = DE \cdot HR \quad (2.7)$$

Limitations in the performance

The performance of ERICA-LAMS throughout the ND-MAX campaign was examined based on the vertical profiles of DE , HR , and CE that are displayed in Fig. 2.3. In general, ERICA-LAMS performed better at high altitude levels than below 5 km due to several factors (Fig. 2.3 (a) and (b)). DE reached values up to 0.68 (1.21) in maximum during the first (second) series of RFs at 7.5 km (10 km). DE values of approximately 40% were achieved above an

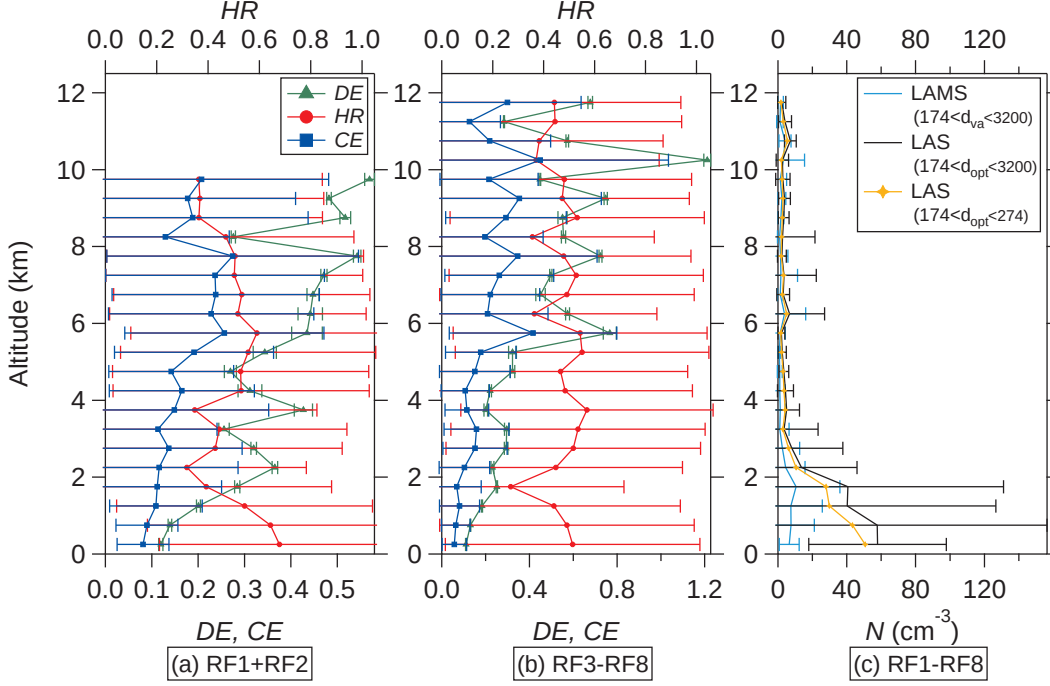


Figure 2.3: Vertical profiles of detection efficiency (DE), hit rate (HR) and collection efficiency (CE) for a lens position of $x_1 = 10.48$ mm and $y_1 = 10.59$ mm on research flight 1 and 2 (RF1+RF2, a) and a new position of $x_2 = 10.22$ mm and $y_2 = 10.59$ mm on RF3-RF8 (b) during the ND-MAX campaign. (c) provides a vertical profile of the recorded number concentration of ERICA-LAMS and the reference instrument LAS for a size range of approximately 175 to 3200 nm. Values are given as mean within altitude intervals of 500 m, error bars correspond to absolute uncertainties ((a) and (b)) and standard deviations (c). The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

altitude level of 5 km, whereas they dropped to 20-30% for an altitude range below 5 km (both series of RFs).

The minima of DE were detected next to the ground and are the result of the limited size detection range of ERICA-LAMS. As sources of primary aerosol particles are widely distributed near the ground, the number of small-sized particles ($d_p \sim 174$ to 275 nm) in the range of interest was larger than for the altitude bins above, and was rather detectable by the reference instrument (LAS) (Fig. 2.3 (c)). This led to a small detection efficiency next to the ground, whereas in a range above 5 km, the aerosol population was dominated by particles of a larger size. In consequence, more large-sized particles were present that were detected by ERICA-LAMS as well, and that led to a larger detection efficiency. A local minimum at 8 km was probably the result of aircraft emissions that also released small-sized aerosol particles and precursor gases, which were in favor of new particle formation but not detectable by ERICA-LAMS.

In addition, the performance was limited by the ablation laser repetition rate. As long as the number of particles was small, which was the case for the lowermost altitude bins, the limitation of particle ablation due to laser limitation was low. Thus, the hit rate reached a maximum of 68% when ERICA-LAMS only detected a small number of particles. For altitude bins above 500 m, DE increased up to 0.37, expanding the potential to reach the maximum laser repetition rate. Accordingly, HR dropped to 0.32. The same effect was also observed for higher altitude levels. Nevertheless, the hit rate did not decrease in the same ratio as the detection efficiency extended. Thus, the combination of both (CE) slightly enhanced with altitude. Analogous trends were observed for the second series of RFs. DE tended to grow with altitude and so the collection efficiency did because the hit rate just slightly shrunk.

2.2 PARTICLE MASS SPECTRUM ANALYSIS

For each particle that was successfully detected by both detection units of ERICA-LAMS, a raw spectrum per polarity was stored on the hard disk drive for later analysis. The raw spectrum provides the ion flight time t_{tof} and the voltage signals of ions detected at the multi-channel plates in the mass spectrometer as a function of t_{tof} . In order to analyze the chemical substances involved in the particle, the voltage signals of the ions need to be converted into a mass to charge ratio m/z . This m/z calibration was conducted using the software package *Concise Retrieval of Information from Single Particles* (CRISP). The calibration obtained by a method of Klimach (2012) is describing the proportionality of t_{ToF} and $\sqrt{m/z}$, which is given by:

$$t_{ToF} = a + b \cdot \sqrt{m/z} \quad (2.8)$$

with the calibration coefficients a and b . The calibration coefficient a describes the shot-to-shot variability of the boundary conditions during ion formation (Brands et al., 2011; Klimach, 2012). The coefficient b (Eq. 2.9) includes the integration of the raw voltage signal over time. The area below the curve of the ion signal is determined in order to gain the so-called particle stick spectra representing the ion peak area. They are provided in $\text{mV} \cdot \text{sample}$, where the term *sample* is referred to the sampling time interval of the oscilloscope that was set to 1.6 ns (Klimach, 2012; Hünig et al., 2022). The corresponding equation is:

$$b = \frac{1}{\sqrt{(2 \cdot e_c)}} \cdot \int \frac{1}{\sqrt{U(s_{ToF})}} \cdot ds_{ToF} \quad (2.9)$$

After the conversion of raw spectra into stick spectra, the final mass spectra were classified into several particle types by analysis and comparison. In detail, each particle mass spectrum was assigned to one out of a set of randomly predefined particle types. Each particle spectrum consisted of several dozen cation and anion peaks and a research flight counted up to thousands of mass spectra. Consequently, an appropriate method was essential to divide this multidimensional set of aerosol particles into a small number of groups.

Different methods have been used in the past to sort the individual mass spectra (Song et al., 1999; Hinz et al., 1999; Murphy et al., 2003; Gross et al., 2010; Klimach, 2012; Reitz et al., 2016; Sultana et al., 2017; Christopoulos et al., 2018). An automated clustering based on *k-means* algorithm (Hartigan and Wong, 1979; Rebotier and Prather, 2007) has been used to analyze mass spectra of ERICA-LAMS in the Ph.D. thesis of Hünig (2021). A detailed description of the *k-means* algorithm and its implementation and performance in CRISP can be found in the Ph.D. thesis of Klimach (2012) and Roth (2014). Briefly, a total number k of clusters and a distance criterion is predefined by the user. In a first iteration, the algorithm sets the first particle spectrum as a reference spectrum for the first group of particles, which is referred to as *Cluster0*. The following spectrum is then compared with the reference spectrum of *Cluster0*. In case the distance criterion is not fulfilled, i.e. the distance between the reference spectrum and the next one is smaller than the preset condition, the spectrum will be also assigned to *Cluster0*. If the distance criterion is fulfilled, i.e. the distance is larger than the preset criterion, the next spectrum will be used as a reference spectrum for a second group of particles, named *Cluster1*. However, this procedure can be repeated only until all predefined clusters k are given a reference spectrum. For all following spectra, the algorithm will assign the current spectrum to the reference spectrum that is showing the smallest distance to the current one. After the first assignment, the mean mass spectrum of each cluster will be updated in a way that it represents all particle spectra belonging to that cluster. In the next iteration, the mass spectra will be assigned for a second time to the clusters, but now regarding the distance to the mean mass spectra of each cluster. Again, a mean mass spectrum will be derived for each cluster. The following iterations will proceed in the same way until the assignment of particle spectra will not change anymore.

A big advantage of the *k-means* algorithm is the assignment of all particles to one of the predefined clusters. Ergo, a cluster of undefined spectra is not existing in the end. However, this advantage results in the assignment of particles

to a certain cluster due to the minimized distance even though the particles might not necessarily fit to the predefined cluster and would rather belong to a different cluster. Furthermore, the *k-means* algorithm shows a bias towards the first hundred to thousand of spectra as it only considers these particles for the definition of reference spectra. In case that an important particle type is not detected within the first thousand of spectra, its mass spectrum might not be declared as a reference spectrum. Moreover, it will probably be assigned to a reference spectrum and cluster that it actually does not belong to.

The mentioned disadvantages have been partly overcome by the use of the *fuzzy c-means* algorithm (Bezdek et al., 1984; Hinz et al., 1999). This algorithm also compares the spectrum of the current particle to the reference spectra of a predefined number of clusters. However, the assignment of a spectrum to a reference is regulated by a larger number of parameters. For each spectrum, a membership coefficient is calculated that considers the distance towards the reference spectrum of, and its affiliation to a certain cluster. These distance functions are based on Euclidian metric or Pearson correlation (Klimach, 2012; Roth, 2014). In the framework of this thesis, the Pearson correlation coefficient (r) was chosen to determine the distance (d_{ij}) between the current spectrum i and the reference spectrum j :

$$d_{ij} = 1 - r_{ij} \quad (2.10)$$

The membership coefficient of a spectrum i towards a reference spectrum of cluster k is defined by Eq. 2.11 (Roth, 2014):

$$m_{ik} = \frac{1}{\sum_{k=1}^C \left(\frac{d_{ij}}{d_{ik}} \right)^{\frac{2}{f-1}}} \quad (2.11)$$

where f (*fuzzifier*) is a measure of the fuzziness of the division into clusters. The value of f is $1 \leq f \leq \infty$. For larger values of f , the division into clusters becomes fuzzier. When the fuzzifier approaches the limit value ($f \rightarrow 1$), the particle spectra will be assigned to only one certain cluster, which is equal to the *k-means* algorithm. Moreover, the sum of all membership coefficients of a certain spectrum i equals 1. Summarizing, the *fuzzy c-means* method has a more sophisticated assignment routine than the *k-means* algorithm.

Next, the *fuzzy c-means* algorithm contains a cluster of undefined particles that are not attributable to any of the reference mass spectra. Consequently, these

spectra may be subclustered in a second iteration allowing for the filtering of rare particle types or individual types which are characterized by less intensive signals.

This describes a general problem of the clustering method. The assignment of mass spectra is affected by dominant ion peaks resulting from composition-dependent ionization efficiencies and matrix effects. As a consequence, mass spectra of particles of different chemical composition may be collected erroneously in the same cluster. This problem may be reduced by a pre-scaling of the ion peak area. Roth et al. (2016) and Schmidt et al. (2017) used the square root of ion peaks in order to decrease the relative differences of the signal intensities but were not able to fully compensate the effect of dominant peaks on the assignment of mass spectra.

Köllner (2020) and Eppers (2023) decided for a *markering* method to overcome the problems mentioned for the clustering algorithms, for which they only regarded the presence of individual ion peaks showing signals above a background threshold. This method may be applicable for the identification of predefined particle types of known nature. However, the focus of this thesis is on the chemical composition of the midlatitude UTLS aerosol particles in general. Since the knowledge of UTLS aerosol is still limited, a clustering method seems to be more appropriate to provide an overview of the individual particle types and their abundance.

Here, the *fuzzy c-means* algorithm was applied to group the mass spectra into clusters of individual particle types. For that, the dataset was clustered with the application of parameters listed in Table 2.1. A detailed description of the parameters is given in Klimach (2012). The *number of clusters* determines how many groups the mass spectra are sorted into. Within the *type of clustering* the user chooses the clustering algorithm. The *initalization type* defines the way the start clusters are set. The reference mass spectra for each cluster may be chosen randomly or by ensuring a difference between the individual clusters. This is defined by the *startcluster difference* which describes the minimum difference between two mass spectra. The larger the value is set, the more features of the mass spectra of the individual clusters are common. With a value of 1, the mass spectra are identical. In the presence of particle types with highly variable chemical composition, a smaller number for the startcluster difference is preferred in order to cover all particle types. The *source for clustering* may be cation and anion signals or only one polarity of them depending on their noisiness. The *normalization type* represents the factor the signal intensities in the mass spectrum are normalized to. This compensates for the highly variable ionisation capability among cations and anions. Further, the mean mass spectrum can be normalized in three different ways. The mass spectrum

Table 2.1: Overview of the parameters applied for the fuzzy c-means clustering of the ND-MAX dataset. Subclustering and sub-subclustering were applied to the cluster of non-assigned mass spectra of the previous clustering routine.

Parameter	Main clustering	Sub-clustering	Sub-sub-clustering
Number of cluster	50	20	20
Type of clustering	fuzzy c-means	fuzzy c-means	fuzzy c-means
Initialization type	find different startcluster	find different startcluster	find different startcluster
Source for clustering	anion + cation	cation	cation
Normalization type	sum	sum	sum
Normalization time	before and after concatenation	after concatenation	after concatenation
Startcluster difference	0.8	0.3	0.7
Pre-processing type	power each mz	power each mz	power each mz
Pre-processing power	0.5	0.5	0.5
fuzzifier	1.7	1.2	1.2
fuzzy abort	0.001	0.001	0.1
Distance mode	correlation	correlation	correlation

may be normalized before the mean cation and mean anion mass spectrum are concatenated, or afterwards. In addition, normalization can be performed twice, before and after concatenation. This is done by adjusting the *normalization time*. The *pre-processing type* "prepares" the mass spectra before normalization in a way that each signal is raised to a given power (*pre-processing power*). As a result, mass lines of lower signal intensity are increased in relation to large signal intensities within one mass spectrum. In the context of calculating the distance of a mass spectrum to a reference spectrum, the presence of an m/z in both mass spectra is given more weight than the correspondence of the signal intensities. Finally, the *fuzzy abort* determines the criterion that is proven for each clustering iteration. This value corresponds to the difference of all m_{ik}

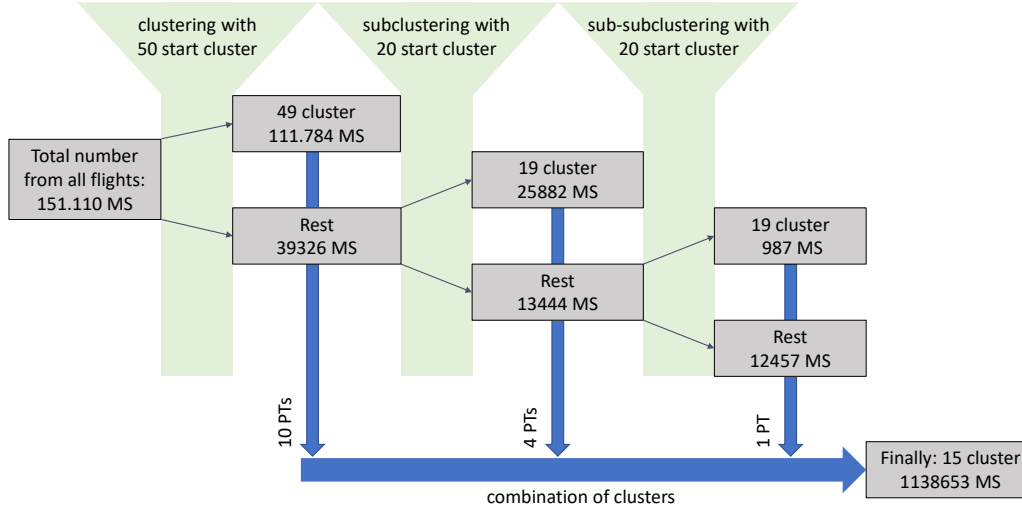


Figure 2.4: Schematic overview of the clustering process in CRISP. Acronyms are defined as follows: MS = Mass Spectra, PT = Particle Type. The process includes three steps. The complete dataset is clustered to ensure congruence of particle types across all research flights. The rest cluster of that dataset is clustered in a subroutine. Once again, a rest cluster of that subroutine remains that is clustered consecutively in a sub-subroutine.

(see. Eq. 2.11) of two consecutive runs. In case it is underpassed, the clustering procedure is stopped (Roth, 2014).

Except for the startcluster difference, the properties for the clustering were set according to Roth (2014). The startcluster difference was set to be 0.8 instead of 0.7 in order to obtain a larger number of clusters of similar spectra characteristics. Using this set of conditions, a number of 50 clusters was found to be appropriate for the clustering of the ND-MAX dataset. A larger number of initial clusters lead to empty clusters. The main clustering routine resulted in 111784 spectra that were successfully assigned to one of the initial clusters. The start clusters were later on merged to a total of 10 clusters referring to 10 individual particle types (see Fig. 2.4). However, more than a quarter of all spectra (39326) was not attributable, mostly due to low signal intensities in the anion spectrum. The clustering routine obviously could not manage the classification of these noisy spectra. As a consequence, the pool of undefined spectra had to be clustered in a subroutine, only considering the cations. An initial number of 20 clusters was observed to be large enough to prove the remaining particles for their spectra characteristics. The clustering parameters were adapted iteratively to gain a minimum of non-assigned spectra in the subroutine. The cluster of non-assigned spectra in the subroutine contained

13444 mass spectra and was clustered consecutively in a sub-subprocedure. By the analysis of this *rest* cluster, the number of non-assigned spectra was reduced to 12457 particles or 8.24 %. Simultaneously, additional five particle types of less abundance were discovered that play an important role for the analysis of the chemical composition in the UTLS region.

2.2.1 Ion peak area threshold

Ion signals in particle mass spectra may be interfered by instrumental background noise. In order to overcome this issue, the ion peak area threshold is determined, which states that a peak is present in case it exceeds the threshold of background noise. Different threshold definitions have been used in the past (e.g. Tolocka et al., 2004; Roth et al., 2016; Eppers, 2023). Köllner (2020) described an experimental method to detect background noise. For that, the ablation laser is triggered at a fixed frequency and does not ablate any particulate material. Consequently, the background noise is not interfered with ions of ablated particles anymore, and is detected by the record of 'background' mass spectra. These test measurements on background noise were not conducted during the ND-MAX campaign. Therefore, the mass spectra of the detected particles were proven to overcome the ion peak area threshold on mass-to-charge ratios that are not affected by ions of ablated and ionized atmospheric particles. As many mass-to-charge ratios are occupied by these ions, certain m/z values have to be considered for the detection of background noise. Here, the mass-to-charge-ratios of m/z 2-11 and m/z 245-250 were taken into account for both polarities, except for m/z +6 and m/z +7, which are assigned to the Li^+ ion. Lithium is a constituent of mineral dust (e.g. Gallavardin et al., 2008) but was also observed in the mass spectra of motor oil particles recorded during ND-MAX (see App. A.2). The background signal peaks were counted and their 99% cumulative probability was defined as the ion peak area threshold (Fig. 2.5). Thus, 99% of all signal peaks below that threshold were defined as background, whereas the 1% overshooting beyond that value was regarded as signal peak of detected ions.

Both, the threshold for anions ($x_{t,an}$) and for cations ($x_{t,cat}$) were six to seven times larger than that value of 7 mV·samples determined by Hünig (2021). An analysis of the threshold with respect to the unoccupied masses mentioned in Hünig (2021), which only regarded m/z +2 to m/z +6 for cations and m/z -2 to m/z -11 for anions, did not result in lower thresholds. An analysis of raw spectra of individual particles revealed that this high background threshold was the result of some electrical noise detected within a few mass spectra. However, this ringing was found to be irrelevant for the clustering routine

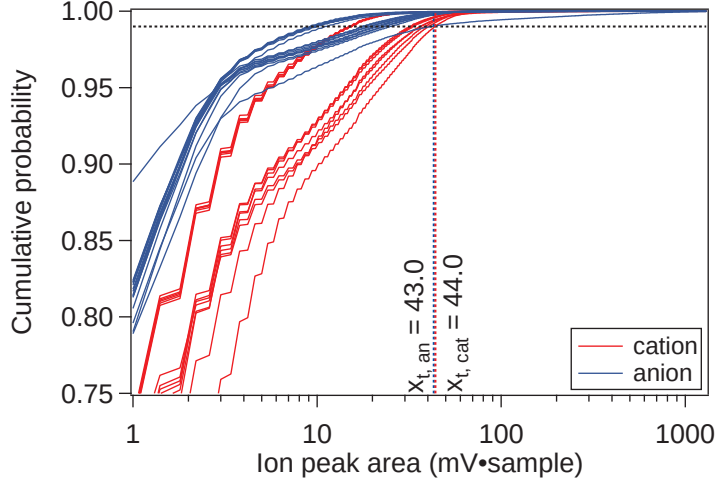


Figure 2.5: Cumulative probability distributions of the anion (negative, blue) and cation (positive, red) ion peak areas at m/z 2-11 and m/z 245-250 (assumed as non-occupied m/z values), except for m/z +6/+7 representing Li^+ . Dashed vertical lines represent the selected threshold values $x_{t,an}$ and $x_{t,cat}$, dashed horizontal line marks the 99% cumulative probability.

and the interpretation of mass spectra in the framework of this thesis. In case of marking methods (see Sect. 2.2), the background noise might affect the filtering with respect to individual masses because this background noise resulted in artificial signals slightly above 10 $\text{mV}\cdot\text{sample}$. Nevertheless, the electrical noise was rarely detected. In 94% of all spectra, the cation signals were below 20 $\text{mV}\cdot\text{sample}$ and the anion signals even below 6 $\text{mV}\cdot\text{sample}$. In consequence, the electrical noise only resulted in a small number of noisy spectra, which was neglectable within this analysis.

2.2.2 Classification of particle types measured during ND-MAX

During the campaign, 15 different particle types were found using the clustering routine of CRISP as mentioned in Sect. 2.2. The rest cluster was sub-clustered two times in order to trace particle types of low frequency and to minimize the number of undefined mass spectra. The particle types were named according to the most intensive ion signal peaks (*markers*) in their mean mass spectrum and were afterwards interpreted with the help of marker peaks provided in literature. This procedure is shown exemplarily for the mineral dust type.

Regarding the mean mass spectrum of the first particle type in Fig. 2.6, large cation signals were detected for sodium, magnesium, aluminium, silicon, potassium, and calcium as well as chemical compounds consisting of them. In addition, the anion spectrum revealed the presence of carbon hydrogens, chloride,

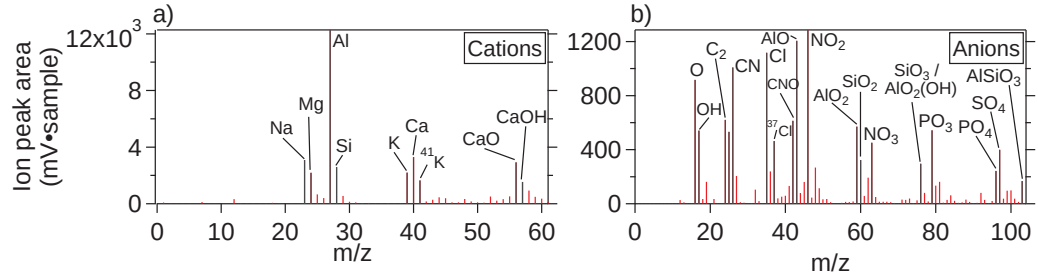


Figure 2.6: Mean mass spectrum of cations (a) and anions (b) for Mineral dust particles detected by ERICA-LAMS during ND-MAX.

aluminium-, and silicon-compounds and further substances involving nitrate, phosphate, and sulphate. As a consequence, the particle type was named previously *AlOrgNOPhoSOCl* in order to highlight the most characteristic chemical species that this type was consisting of. Silva et al., 2000 presented mass spectra of soil dust particles detected in Southern California, exhibiting dominant peaks at the mass-to-charge ratios (m/z +23, +27, +39, and +56) that referred to the common isotopes of sodium, aluminium, potassium, and iron. Further peaks of silicate (m/z +28 and -60, -76, -103) and calcium components were indicative for dust (e.g. Skorbilowicz and Skorbilowicz, 2019), too. Therefore, the particle type was interpreted as *mineral dust*. Moreover, the chemical constituents of nitrate (m/z -46 and -62), phosphate (m/z -76 and -95), and sulphate (m/z -80, -81, -96, and -97) signified a processing of the particle type. Despite the intense nitrate signal on m/z -46, the particle type was not defined as a nitrate particle type due to a lack of the confirming nitrate signal in the cation spectrum. Analogously, all particle types were analyzed for their characteristic ion signal peaks. Table 2.2 provides an overview of the individual particle types, their characteristic signal peaks, and interpretation according to the referenced literature. A quick analysis and interpretation of the mean mass spectra of each single particle type is conducted in App. A.2.

Table 2.2: Overview of the classified particle types detected by ERICA during the ND-MAX campaign, including their predefined names, interpretation, absolute and relative abundance, and literature for interpretation.

Particle type	Ion marker peaks*	Interpretation	Literature/ Comments
AlOrgNO- PhoSOCl	m/z +23 (Na^+), +28 (Si^+), +39/41 (K^+), +40 (Ca^+), +54/56 (Fe^+), -60 (SiO_2^-), -76 (SiO_3^-), -103 (AlSiO_3^-)	Mineral dust	Silva et al., 2000, Lee et al., 2002; Gallavardin et al., 2008

To be continued.

Particle type	Ion marker peaks*	Interpretation	Literature/ Comments
CaKNaClMg	$m/z +23$ (Na^+), $+24/25/26$ (Mg^+), $+39/41$ (Ka^+), $+40$ (Ca^+), $+83$ (Na_2Cl^+), $-35/37$ (Cl^-), -93 (NaCl_2^-)	Sea spray	Prather et al., 2013; Su et al., 2023
EC	$m/z +n \cdot 12$ (C_n^+) and $m/z -n \cdot 12$ (C_n^-) for $n=1,\dots,12$	Elemental carbon (EC)/ fresh soot	Moffet and Prather, 2009; Pratt et al., 2009
Hydrocarbons	$m/z 30$ (CH_4N^+), $+58$ ($\text{C}_3\text{H}_8\text{N}^+$), $+59$ ($(\text{CH}_3)_3\text{N}^+$), $+70$ ($\text{C}_4\text{H}_{10}\text{N}^+$)	Amine	Angelino et al., 2001; Healy et al., 2015
KNaClMet-NOSO	Sea spray and $m/z +64/66/68$ (Zn^+), $+85/87$ (Rb^+), $+136/137/138$ (Ba^+), $+206/207/208$ (Pb^+), -46 (NO_2^-), -62 (NO_3^+)	Processed sea spray	Similar to sea spray, incl. zinc, rubidium, barium, lead Cornwell et al., 2020
KOrgNOSO1	$m/z +12$ (C^+), $+23$ (Na^+), $+39/41$ (K^+), -46 (NO_2^-), -62 (NO_3^-), -81 (HSO_3^-), $-97/99$ (HSO_4^-)	Biomass burning (BB) type 1	Pratt et al., 2009
KOrgNOSO2	KOrgNOSO1 and $m/z -60$ (SiO_2^-), -76 (SiO_3^-), -79 (PO_3^-)	Biomass burning (BB) type 2	Pratt et al., 2009/ low anion signals compared to KOrgNOSO1
KOrgNOSO3	KOrgNOSO1	Biomass burning (BB) type 3	Pratt et al., 2009/ mostly detected in UTLS-region
MetOrgNO- PhoSOCl	Mineral dust and $m/z +52/53/54$ (Cr^+), $+56$ ($\text{Fe}^+/\text{CaO}^+/\text{KOH}^+$), $-35/37$ (Cl^-), -42 (CNO^-), -43 (AlO^-), -84 (CrO_2^-), -100 (CrO_3^-)	Internal mixture of mineral dust, salt, metal	Similar to min. dust, but also contains fluor, chloride, chrome

To be continued.

Particle type	Ion marker peaks*	Interpretation	Literature/ Comments
MetOrg-PhoSO	m/z C_n^+ for $n=1,2,3$, and +15 (CH_3^+), +27 ($C_2H_3^+$), +37 (C_3H^+), +39 ($C_3H_3^+$), +57 ($C_4H_9^+$), +85 ($C_6H_3^+$), -143 ($C_6H_7O_4^-$), -159 ($H(PO_3)_2^-$)	Motor oil	Clemen et al., in preparation
NaMgFe	m/z +23 (Na^+), +24/25/26 (Mg^+), +40 (Ca^+), +54/56 (Fe^+), +72 (FeO^+), +73 ($FeOH^+$), -44 (SiO^-), -97/99 (HSO_4^-)	Meteoric material**	Schneider et al., 2021
NOSO	m/z +18 (NH_4^+), +30 (NO^+), -46 (NO_2^-), -62 (NO_3^-), -96 (SO_4^-), -97/99 (HSO_4^-)	Nitrate-rich	Appel et al., 2022
OrgNOSO	m/z +12 (C^+), +24 (C_2^+), +18 (NH_4^+), +30(NO^+), +32 (S^+), +48 (SO^+), +99 ($H_3SO_4^+$), -97/99 ($H_3SO_4^-$)	Internally mixed elemental and organic carbon (ECOC) with nitrate and sulphate	Gunsch et al., 2018
OrgNOSO2	m/z +12 (C^+), +18 (NH_4^+), +30 (NO^+), m/z +39 ($C_3H_3^+$), -26 ($CN^-/C_2H_2^-$), -46 (NO_2^-), -62 (NO_3^-), -80 (SO_3^-), -97/99 (HSO_4^-), -125 ($HN_2O_6^-$)	Processed organic carbon (OC)	Pratt et al., 2009
OrgSO	m/z +n· 12 (C_n^+) for $n=1,...,4$ and m/z +27 ($C_2H_3^+$), +39 ($C_3H_3^+$), -79 (PO_3^-), -80 (SO_3^-), -97/99 (HSO_4^-)	Coated soot	Moffet and Prather, 2009

* Note: Ion marker peaks refer to the mean mass spectra of individual particle types detected during ND-MAX. For ion marker peaks provided by references, see App. A.2.

** For simplicity, particles containing meteoric material are referred to as *meteoric material*.

2.2.3 Definition of chemical composition and particle fraction

The term *chemical composition* is generally used to describe the chemical components of a certain measurement interval (e.g. exhaust plume) or object (e.g. aerosol particle). Absolute values are provided by measurement instruments in terms of number (counts), volume, or mass that are often normalized to a reference volume and, thus, provided as number, volume, or mass concentration, respectively. However, when comparing the abundance of two or more constituents, their occurrence needs to be based on the same reference. Therefore, the absolute number of a certain constituent is divided by a parent population, providing a proportion for each constituent. Referring to the chemical composition of the UTLs region, which that thesis is focused on, the contribution of each individual particle type is defined as the number of particles of that type divided by the number of all particles, and is called *particle fraction* (PF) (Eq. 2.12). In detail, the number of mass spectra of a certain particle type (cluster) is divided by the number of all mass spectra detected with ERICA-LAMS. This term describes the relative contribution of the individual particle type to a pre-defined event of exhaust plume, free troposphere, cirrus, or contrail. Moreover, this term is used to describe the relative occurrence of particles with respect to binned variables such as altitude, distance, potential temperature, and other meteorological parameters. Analogously, this concept is used to analyze the contribution of potential source regions to the air masses detected along the flight track. The uncertainty of this statistical approach is mainly affected by the number of collected and assigned particles. As low particle numbers lead to large uncertainties, a sufficient particle number is required per bin and in total to achieve a good statistical representation. In the framework of this thesis, only bins of more than 20 counts were taken into account. The particle fraction is given by:

$$PF_{Type} = \frac{C_{Type}}{C_{All}} \quad (2.12)$$

with the aerosol particle counts of a certain particle type (C_{Type}) and the counts of all aerosol particles (C_{All}).

2.3 SAMPLING INLET FOR AMBIENT AIR

The ND-MAX campaign did not only focus on exhaust aerosol particles emitted by the aircraft but also on the cloud residuals of freshly formed contrails generated upon this exhaust particulate matter. Both types differ in size, shape, and inertia, and thus are difficult to detect by just one inlet type. Therefore, two different aerosol inlet systems were operated throughout the campaign, of which one is specialized on nanometer sized particles, whereas the second system is focused on cloud residuals in the size range of micrometers. Especially, when sampling cloud residuals, the inlet system has to ensure the deceleration of large particles and evaporation of water residue surrounding the core in order to avoid inertial deposition and droplet shattering (Shingler et al., 2012). Both systems are shortly described in the following subsections.

2.3.1 *Aerosol sampling inlet "Scoop"*

The aerosol inlet is a “scoop”-style inlet system providing aerosol particles up to $1\text{ }\mu\text{m}$ in size as well as small contrail ice particle residuals. Larger cloud droplets and supermicron ice particles are deflected away from the sampling line (Moore et al., 2004; Voigt et al., 2021). Interstitial aerosol may even be collected inside clouds due to minimized precipitation particle shattering (Anderson et al., 2015). The scoop inlet is mounted on the forward zenith port of the NASA DC-8 and tapered from the inlet towards the exhaust in order to provide a boost in ram pressure (Anderson et al., 2018). The sample air is introduced and guided non-isokinetically through a probe towards a manifold containing a sample extraction orifice. Supermicron particles are turned aside by a deflector before reaching the sample extraction tube. A small fraction of the extracted sample air is subsequently diluted with a concentric flow of filtered air and directed to the research instruments. The dilution flux is adaptable to maintain a constant pressure level of 160 Torr regardless of aircraft altitude. The excess air flux is released through a rear-facing tube, which is mounted on an aircraft window plate (Anderson et al., 2015, 2018).

2.3.2 *Counterflow Virtual Impactor "CVI"*

The inlet for sampling of cloud residuals is a Counter-flow Virtual Impactor (CVI) from Brechtel Manufacturing Incorporated (BMI Model 1204, Hayward, CA, USA), which was mounted in a starboard side window of the NASA DC-8. The CVI was used for the collection and evaporation of cloud particles larger

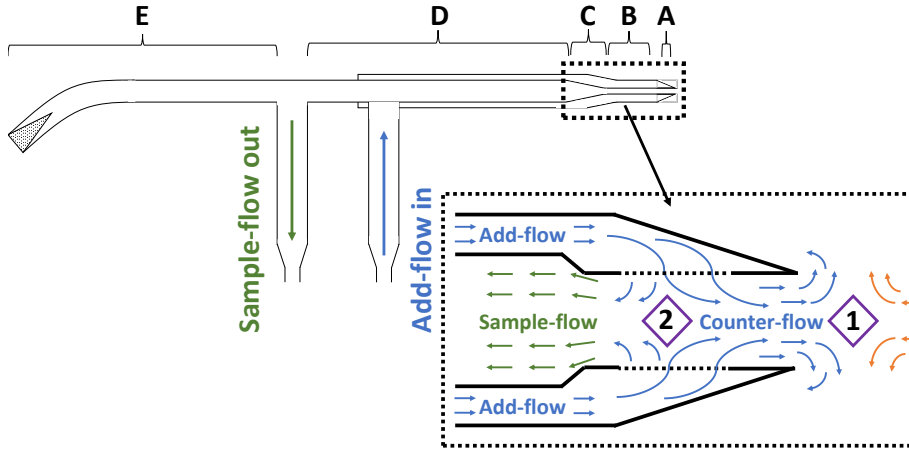


Figure 2.7: Schematic depiction of the CVI inlet and involved flows (adapted from Shingler et al., 2012). Sample air enters the inlet nozzle and streams into the probe tip where the heated counter-flow is introduced through a porous tubing (A). The final sample flow is guided to the extension tube (B) and later on to the expansion region (C). In a last sequence, the cloud residuals are directed to the instruments through a long plumbing (D). The particle trap (E) collects particles of too large size and inertia to follow the tubing towards the instruments.

than approximately $5\text{ }\mu\text{m}$. The core residuals are enriched by a factor of 8 in minimum above ambient concentrations due to a sub-isokinetic inlet flux and provided to ERICA and further particle detection and sizing instruments (Anderson et al., 2018).

For entering the CVI, the sample air passes the inlet nozzle and streams into the probe tip where it hits the dry and heated counter-flow that is introduced by a porous tubing (see Sect. A in Fig. 2.7). Small particles and interstitial aerosol are rejected, whereas the large and inert cloud residuals overcome the counter-flow and continue their way into the extension tube (Sect. B in Fig. 2.7) and the expansion region (Sect. C in Fig. 2.7). The newly formed sample flow consists of the cloud residuals and a flux of warm and dry, filtered air provided by the counter-flow. Exposed to the dry and warm ambient conditions, the cloud residuals evaporate as they travel through the plumbing (Sect. D in Fig. 2.7) before the residual cores are guided into the aircraft body towards the research instruments. Large-sized residuals that tend to impact are collected in a particle trap (Sect. E in Fig. 2.7). The cut-off size of the residual cores depends on the velocity of the ambient air flow outside the probe tip and the distance between the two stagnation planes (labelled 1 and 2 in Fig. 2.7) which appear between two opposite flow directions (Shingler et al., 2012).

2.4 COMPLEMENTARY MEASUREMENTS DURING ND-MAX

Throughout the ND-MAX campaign, a large dataset of variables has been recorded, containing aerosol number, size, and chemical information as well as trace gases and water vapor regarding their concentrations. The instruments and the corresponding parameters recorded by complementary measurements are introduced briefly in this section.

Table 2.3 lists all variables of complementary datasets used in the framework of this thesis including their accuracy and corresponding research instruments as well as references.

2.4.1 *Condensation Particle Counter (CPC)*

The Condensation Particle Counter is a CPC model 3010 by TSI Instruments Ltd, Shoreview, MN, USA, which was modified and optimized for airborne application. The particles enter a non-isokinetic, forward-facing aerosol inlet and undergo a shock-front where ice and water constituents are expected to evaporate completely. In a second step, the particles pass a thermodenuder heated to 250 °C, which ensures the volatile material to be removed. Thus, only the non-volatile particulate matter remains and is recorded by the detection unit. Corrections were applied to the dataset concerning the reduced detection efficiencies in low pressure environments and particle losses in the thermodenuder (Bräuer et al., 2021a; Noone and Hansson, 1990). The aerosol number concentration of particles larger than 10 nm in size, normalized to standard temperature (273.15 K) and pressure (1013.25 hPa), was adopted for the purpose of event definition (see Sect. 2.6).

2.4.2 *Laser Aerosol Spectrometer (LAS)*

The Laser Aerosol Spectrometer LAS model 3340 by TSI Instruments Ltd, Shoreview, MN, USA delivered information about aerosol particle concentration and size distribution in a range between 90 and 7500 nm. The particles are guided into the instrument and pass a helium-neon gas laser. The scattered light is focused and redirected by two pairs of wide-angle mirrors towards an avalanche photo diode and a low-gain photo diode. Four different gain stages are fed with the voltages transmitted from the photocurrent signals and undergo a pulse height analysis to find the first unsaturated gain stage and the corresponding size bin to count up the number for that bin (Moore et al., 2021). The spectrometer drew sample from the same inlet line as ERICA that

Table 2.3: Overview of the instrumentation and parameters during the ND-MAX research campaign including information on time resolution and data accuracy or uncertainty.

Instrument	Parameter used in this study (unit)	Particle size range	Time resolution	A/P: accuracy / precision		Operator	Reference
				T: total uncertainty	CE: collection efficiency		
CPC	$N_{10,STP}$ (cm^{-3})	10 - 3000 nm	1 s	A/P: 10 % (TSI1999)		DLR	^a
LAS	$N_{LAS,STP}$ (cm^{-3})	90 - 7500 nm	1 s	A/P: <5 % (TSI2017)		NASA LaRC	^b
FFSSP	N_{ice} (cm^{-3})	1 - 25 μm	1 s	T: 10 - 35% (Braeuer2021b)		DLR	^c
DLH	$VMR_{\text{H}_2\text{O}}$ (ppmv)		1 s	T: 5 %		NASA LaRC	^d
CIP	IWC (g m^{-3})		1 s	T: 20 %		NASA LaRC	^e
CRDS	VMR_{CO_2} (ppmv)		1 s	A/P: 0.3 ppmv		DLR	^f
O ₃ -analyzer	VMR_{O_3} (ppbv)		1 s	A/P: 5 % or 3 ppbv		DLR	^g
DDS	T ($^{\circ}\text{C}$); p (hPa); z_{DC-8} (m a.s.l.); Lat_{DC-8} ($^{\circ}\text{N}$); Lon_{DC-8} ($^{\circ}\text{E}$)		1 s	A/P: 0.5 $^{\circ}\text{C}$; T: 2.5 hPa; T: ~ 5 m; A/P: 0.01 $^{\circ}\text{N}$; A/P: 0.01 $^{\circ}\text{E}$		NASA	^h
FTI	z_{ATRA} (m a.s.l.); Lat_{ATRA} ($^{\circ}\text{N}$); Lon_{ATRA} ($^{\circ}\text{E}$)		1 s	T: ~ 52 m; A/P: 69 m; A/P: 69 m		DLR	ⁱ

References: ^a Noone and Hanson, 1990 ^b Moore et al., 2021 ^c Baumgardner et al., 1992 ^d Diskin et al., 2002; Vay et al., 1998 ^e Baumgardner et al., 2001 ^f Voigt et al., 2021 ^g Schlager et al., 1997 ^h NASA, 2011 ⁱ maximum value of standard deviation of processed uncertainty data J. T. Bräuer, personal communication, March 25, 2024

was adjustable between the scoop inlet (see Sect. 2.3.1) and the CVI (see Sect. 2.3.2).

2.4.3 *Cavity Ring Down Spectroscopy (CRDS)*

A Cavity Ring Down Spectroscopy (CRDS) instrument by Picarro Inc., Santa Clara, CA, USA (model: G2301-m flight analyzer) was used to detect carbon dioxide. The measurement principle is based on a pulsed laser beam with the wavelength of a CO₂ absorption line, which is emitted into a three-mirror cavity. The mole fraction of CO₂ in the sample air is proportional to the attenuation time of the laser beam. Thus, the CO₂ concentration can be derived by measuring the required time interval to attenuate the pulses. The cavity is operated at a stable pressure of 140 Torr, which is regulated by an inlet valve and achieved by a pump in the sample air inlet line. The measurement interval is 2 s and the data accuracy is 0.3 ppmv. The CO₂ signal rise time (10-90 %) and fall time (90-10 %) is 1.5 s. The sample air is provided by a backward-facing inlet mounted to the upper part of the fuselage of the NASA DC-8 (Bräuer et al., 2021a; Voigt et al., 2021).

2.4.4 *Fast Forward Scattering Spectrometer Probe (FFSSP)*

The Fast Forward Scattering Spectrometer Probe FFSSP (Baumgardner et al., 1992; Brenguier et al., 1998) measures the ice particle concentrations inside clouds in a diameter range between 1 and 25 μm . The instrument was installed on the upper fuselage of the NASA DC-8 next to the inlet for the CRDS in order to derive ice emission indices (EI) with respect to carbon dioxide (CO₂). Additionally, it was placed close to the aerosol inlet allowing for comparison between soot and ice measurements (Bräuer et al., 2021a). The ice particles enter the ice inlet and are guided to the focus of a He-Ne laser beam inside the FFSSP with a wavelength of 632.8 nm. The scattered light intensity in forward direction is measured by a photo detector to derive the particle size and concentration. A size-calibration was conducted previously on the basis of a T-matrix calculation (Borrmann et al., 2000; Rosenberg et al., 2012) for an ice particle aspect ratio of 0.5 to incorporate nonspherical ice crystals. A size-dependent correction function was applied to the data of small particles between 0.5 and 1 μm (Bräuer et al., 2021a). The probe took also part in other contrail measurements (Voigt et al., 2010, 2011; Gayet et al., 2012; Jeßberger et al., 2013; Chauvigné et al., 2018). In 2017, its electronics received an update allowing for recording of single particles (Bräuer et al., 2021a).

2.4.5 *UV absorption photometer*

A UV absorption photometer (Model 49TE by Thermo Fisher Scientific Inc., MA, USA) was deployed to detect ozone data. The analyzer runs in a measurement and a purging mode and switches every second between both modes. In the first one, ambient sample air is introduced to an absorption chamber of 300 mm length and 5 mm inner diameter. A temperature-controlled mercury lamp irradiates the sampled air and the transmitted light is detected by a silicon-photodiode. In the purging mode, the ozone is eliminated from the air sample and a reference measure is recorded. The instrument has a time resolution of 2 s and an accuracy of 5 % or 3 ppbv depending on which value is larger (Schlager et al., 1997).

2.4.6 *Diode Laser Hygrometer (DLH)*

The water vapor content in the ambient air was observed using the NASA Langley/ Ames Diode Laser Hygrometer (DLH), which is based on a fast response near-infrared diode laser sensor. The custom-built instrument mainly consists of a compact laser transceiver mounted on a window and a sheet of high-grade retroreflector applied to the NASA DC-8 engine nacelle (Diskin et al., 2002; Anderson et al., 2018). The water vapor is sensed along the path between the sheet and the transceiver, based on the absorption by one of three separate spectral lines near $1.4\ \mu\text{m}$, and differential absorption detection techniques (Vay et al., 1998). Using the ambient pressure and temperature as well as spectroscopic parameters of previous research studies, the mixing ratio of water vapor ($\text{H}_2\text{O}_{\text{vap}}$) is calculated by an algorithm and provided in real-time to the investigator (Vay et al., 1998; Alfter, 2023).

2.4.7 *Cloud Imaging Probe (CIP)*

The Cloud Imaging Probe (CIP) is an instrument for detection of large particles in a size range from 15 to $900\ \mu\text{m}$ at a resolution of $15\ \mu\text{m}$ and belongs to the Cloud, Aerosol and Precipitation Spectrometer (CAPS, model by Droplet Measurement Technologies, Boulder, CO, USA). A detection mode in a size range of 25 to $1550\ \mu\text{m}$ with a resolution of $25\ \mu\text{m}$ is also practicable. The CIP operates on the detection of shadow images projected onto a linear array of 64 photodetectors. The shadow is created as the particle moves through a collimated laser beam and a reduced light level is recorded on each diode at a rate according to the probe velocity and the size resolution of the instrument. In the end, the subsequently determined shadow drawings of the particle are

combined to a particle image (Baumgardner et al., 2001; Frey et al., 2011; DMT, 2014; Molleker et al., 2014; Klingebiel et al., 2015). CAPS was mounted on the left-wing tip of the NASA DC-8 next to a Cloud Droplet Probe (Anderson et al., 2018).

2.4.8 *DC-8 Data Distribution System (DDS)*

Several parameters concerning time, GPS, navigation, and weather parameters were recorded by permanently installed onboard instruments and provided to the NASA DC-8 Data Distribution System (DDS): The Applanix POS AV inertial navigation and GPS system (by Applanix, Richmond Hill, Ontario, Canada) tracked the aircraft position, velocity, axis orientation, and rates with a maximum frequency of 100 Hertz. Meteorological parameters such as total and static air temperature, potential temperature, pressure altitude and aircraft data including vertical speed, indicated and true air speed were detected by an infrared radiometer. Together with dew point measurements from a General Eastern frost-point hygrometer (General Electric Corp., Boston MA, USA), the data were recorded by the Air Data Computer at a resolution of 0.05 s (NASA, 2011; Anderson et al., 2018).

2.4.9 *ATRA Basic Measurement System*

The DLR-ATRA Basic Measurement System is another flight test instrumentation and acts in a similar way to the DDS. It records all aircraft data related to the experiments as well as meteorological data and provides them for experimental users (DLR, 2016). Engine parameters such as inlet temperatures and pressures, engine pressure ratio and gas temperature, speed of turbofan engines, and fuel flow are tracked for aircraft research on noise, acoustics, aeroelasticity, lift, wake turbulence, and evaluation of flight systems (Anderson et al., 2018).

The aircraft and atmospheric state parameters of both airplanes were provided in a merged *Meteorological and Navigation* (short: *MetNav*) dataset by the American National Suborbital Research Center (Bennett and Yang-Martin, 2021).

2.5 TROPOPAUSE DERIVATION

This section describes the estimation of the location of the tropopause, which is needed for the determination of the UTLS region throughout the RFs of ND-MAX and for the analysis of the atmospheric vertical profiles with respect to the abundance of individual particle types in the UTLS, and cloud formation region. The location of the tropopause is derived using several markers such as potential temperature, ambient temperature and its gradient as well as the volume mixing ratio of ozone, and water.

Several different definitions of the tropopause exist that are based on the dissimilar chemical and physical properties of the adjacent atmospheric layers *troposphere* and *stratosphere*. For example, the *cold point tropopause* is predicated on a physical property, the local minimum in the vertical temperature profile (e.g. Highwood and Hoskins, 1998 and therein) and often used for the investigation of the tropical tropopause. The World Meteorological Organization defines the tropopause by the vertical temperature gradient that has to undershoot a value of 2 K km^{-1} at the lowest temperature level. In addition, the definition of this *lapse rate tropopause* demands that in a range of 2 km above the tropopause level the temperature gradient does not exceed 2 K km^{-1} again (WMO, 1957). The potential vorticity (*PV*) is considered for the description of the *dynamic tropopause* and divides the UTLS-region into a regime of low PV referring to the troposphere and a regime of high PV above (Reed, 1955). The values of PV defining the frontier vary in a large range between 0.6 and 7 PVU (1 standard potential vorticity unit (PVU) = $10^{-6} \text{ K m}^2 \text{ kg}^{-1} \text{ s}^{-1}$) depending on the geographic location. In literature, the 2 PVU surface is the most common choice above which the stratospheric regime takes over (Kunz et al., 2011).

Returning to the chemical properties, the two spheres are of different chemical composition, which is evident for the comparison of the amounts of trace gases such as water vapor or ozone. Besides the oxidation of methane, stratospheric water vapor is a result of the troposphere-stratosphere-exchange. Thus, it is limited in the stratosphere and an appropriate tracer to differentiate air masses of stratospheric origin from those of tropospheric regions (Seinfeld and Pandis, 2016). Besides, ozone is also a good indicator for the detection of stratospheric air masses since it is naturally formed in the so-called *ozone layer* via photolytic decomposition of atmospheric oxygen (O_2). The solar radiation of wavelengths less than 242 nm, which is required for the photolysis process, is only available above an altitude level of approximately 30 km (Seinfeld and Pandis, 2016). Further appropriate trace gases to distinguish both regimes are carbon monoxide and dioxide, nitrous oxide, or methane. All of them originate from natural or anthropogenic emissions close to the ground and reveal stratospheric sinks.

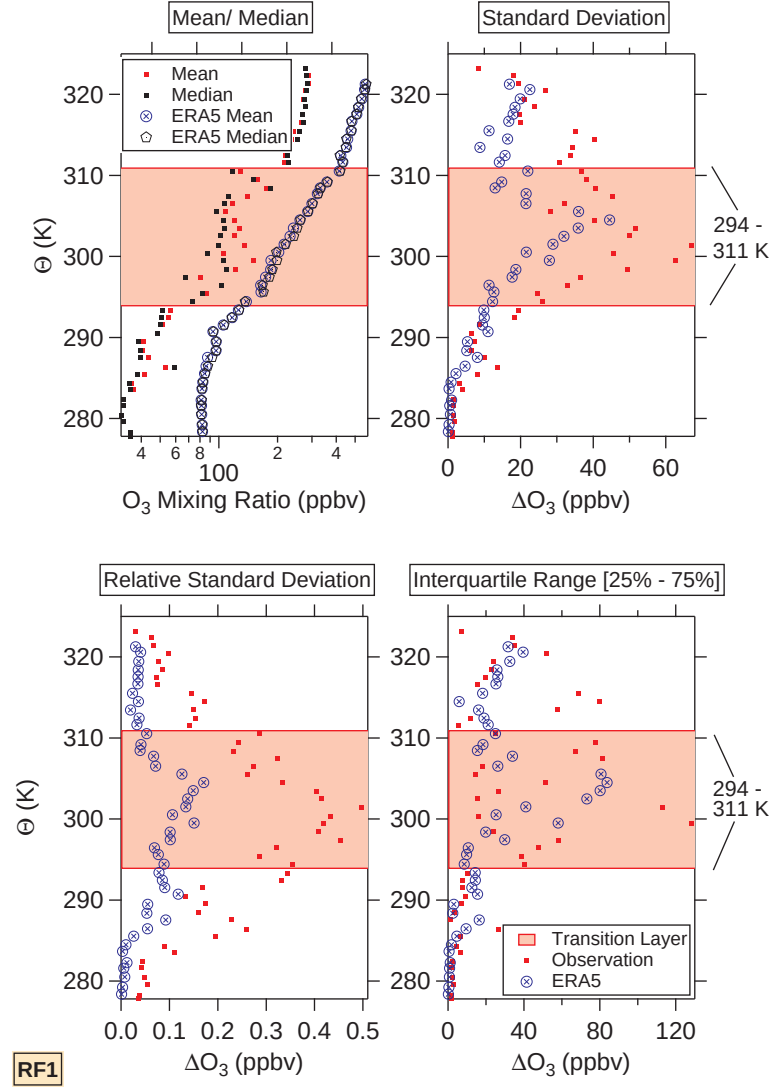


Figure 2.8: Vertical profile of the statistic parameters mean, median, and absolute standard deviation (a) as well as relative standard deviation and the interquartile range (b) of the O_3 volume mixing ratio during RF1. Red and black dots depict observational data, blue and grey circles denote ERA5 reanalysis data provided by Hersbach et al. (2018) interpolated on the flight track. The reddish area represents the 1.2 km thick transition layer between 294 and 311 K in potential temperature.

Consequently, they are in favor for the analysis of atmospheric transport and life times (Boering et al., 1996; Park et al., 2007; Seinfeld and Pandis, 2016).

In the framework of this thesis, the scanned altitude range was divided into three sections based on their chemical signatures. Of the trace gases mentioned above, the volume mixing ratio of ozone and water vapor were adopted to assess the three regimes *troposphere*, *transition layer*, and *stratosphere*. For bins of 1 K, the statistic parameters mean, median, absolute and relative standard

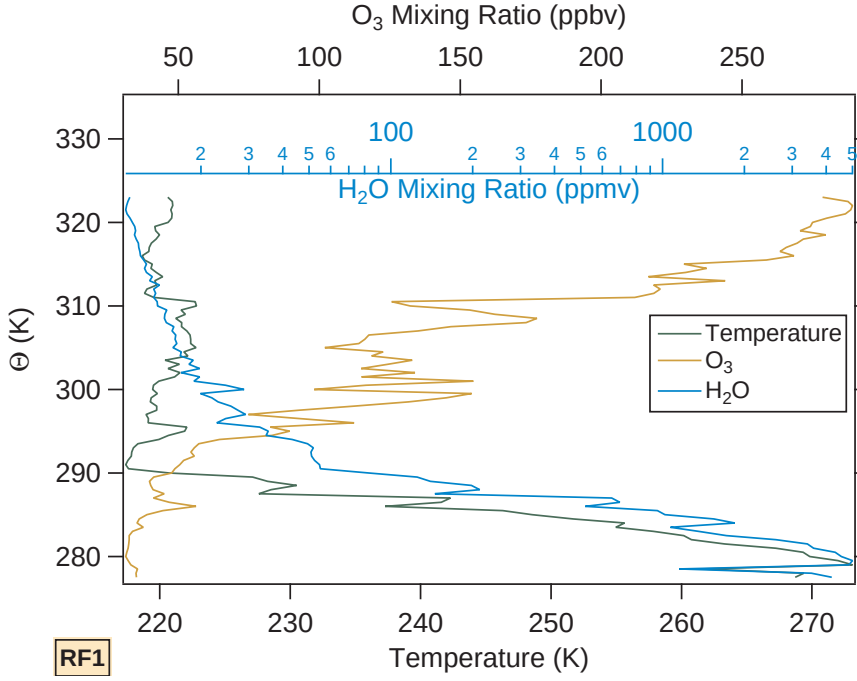


Figure 2.9: Exemplary vertical profiles of the temperature, and the volume mixing ratios of H_2O , and O_3 for RF1.

deviation, and the interquartile range (25-75%) were computed for the potential temperature Θ and the volume mixing ratio of O_3 . A plot of the vertical distribution of the statistic parameters for O_3 is provided in Fig. 2.8. The statistic parameters denote ozone values below 60 ppbv up to 294 K potential temperature, which refers to the troposphere, and a high-level sector of ozone values above 200 ppbv. This sector appears in a potential temperature range of 311 K in minimum and is attributed to the stratosphere. The section located between the aforementioned represents the transition layer (TL)¹, which exhibits characteristics of both spheres. This leads to a strong variability in the mixing ratio of ozone, as depicted by the standard deviation and interquartile range. These findings are confirmed by the vertical profile of the ambient temperature and the water vapor mixing ratio. The temperature profile in Fig. 2.9 depicts a minimum around 291 K, which marks the cold point tropopause. As well, the water vapor profile indicates a transition from a strong gradient in a θ - range between 279 K and 295 K to a moderate lapse rate higher above. Finally, the potential temperatures framing the transition region were read out for every RF in order to assign each data point to one of the predefined atmospheric regimes. The analysis of the TL for the other RFs based on recorded ozone data is provided in App. A.1.

¹ In literature, the transition layer is often referred to as *Extratropical Transition Layer* or *Extratropical Tropopause Layer (ExTL)*.

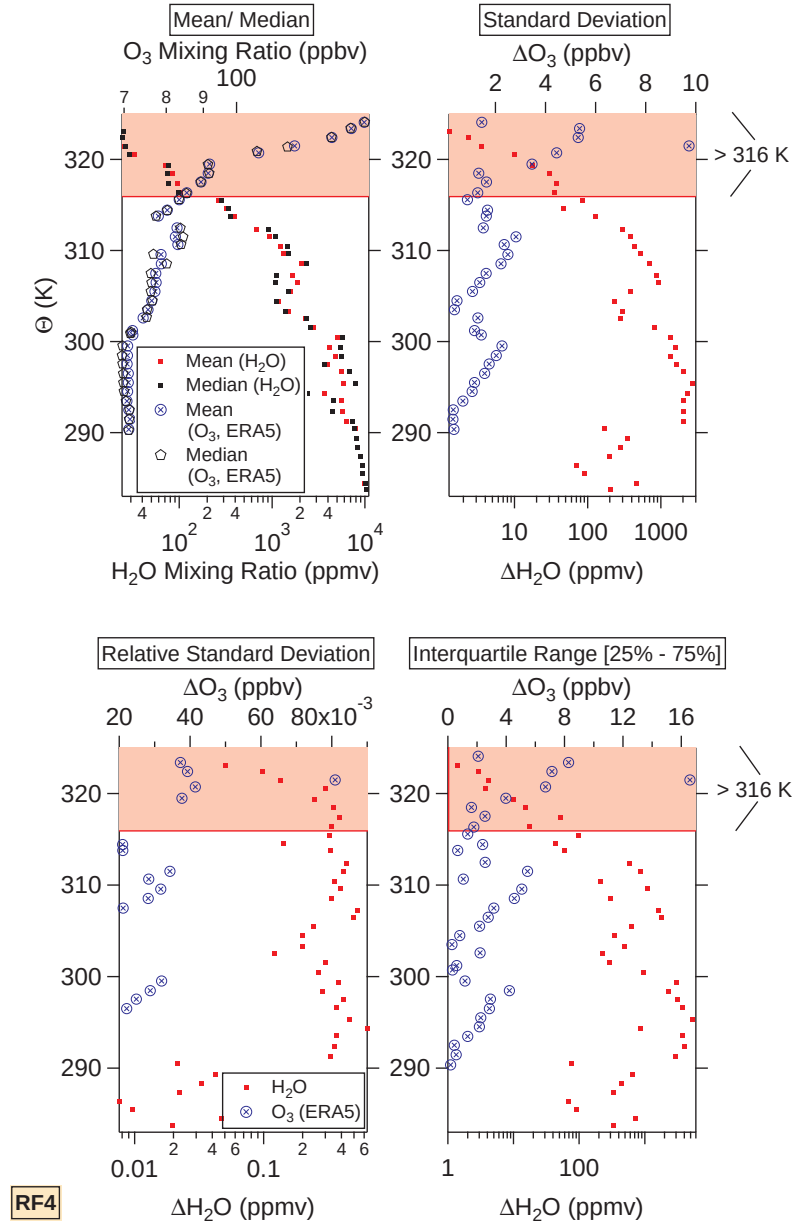


Figure 2.10: Vertical profile of the statistic parameters mean, median, absolute and relative standard deviation, and the interquartile range of the H_2O volume mixing ratio at RF4 instead of the missing O_3 data. Red and black dots depict observational data, blue and grey circles denote ERA5 reanalysis data of O_3 provided by Hersbach et al. (2018). The reddish area marks the transition layer, located above 316 K potential temperature or 9.7 km.

The reanalysis data (ERA5) of the European Centre for Medium-Range Weather Forecasts (ECMWF) provided estimates of the ozone mixing ratio along the flight path. The data were plotted additionally into the vertical profile in Fig. 2.8 and reveal a shift towards larger values of ozone throughout the atmosphere.

However, the vertical profile of the ERA5 ozone agrees on the derivation of the TL position.

Due to an instrumental issue, no ozone data were recorded on RF4. As a consequence, the data of the water vapor mixing ratio were used to estimate the lower and upper bounds of the TL. Fig. 2.10 displays the vertical profile of the statistic parameters of H_2O . With the aid of the temperature profile of RF4 and the knowledge about the position of the TL on the previous day when RF3 took place, the lower limit of the TL was determined as 316 K. The upper limit was not detectable as this altitude level was not reached during RF4.

In summary, the probed section of the atmosphere was divided into the troposphere, stratosphere, and a TL showing characteristics of both. The thresholds for the several spheres were detected by means of chemical tracers such as ozone and water vapor, and the vertical profile of the ambient temperature. The position of the TL was found to be consistent with the ERA5 ozone data estimates although the absolute values differed.

2.6 DEFINITION OF EVENTS IN ND-MAX

One aim of the ND-MAX campaign was the analysis of aircraft exhaust and its contribution to the formation on contrails at the typical cruise altitude levels in the UTLS-region. For that, the particle measurements conducted aboard the aircraft had to be divided into several periods of comparable conditions regarding the sample inlet, aircraft impact, and cloud types. The events were defined by the recorded data of complementary measurements described in Sect. 2.4. Of actually four parameters, finally three were taken into account for the definition of several events as Fig. 2.11 depicts.

The aerosol particle number concentration detected by a CPC is the major indicator for the periods of interest that differ from background conditions. It is a good measure for the tracing of aircraft exhaust plumes as the burning process of aircraft fuel in the aircraft turbines creates a large amount of soot and sulphate particles (Hendricks et al., 2004; Kärcher and Yu, 2009; Lee et al., 2009). However, the presence of clouds also implies the necessity of a second criterion. With respect to plumes, the volume mixing ratio of carbon dioxide is considered a confirming condition because CO_2 is a typical byproduct of combustion processes and thus a good indicator for aircraft exhaust (Lee et al., 2009; Bräuer et al., 2021a). For clouds, the ice particle number is counted by the FFSSP in order to distinguish between cloudy and cloud-free regimes in the atmosphere.

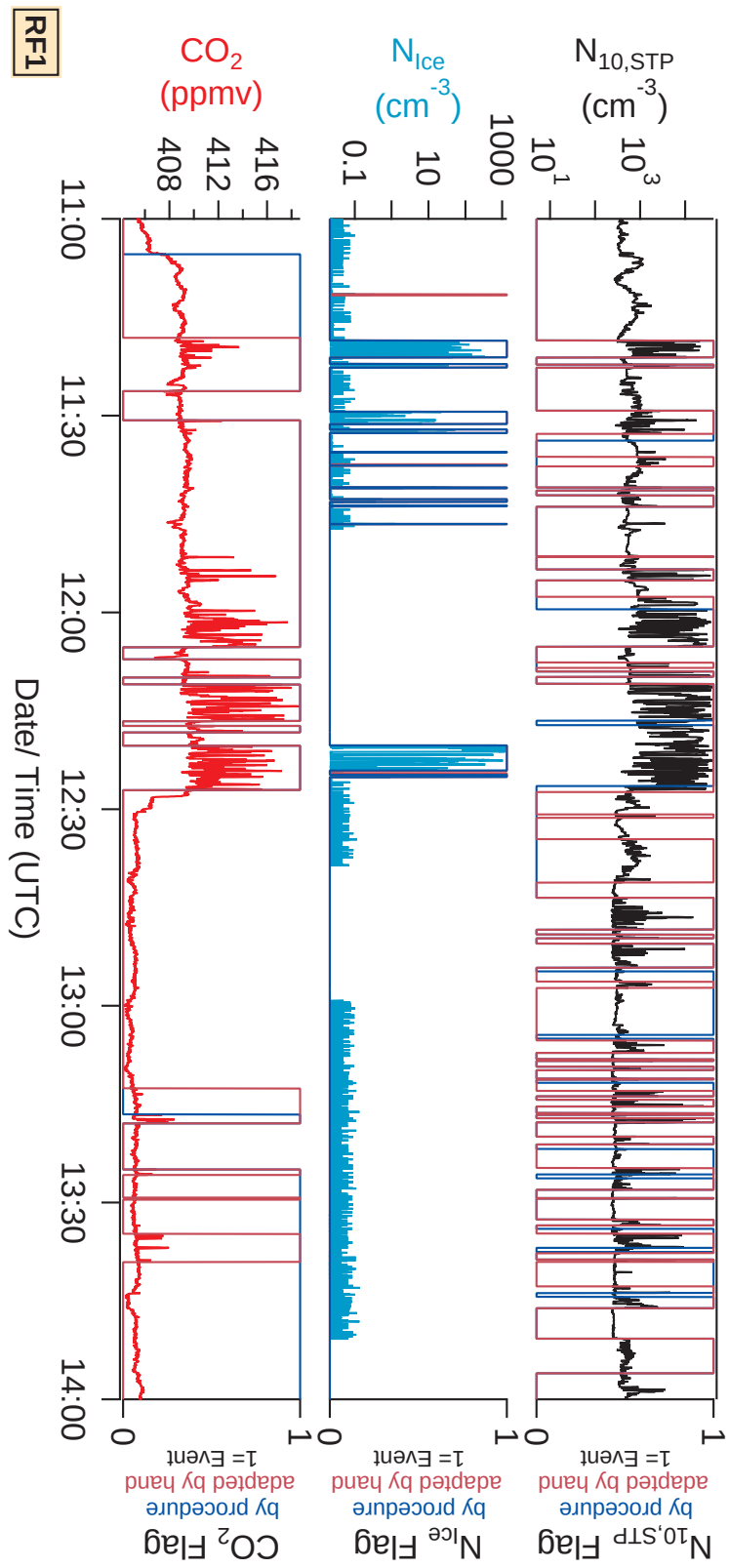


Figure 2.11: Overview of the event parameter and corresponding flags of aerosol particle event, ice particle event, and CO_2 event determined by the procedure (in blue) and manually adapted by hand (in red). The timeseries refer to RF1, January 17th 2018.

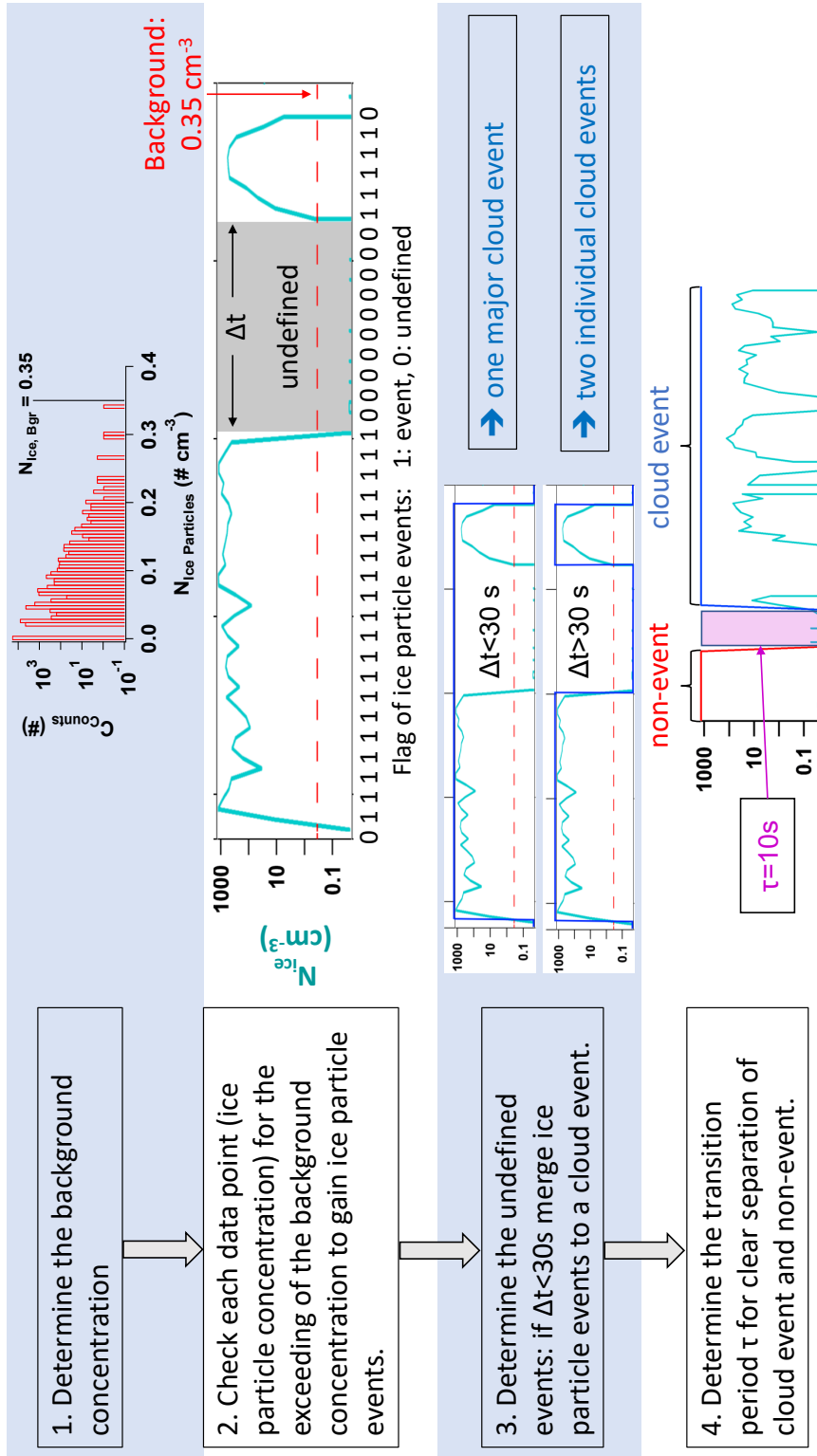


Figure 2.12: Exemplary procedure of the characterization of ice particle events and merged cloud events.

An enhanced aerosol particle concentration was observed with the CPC within cirrus and contrails. As the CPC was operated continuously at the scoop inlet, the increase in aerosol number is assumed to result from ice crystal shatter. It is likely that the ice crystals absorbed aerosol particles on their surfaces which were released when the ice crystals shattered inside the inlet tubing. Also, the number of aerosol particles was approximately one order of magnitude greater than the number of ice particles detected in cirrus and contrails, implying the presence of interstitial aerosols which have not been activated to ice crystals and, thus, were sampled via the scoop inlet. However, the processes leading to such an enhancement in aerosol number are still unclear and need further research.

For each parameter, a similar procedure was set up to capture the events of interest in a flag, denoting a 1 for an event and a 0 for an undefined state (Fig. 2.12). The term *non-event* is explicitly not used in this notation since the remaining points may be assigned as transition or non-event. The procedure starts with the determination of a background concentration. In a second step, the threshold and a corresponding condition are defined and have to be fulfilled in order to denote an event. Further properties describe the maximum length of undefined periods between two surrounding events, i.e. that the surrounding events are merged together if the time span between them is smaller than a certain period. Moreover, the transition time between the event and non-event needs to be estimated. An overview of the conditions and parameters used for the external data is provided in Table 2.4.

2.6.1 *Analysis of background periods and air mass events*

Ice particle events

The derivation of ice particle events begins with the investigation of the instrumental background noise. A major advantage of the ice particle data is the constant level of background signals due to electrical noise that is independent from altitude and pressure. It is found to be close to zero throughout the entire research campaign. In consequence, a single threshold regarding the ice particle concentration was determined for the entire campaign. This requires much less effort than the analysis of the variable background concentration of the aerosol particle number and the volume mixing ratio of CO₂ that are presented below.

Table 2.4: Comparison of routines for the determination of background concentrations of aerosol particle concentration, ice particle concentration, and CO₂ volume mixing ratio.

Parameter	N _{Ice}	CO ₂	N ₁₀
Routine	- assembly of all "background" periods - calculation of a histogram - determination of a threshold for event/non-event	- definition of discrete events - calculation of a histogram per event - generation of a fit for the background mode - determination of a threshold for event/non-event	equal to the CO ₂ routine
Differentiation between events?	no	yes	yes
Fit	/	Gaussian fit	lognormal fit
Threshold	maximum of the histogram	mean plus threefold standard deviation of the histogram fit	mean plus threefold standard deviation of the histogram fit
Start condition for the event	$N_{Ice}[i] > N_{Ice,Bgr}$	$\frac{CO_2[i]}{\overline{CO_2}(i-30, i-1)^a} > + 3 \cdot \sigma_{ref}$	$\frac{N_{10}[i]}{\overline{N_{10}}(i-30, i-1)^b} > + 3 \cdot \sigma_{ref}$
Max. length of neglected non-event periods between two surrounding events	30 s	40 s	30 s
Transition period between event and non-event periods	10 s	10 s	10 s
Further corrections by hand	events partly adapted by hand for erroneous classifications; 1 event manually added for RF7	events partly adapted by hand for erroneous classifications	events partly adapted by hand for erroneous classifications

^{a)} $\overline{CO_2}(i-30, i-1)$: arithmetic mean of CO₂ of the previous 30 s

^{b)} $\overline{N_{10,STP}}(i-30, i-1)$: arithmetic mean of CO₂ of the previous 30 s

In a first step, the timeseries of the ice particle number concentration of all eight research flights were concatenated. Periods of obviously increased

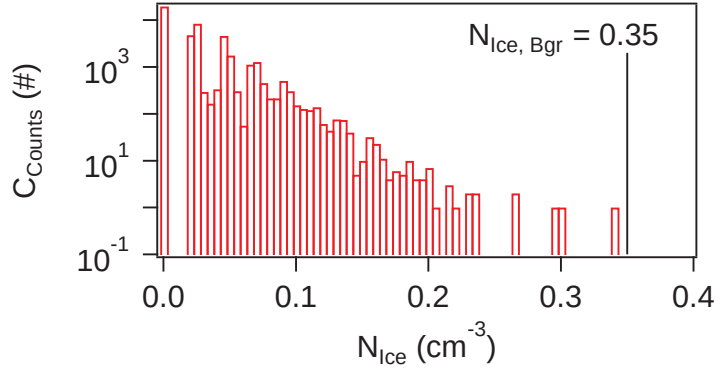


Figure 2.13: Histogram of the background ice particle concentration. C_{Counts} represents the absolute frequency of the ice particle concentration values recorded outside clouds for a bin width of 0.005 cm^{-3} . A concentration above 0.35 cm^{-3} has been classified as an ice particle event.

ice number concentrations were excluded to focus on background conditions. Second, a histogram of the merged background periods was calculated in order to determine the maximum background concentration. This is the threshold above which a data point is declared as an ice particle event. The histogram, which is based on 150 size bins of a width of 0.005 cm^{-3} , is presented in Fig. 2.13. The maximum of 0.35 cm^{-3} of the histogram's abscissa was defined as the maximum value of the ice particle background concentration $N_{Ice, Bgr}$. In a third step, this value was inserted into a routine to check each data point of the ice particle concentration for an ice particle event. If the current data point hit the threshold ($N_{Ice}[i] > N_{Ice, Bgr}$), the data point was defined as an ice particle event. As these ice particles are usually detected within clouds, they appear as an ensemble and refer to one certain cloud event. Nevertheless, these cloud events may contain single data points or even a series of up to 30 data points that are not classified as ice particle events. Such data points will be attributed to the surrounding cloud events then, and the two cloud events ahead and afterwards are merged to one event. Next, for each of the final cloud events a transition flight time period of 10s was introduced to separate the event from the previous and subsequent non-events. The data points in that transition period are neither defined as event nor defined as non-event and remain unspecified.

Despite the large accuracy of the procedure mentioned above, some events were classified erroneously and had to be corrected by hand. For RF1, the ice particle flags determined by the procedure (blue) and adapted by hand (red) are shown in Fig. 2.11. Furthermore, one event was introduced manually for RF7 (not shown). Finally, a flag of ice particle events was generated that can be combined with other event flags later on.

Aerosol particle events

The events of enhanced aerosol particle concentration were detected in a similar way to the detection of ice particle events. However, the variable background concentration complicated the characterization of the particle events because the concentration level is a complex function of the prevailing air mass, altitude, and meteorological situation. Therefore, several periods of interest were specified according to the cruise altitude, the particular legs of the research flights, and the level of aerosol particle concentration as shown in Fig. 2.14. In a second step, a histogram was plotted for each period of interest to analyze the level of background concentration and spikes due to aircraft exhaust. Fig. 2.15 displays exemplarily the mode of the background concentration and counts of enhanced aerosol number for the period of RF1 on January 17th 2018, 11:16 – 11:22 UTC. Since the aerosol number concentration is varying over orders of magnitude between exhaust plumes and undisturbed air masses, the lognormal distribution is the appropriate method to describe the distribution of the aerosol number concentration.

The lognormal fit ¹ was calculated in Igor using Eq. 2.13 (Balakrishnan and Chen, 1999). The boundary conditions were preset: a fixed value of 0 for the baseline (y_0) and an expected value (x_0) of the background mode that was given by the statistics of the measurement data:

$$f(x) = y_0 + \frac{1}{\sqrt{2\pi}\sigma x} \exp\left(-\frac{(\ln(x) - \mu)^2}{2\sigma^2}\right) \quad (2.13)$$

with the fit parameters:

$f(x)$: fit for the absolute frequency of aerosol particle concentration values (C_{Counts})

μ : expected value of the natural logarithm of x , cm^{-3}

σ : standard deviation of the natural logarithm of x , cm^{-3} .

The background mode may be expressed in terms of the mean aerosol number concentration, referred to as expectation E , and a standard deviation SD of the lognormal distribution that depend on μ and σ , the expectation and standard deviation of the normal distribution (see Eq. 2.17):

$$E = e^{\mu + \frac{\sigma^2}{2}} \quad (2.14)$$

$$SD = \sqrt{e^{2\mu + \sigma^2} \cdot (e^{\sigma^2} - 1)} \quad (2.15)$$

¹ The lognormal fit only refers to the background mode ($\sim 320 \text{ cm}^{-3} < N_{10,STP} < 600 \text{ cm}^{-3}$), not to the whole histogram.

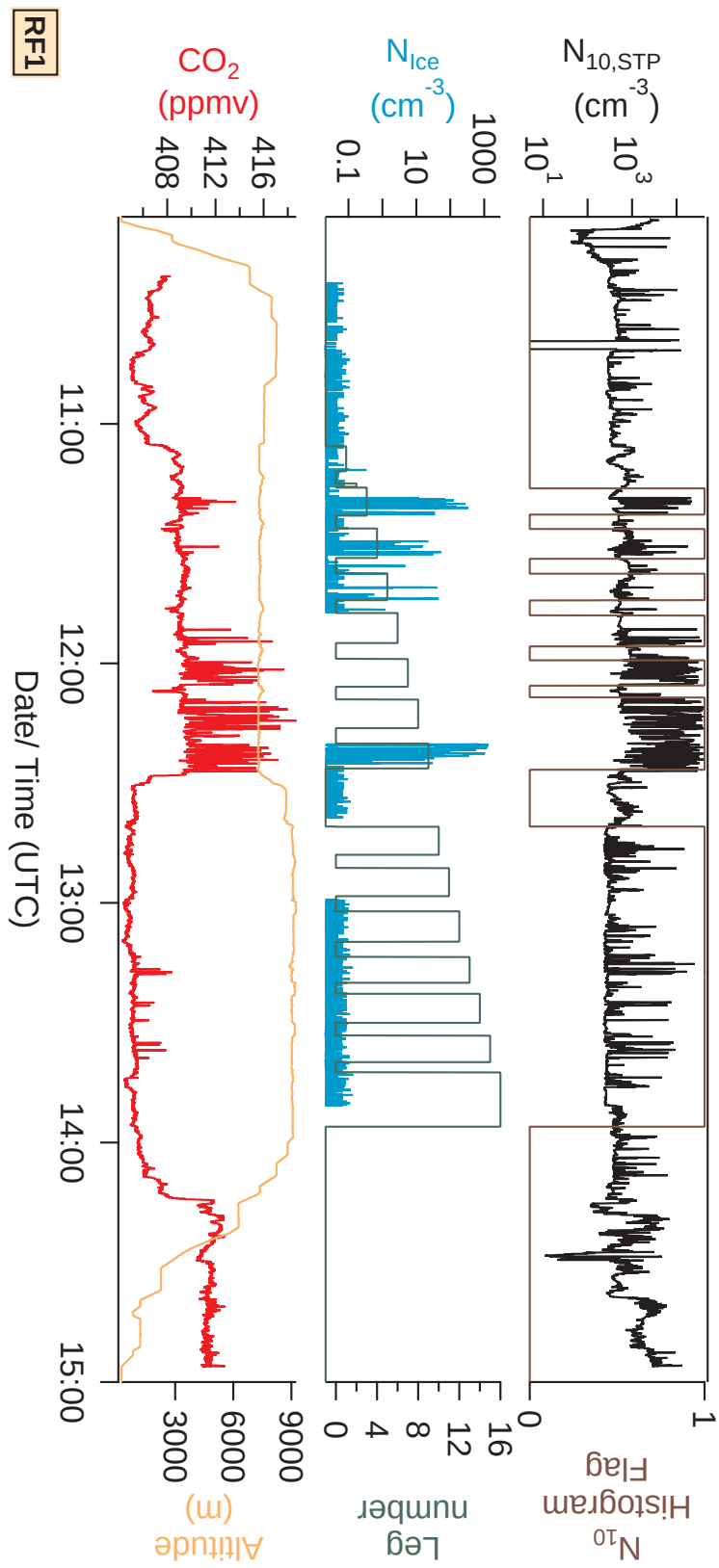


Figure 2.14: Overview of the event parameters aerosol particle number concentration $N_{10,STP}$, ice particle number concentration N_{ice} , CO_2 volume mixing ratio, cruise altitude, flight legs, and selected histogram periods for the background concentration analysis. The timeseries refer to RF1, January 17th 2018.

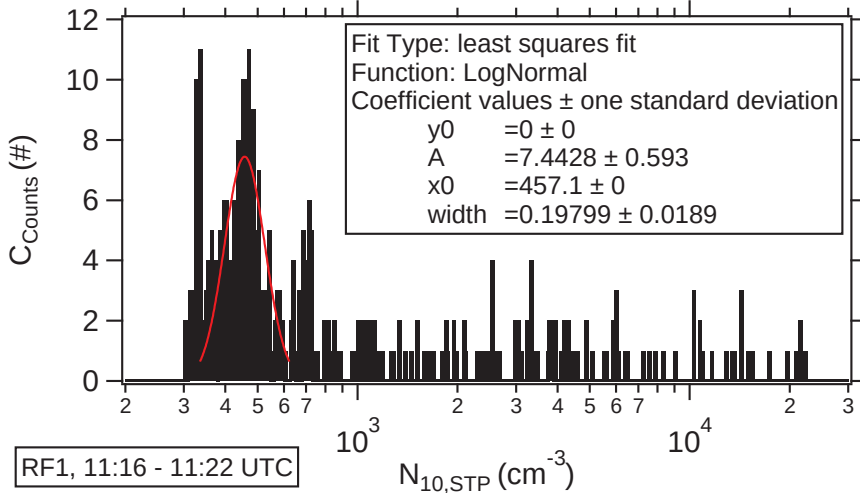


Figure 2.15: Histogram of the aerosol particle number concentration $N_{10,STP}$ for a selected period from 11:16 to 11:22 UTC on RF1 for the analysis of the background concentration. C_{Counts} illustrates the absolute frequency of the aerosol particle concentration values per equidistant bins of 0.0141 cm^{-3} .

The empirical rule in statistics states that in a normal distribution 68%, 95%, and 99.7% lie within one, two, and three standard deviations of the mean, respectively. With regard to the distribution of the aerosol particle number concentration, 99.7% of all data points belonging to the background mode are detected within three standard deviations of the expectation value of the background mode (e.g. Bevington and Robinson, 2003). Thus, the sum of both, the expectation and the threefold standard deviation was taken as the lower limit for the definition of particle events. As soon as the aerosol number concentration exceeds the expectation including the threefold standard deviation, the data point no longer seems to be of background condition and is attributed to a particle event. In detail, the current number concentration is compared to the mean concentration of the previous 30 s and the threefold standard deviation of the reference period. In case the detected concentration overshoots the mean including the deviation, a particle event starts as stated by Eq. 2.16.

$$N_{10,STP}[i] > \frac{1}{30} \sum_{n=i-30}^{i-1} N_{10,STP}[n] + 3 \cdot \sigma_{ref} \quad (2.16)$$

with σ_{ref} as the standard deviation of the reference period histogram.

Contrary, the end of the particle event is defined by the difference between the averaged concentration of the current particle event and three times the standard deviation of the reference period. If this difference is undershot, the particle event is concluded. The considered average particle concentration only includes a maximum of the last 30 s. Lastly, the particle events were transferred

into a flag that had to be corrected manually alike the ice particle flag. A comparison of both flags is provided in Fig. 2.11.

CO₂ events

The plumes of carbon dioxide were detected in the same way as the aerosol particle events. Beginning with specified time slots of interest that share similar boundary conditions for the determination of a background level of CO₂, histograms were assembled and analyzed. Using the provided information about the volume mixing ratio of carbon dioxide in the free troposphere and inside aircraft exhaust plumes, thresholds were derived to distinguish phases of increased carbon dioxide from a background mixing ratio. In contrast to the particle events, the background mode in the histogram is expressed in terms of the normal distribution (e.g. Bronstein et al., 2012) because variations in the CO₂ mixing ratio happen on a linear scale and not on log scales like the aerosols. The normal distribution is given by:

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{(x - \mu)^2}{2\sigma^2} \right] \quad (2.17)$$

with the expectation μ and the standard deviation σ .

Consequently, the background amount of carbon dioxide is described by the mean volume mixing ratio of CO₂ and its threefold standard deviation. As soon as the current mixing ratio exceeds the background, a CO₂ event starts according to:

$$CO_2[i] > \frac{1}{30} \sum_{n=i-30}^{i-1} CO_2[n] + 3 \cdot \sigma_{ref} \quad (2.18)$$

Analogously, the CO₂ event only lasts as long the current mixing ratio does not drop below the average mixing ratio of the event minus three times the standard deviation of the reference period. The flag that is produced by this procedure needs to be adapted manually as some of the events are placed mistakenly. Both flags are depicted in Fig. 2.11. The adapted flag can be combined with other flags to define the events of interest such as exhaust, cirrus or contrails.

2.6.2 *Combination of flags*

So far, the recorded measurement data were analyzed to determine periods of increased aerosol, and ice particle concentration beside the enhanced carbon

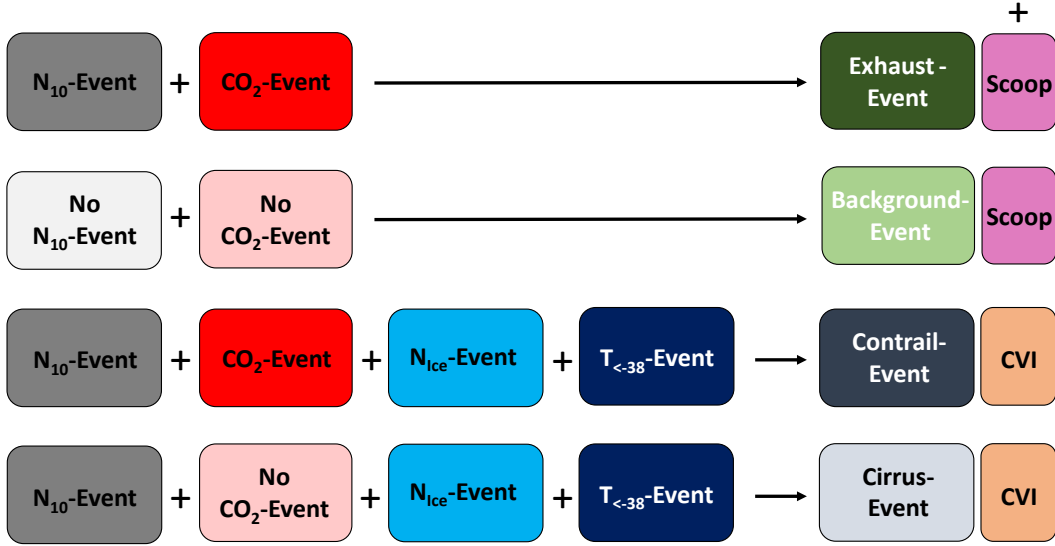


Figure 2.16: Definition of *exhaust*, *background*, *contrail*, and *cirrus* events by combination of periods of raised or background aerosol, ice particle number concentration, and CO₂ level.

dioxide volume mixing ratio. However, the focus of the dissertation lies on the analysis of aerosol particles which contribute to the cirrus and contrail formation. Thus, the events of enhanced aerosol particle concentration, CO₂ volume mixing ratio, and ice particle concentration need to be combined in order to identify the events related to aircraft emissions such as exhaust plumes and contrails as well as their counterpart, the background air and naturally formed cirrus clouds.

As mentioned in Sect. 2.6, the phases of exhaust plumes are characterized by periods of elevated aerosol number concentration and CO₂ level. Hence, a combination of both phenomena reveals a flag of *exhaust* events as depicted in Fig. 2.16. In contrast, the alignment of periods of non-elevated aerosol numbers and CO₂ concentration result in a flag denoting *background* periods. *Contrails* are defined by the same conditions as *exhaust* but they also provide an enhanced number of ice particles. In order to exclude non-ice-phase clouds in the analysis, an additional temperature condition ($T < -38^{\circ}C$) was introduced. This is due to supercooled water droplets which can only exist down to temperatures of $-38^{\circ}C$ before homogeneous freezing takes place. Finally, *cirrus* clouds are indicated by the same conditions as contrails with the exception of carbon dioxide. Since these clouds are formed in the absence of aircraft emissions, they are only characterized by a raised number of aerosol (see Sect. 2.6), and ice particles as well as the temperature criterion as with contrails. Additionally, an enhanced aerosol particle concentration was adopted as tracer.

Finally, the event flags need to be combined with the appropriate inlet flag adopted from the merged dataset of meteorological parameter and measurement data managed by Ryan Bennett and Melissa Yang-Martin (both NASA) (for data availability, see Bennett and Yang-Martin (2021)). For the cloud-free periods, the exhaust flag and background flag are combined with the flag of the scoop inlet to ensure the sampling of interstitial aerosol particles in these periods. In contrast, the cirrus and contrail flag are combined with the CVI flag in order to focus on the ice particle residuals that have already undergone the cloud processing.

2.6.3 Atmospheric conditions for contrail formation

The formation process of contrails depends on several natural and anthropogenic variables. Since contrails are formed by the isobaric mixing of aircraft exhaust plumes with ambient air, they are driven by the characteristics of both air masses. As already stated by Schmidt (1941) and Appleman (1953), contrails can appear as long as supersaturation with respect to liquid water is reached during the mixing event. The water vapor saturation in the atmosphere is controlled by the atmospheric pressure p , temperature T , and relative humidity r . Given the environmental conditions in terms of p and r along with the aircraft engine parameters, the *Schmidt-Appleman-Temperature* (T_{SA}) can be inferred. This threshold temperature ensures water vapor saturation and, thus, sufficient boundary conditions for contrail formation.

The contribution of the aircraft engines to the mixing event is determined by the emitted water vapor and heat energy. The water vapor released by the aircraft is a byproduct of the aviation fuel combustion and characterized by the emission index of water (EI_{H_2O}). It is defined as the produced mass unit of water vapor per burned mass unit of aviation fuel and has a typical value of approximately 1.23 kg kg^{-1} for kerosene. Similarly, the net heat Q is specified by the released combustion heat per mass unit of aviation fuel and is around 43 MJ kg^{-1} for kerosene (Schumann et al., 2000). The propulsion efficiency η defines the fraction of the fuel energy that is converted into the propulsion of the aircraft and is given as 0.29 (e.g. Bräuer et al., 2021a). The rest of the fuel energy is released as heat energy then.

Here, T_{SA} is derived in a short way. A more detailed derivation is provided in Schumann (1996) and Dischl et al. (2022). The isobaric mixing process between the air of the environment (of temperature T_E and water vapor partial pressure

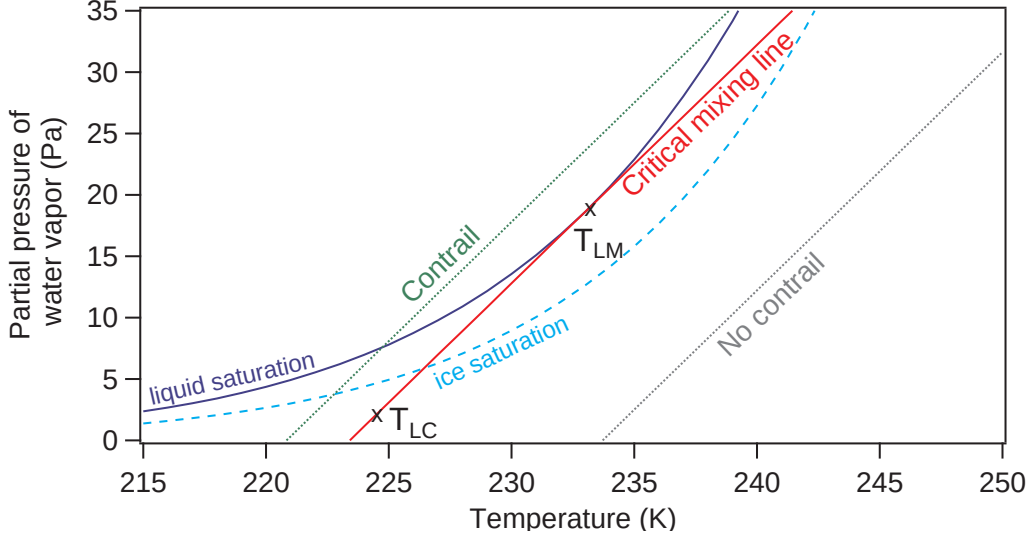


Figure 2.17: Partial pressure of water vapor vs. temperature, including saturation vapor pressure of ice (light blue) and liquid phase (blue). The critical mixing line at $p = 300$ hPa is depicted in red and defined by the tangential contact point T_{LM} with the curve of liquid saturation. Contrails form as long as the ambient temperature undershoots the threshold temperature T_{LC} , which is illustrated by the green mixing line of $T_{ambient} = 222.5$ K and relative humidity of 100%. No contrail is formed at conditions above T_{LC} (grey mixing line, adapted from Dischl et al. (2022)).

e_E) and the exhaust plume (of temperature T_P and water vapor partial pressure e_P , respectively) is described by

$$\frac{e_P - e_E}{T_P - T_E} = \frac{\Delta e}{\Delta T} = \frac{EI_{H2O} \cdot c_p \cdot p}{0.622 \cdot Q \cdot (1 - \eta)} = G, \quad (2.19)$$

where c_p is the specific heat capacity of air at constant pressure. For $T < 50^\circ\text{C}$, a constant value of $c_p \approx 1004 \text{ J kg}^{-1}\text{K}^{-1}$ may be used (Schumann, 1996). G is the slope of the mixing line along which the mixing process takes place (Fig. 2.17). In order to form contrail droplets, the mixture needs to be saturated with respect to water. Thus, the mixing line (red line in Fig. 2.17) needs a tangential contact point (T_{LM} in Fig. 2.17) with the saturation curve of liquid water (blue curve in Fig. 2.17), which is given by the relation

$$\frac{dp_L(T_{LM})}{dT} = G \quad (2.20)$$

including the saturation vapor pressure of liquid water p_L , which is provided in parameterized form by Murphy and Koop (2005):

$$\begin{aligned} p_L \approx \exp \Big\{ & 54.842763 - 6763.22/T - 4.210 \cdot \ln(T) + 0.000367 \cdot T \\ & + \tanh(0.0415 \cdot (T - 218.8)) \cdot (53.878 - 1331.22/T \\ & - 9.44523 \cdot \ln(T) + 0.014025 \cdot T) \Big\} \end{aligned} \quad (2.21)$$

This saturation curve only depends on the temperature T provided in Kelvin and is valid in a temperature range of 123 to 332 K. In order to obtain the temperature T_{LM} of the contact point, Eq. 2.20 needs to be solved numerically. Schumann (1996) published a good approximation for T_{LM} that has been verified later on by Ferrone (2011) for its low absolute errors and is also used here:

$$T_{LM} = -46.46 + 9.43 \cdot \ln(G - 0.053) + 0.720 \cdot [\ln(G - 0.053)]^2 \quad (2.22)$$

With the knowledge about the contact point T_{LM} (Eq. 2.22), the slope G (Eq. 2.19), and the parity of the partial and saturation pressure of liquid water at T_{LM} , the e-axis intercept e_0 of the mixing line can be derived as:

$$e_0 = e(T_{LM}) - G \cdot T_{LM} = p_L(T_{LM}) - G \cdot T_{LM} \quad (2.23)$$

Finally, the mixing line is determined and T_{LC} can be inferred. Following the convention in Schumann (1996), the Schmidt-Appleman Temperature can be calculated by:

$$T_{LC} = \frac{e_{ambient} - e_0}{G} \quad (2.24)$$

T_{LC} provides a complex but useful measure to prove the atmospheric boundary conditions for the potential of contrail formation. As soon as the ambient air is mixed into the exhaust plume, and supersaturation with respect to water is approached, contrail droplets can form. Due to environmental temperatures below -38°C , the droplets tend to freeze to ice crystals homogeneously. Since the saturation pressure of ice is lower than that of liquid water (light blue and blue curve in Fig. 2.17), the ice crystals persist while the air is supersaturated with respect to ice. Therefore, the persistence of contrails is already provided by saturation in the ice phase. A second threshold temperature ensuring the saturation concerning the ice phase can be derived analogously in order to provide assurance of the contrail persistence.

2.7 AIR MASS ANALYSIS

The analysis of the air mass history is essential for the interpretation of aerosol particle measurements as it provides information about their potential sources and origin. In this study, the *Hybrid Single-Particle Lagrangian Integrated Trajectory Model* (HYSPLIT), developed by the American NOAA and Australia's Bureau of Meteorology, was applied for the simulation of backward trajectories along the flight track. In general, the tool is applicable for backward and forward trajectories in order to study the advection of air masses and the transport of

aerosol particles over long distances (Draxler and Hess, 1998; Fleming et al., 2012). The calculation of the advection is based on the following Eq. (2.25):

$$\vec{P}(t + \Delta t) = \vec{P}(t) + 0.5 \left[\vec{v}(\vec{P}, t) + \vec{v} \left(\left\{ \vec{P}(t) + [\vec{v}(\vec{P}, t) \cdot \Delta t] \right\}, t + \Delta t \right) \right] \cdot \Delta t \quad (2.25)$$

where $\vec{P}(t + \Delta t)$ is the final position of the air parcel or aerosol particle, $\vec{P}(t)$ is the initial position, and $\vec{v}(t)$ is the average of the three-dimensional velocity (Draxler and Hess, 1998; Stein et al., 2015).

Besides the calculation of simple air parcel trajectories, the HYSPLIT model has been used in the simulation of dispersion, chemical transformation, and the deposition of pollutants and hazardous materials (Stein et al., 2015; Rolph et al., 2017 and therein).

In the framework of this study, the HYSPLIT model ran in the latest desktop version (v5.2.1) with a set of operational data from the *Global Data Assimilation System* (GDAS) of the American National Centers for Environmental Prediction (NCEP). The dataset has a horizontal resolution of $0.5^\circ \times 0.5^\circ$ and consists of 55 vertical hybrid sigma-pressure levels. The meteorological data were provided on a regular base of three hours and contain the wind components (u, v, and w), temperature, specific moisture, and the pressure at ground level (NOAA-ARL, 2024). For every RF, the trajectories were calculated beginning with the GPS position of the NASA DC-8 and traced back up to 10 days in the past. This resulted in a total of 2670 trajectories and 240 time stamps per trajectory. The aircraft position can be regarded as the test site of air masses of variable origins and the suspended aerosol particles therein.

The contribution of predefined regions to the air mass characteristics and chemical signature of aerosol particles is of particular interest. Therefore, the northern hemisphere was divided into 14 regions as illustrated in Fig. 2.18. Besides the Arctic, four oceanic sectors and nine continental areas were defined as potential source regions. In a second step, the trajectory points reaching the BL were summed up per source region and their relative contribution to the air masses detected along the flight track was analyzed for each of the three prevailing weather periods (see Sect. 4.1.3).

The HYSPLIT model reveals an irregular behavior at the boundary areas which have to be excluded from the interpretation. First, backward trajectories starting below 50 m a.s.l. tend to stay in the boundary layer and touching the ground. As this behavior does not express a realistic scenario, those trajectories are neglected for further analysis. Next, trajectories reaching back to the lowermost 50 m above the ground for a time frame of more than 12 hours are terminated and not traced back any longer because they adapt to the properties of the BL

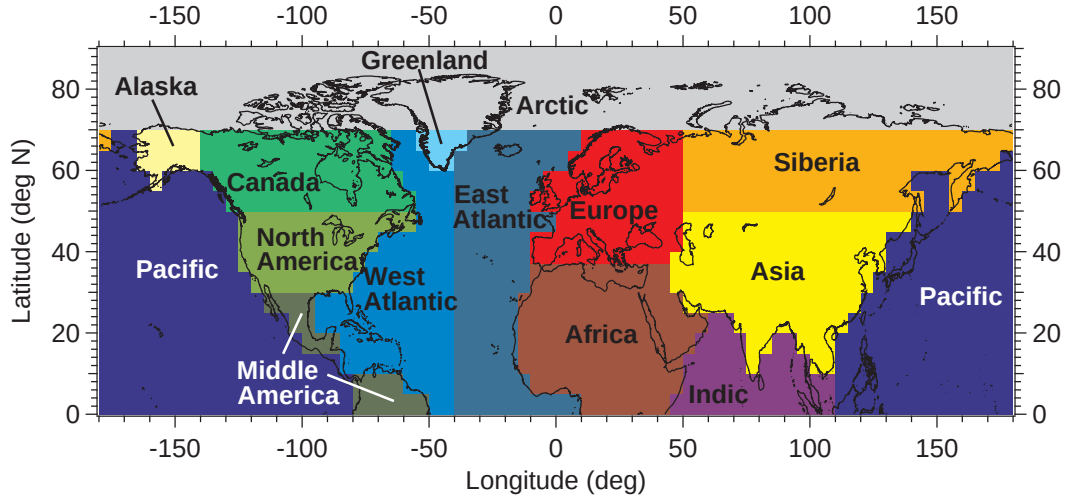


Figure 2.18: Map of potential source regions for backward HYSPLIT air mass trajectories during ND-MAX.

they have passed before reaching the test site. Third, trajectories that never crossed the BL do not provide any information about the air mass origin and particle source and are, thus, disregarded.

Another issue is the backward propagation of trajectories above an altitude level of 20 km, and thus out of the modelling area. In fact, 0.94% of the already filtered trajectories left the model frame, especially during the days of warm period, which are actually attributed to ascending, low-level air masses. As the GDAS data of 0.5° horizontal resolution do not provide a vertical velocity to the HYSPLIT model, the vertical movement is calculated from the divergence, resulting in a strange behavior of a certain fraction of trajectories. In consequence, the dataset of a horizontal resolution of 1° (GDAS1) was applied to the HYSPLIT model to overcome the issue of backward propagation out of the model frame. This dataset provides data of vertical velocity and was assumed to create a more realistic scenario of air mass trajectories. Indeed, the number of trajectories calculated upon this dataset show a smaller fraction of trajectories running towards the stratosphere. Yet, the backward propagation of trajectories failed at the model boundaries. The trajectories bounced into the model frame, were reflected and remained in the UTLS-region, which does not agree with reality. In addition, the number of trajectories that can be attributed to individual source regions, is limited compared to those calculated with GDAS 0.5 data. This results in less favourable statistics. In detail, the contribution of source regions underlies a lower resolution, and the vertical profile of air mass origins provides less information due to a lack of reliable statistics. In conclusion, the analysis of air mass history was conducted using GDAS 0.5 data and neglecting those trajectories that leave the model frame during backward

propagation. Also, the mentioned caveats have been carefully considered for the analysis of the ND-MAX data.

CAMPAIGN AND METEOROLOGICAL OVERVIEW

3.1 AIRCRAFT-BASED ND-MAX CAMPAIGN 2018

The aerosol data analyzed in the framework of this thesis were recorded during a collaborative campaign between the US American *National Aeronautics and Space Administration* (NASA) and the German aerospace center (*Deutsches Zentrum für Luft- und Raumfahrt*; DLR). The ND-MAX campaign (ND-MAX: NASA/ DLR Multidisciplinary Airborne eXperiments) was part of the “Emission and Climate Impact of Alternative Fuels” project (ECLIF2). The airborne field experiments of ND-MAX were conducted out of the US and NATO *Air Base Ramstein* close to Kaiserslautern in Rhineland-Palatinate (LeClercq et al., 2022). The goal was to investigate the effects of alternative fuel blends on aircraft soot emissions and their impact on climate-relevant properties of the resulting contrail cirrus clouds (Voigt et al., 2021).

Two aircraft were involved in the airborne research campaign: the DLR Advanced Technology Research Aircraft (DLR-ATRA) was fueled with various mixtures of the standard kerosene type Jet A-1 and bio-based alternative jet fuel (Voigt et al., 2021). The DLR-ATRA and its exhaust plume and contrail, was "chased" by the aircraft NASA DC-8 that contained a large set of physico-chemical aerosol analysis instruments, several trace gas measurements, and basic meteorological parameters. Both aircraft were equipped with instruments for the detection of several engineering aircraft parameters such as Mach number, fan speed, fuel flow, fuel temperature, and engine inlet temperature. Additionally, meteorological and geophysical variables including pressure altitude, temperature, wind speed and direction as well as potential temperature were logged at a frequency of 1 Hz.

In total, eight research flights (RFs) were conducted between January 17th and February 1st 2018 (see App. B.1). The majority of more than 44 flight hours took place in two restricted air space areas over Northern Germany close to the seaside (LeClercq et al., 2022) at three distinct flight levels of 26000, 32000, and 38000 ft (approximately 7900, 9800, and 11600 m). As the flight map in Fig. 3.1 shows, the first flights (RF1 to RF4) were located over Mecklenburg-West Pomerania close to the Baltic Sea. The tracks of the following flights including RF4 ranged from Lower Saxony up to Schleswig-Holstein along the North

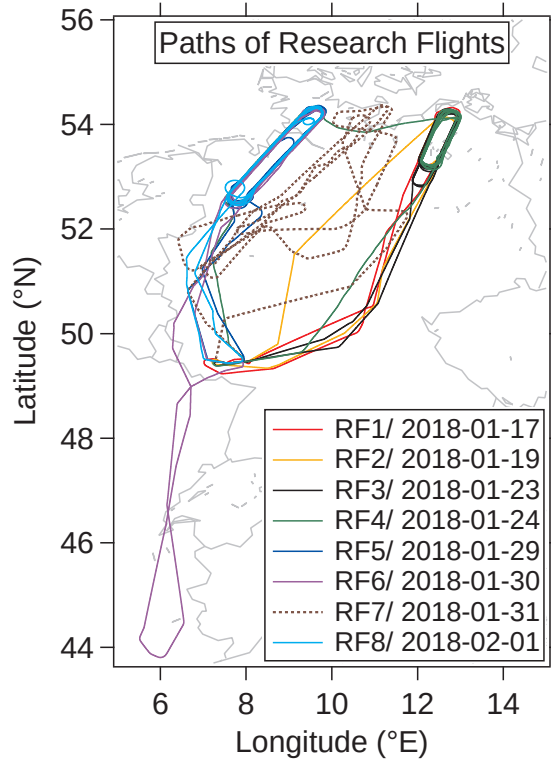


Figure 3.1: Map of all eight research flights during ND-MAX. The solid lines (differentiated by color) demonstrate flight paths when following the DLR-ATRA. The dotted line depicts the particular chase flight of civil aircraft on January 31st 2018. The two elongated, oval flight pattern over North-Germany represent the two restricted air space areas.

Sea. RF7 is the only flight not sampling the exhaust plume of the DLR-ATRA. Instead, the NASA DC-8 *Flying Laboratory* trailed several commercial passenger aircraft in order to determine their emissions and impact on contrail formation including its properties (LeClercq et al., 2022).

A further goal was to sample aerosol particles and trace gases in the UTLS region over Germany. In more detail, the local tropopause level ranged between 7.7 and 12.0 km due to the northern hemispheric winter season and the temporal weather situation during ND-MAX (see Sect. 3.3). Thus, the recorded data allow for an analysis of the background particle chemical composition and its contribution to the formation of cirrus and contrails.

3.2 RESEARCH AIRCRAFT AND POWER FUEL TYPES

Research aircraft

The airborne research campaign based on two distinct research aircraft. The DLR-ATRA is a state-of-the-art Airbus A320-232 equipped with International Aero Engines IAE V2527-A5. The DLR-ATRA has a maximum speed of 840 km h^{-1} and a maximum flight level of 39000 ft (approx. 11900 m). As the largest aircraft of the DLR, it is deployed for wake vortex research, airflow noise measurements, and engine measurements among other research topics. Aircraft data are recorded by the implemented basic measurement system (DLR, 2016, 2023). During ND-MAX, the DLR-ATRA flew up to altitudes of 38000 ft ($\approx 11500 \text{ m}$) in a ground speed range of approximately $180 - 262 \text{ m s}^{-1}$.

The NASA DC-8-72 is a highly modified McDonnell Douglas DC-8 jetliner, which is used as a flying science laboratory (NASA, 2008). It is powered by four CFM International engines CFM56-2-C1 and reaches a true air speed of 450 kts (roughly 835 km h^{-1}) in maximum above an altitude of 30000 ft ($\approx 9100 \text{ m}$). The maximum altitude level is at 42000 ft ($\approx 12800 \text{ m}$) and can be held for up to 12 hours. For ND-MAX, the NASA DC-8 flew in a ground speed range of $137 - 294 \text{ m s}^{-1}$. Besides research studies of the Earth's surface and atmosphere, the aircraft also participates in missions of sensor development, satellite sensor verification, and space vehicle launch or re-entry telemetry data retrieval and optical tracking (Conner, 2023).

Power fuel types

One of the major goals of this campaign was the investigation of aircraft emissions regarding carbon dioxide and particulate matter for several fuel types. As a consequence, the source aircraft DLR-ATRA burned two fossil reference kerosenes (Jet A-1) and three blends with the renewable fuel component HEFA-SPK (Hydroprocessed Esters and Fatty Acids Synthetic Paraffinic Kerosene) during the chase with the NASA DC-8. The naphthalene and aromatic content of the fuel and the corresponding fuel hydrogen content were chosen to be variable in order to analyze its effect on non-volatile particle number and mass emissions (Schripp et al., 2022), as well as ice particle formation in contrails (Voigt et al., 2021). The aviation fuel consists to a large degree of aliphatic hydrocarbons known for their chain structure and aromatic hydrocarbons featuring a cyclic structure. Aromatic rings need higher energies for oxidation and fragmentation, and have been identified as major soot precursors (Lobo et al., 2011; Brem et al., 2015; Voigt et al., 2021).

Table 3.1: Properties of fuels burned during the ND-MAX experiments (adapted from Voigt et al., 2021)

ECLIF Fuels	Ref3¹	Ref4¹	SAF1	SAF2	SAF3
Fuel com- position	100% Jet A-1	100% Jet A-1	51% Ref3+ 49% HEFA ²	70% Ref4+ 30% HEFA	49% Ref3+ 34% Ref4+ 17% HEFA
Aromatics (vol%)	18.6 (± 2.5)	16.5 (± 2.5)	8.5 (± 1.5)	9.5 (± 1.5)	15.2 na ³
Naphthalenes (vol%)	1.17 (± 0.06)	0.13 (± 0.02)	0.61 (± 0.04)	0.045 (± 0.01)	0.64 na
Hydrogen content (mass%)	13.65 (± 0.05)	14.08 (± 0.18)	14.4 (± 0.07)	14.51 (± 0.04)	14.04 na
H:C ratio ⁴	1.88 (± 0.01)	1.95 (± 0.01)	2.00 (± 0.02)	2.02 (± 0.01)	na na

¹ Ref3, Ref4: Reference fuel, standard kerosene Jet A-1. The nomenclature refers to the reference fuels used throughout the ECLIF campaigns.

² HEFA-SPK: Hydroprocessed Esters and Fatty Acids Synthetic Paraffinic Kerosene

³ not available

⁴ Hydrogen:Carbon ratio

In contrast to aliphatic hydrocarbon chains of high hydrogen to carbon ratios ($\text{H:C} \sim 2 : 1$), the aromatic molecules exhibit a H:C -ratio of $\sim 1 : 1$. Consequently, the hydrogen content or ratio is a suitable measure to estimate the sooting tendency of a fuel (Cain et al., 2013; Schripp et al., 2018; Voigt et al., 2021). Naphthalenes are bi-cyclic aromatic hydrocarbons and their role in soot formation is a matter of current research (Schripp et al., 2018; Voigt et al., 2021). The fuel composition regarding aromatic, naphthalene, and hydrogen content is listed in Table 3.1.

3.3 METEOROLOGICAL CONTEXT

Meteorological conditions were found to play a major role for the presence of individual particle types during the ND-MAX campaign, and thus, had an impact on the chemical composition of aerosol particles in the UTLS region.

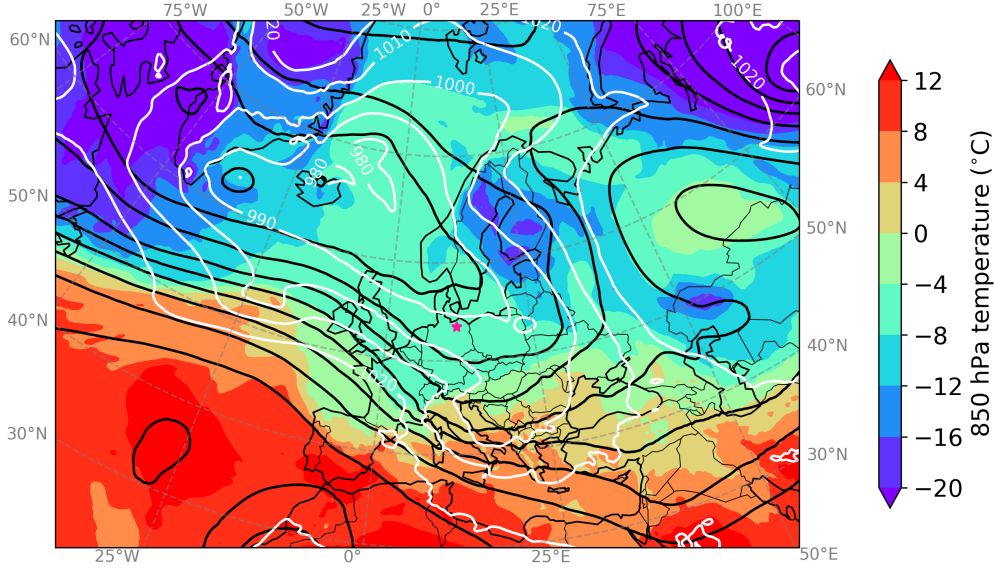


Figure 3.2: Weather map of 17th January 2018, 12:00 UTC including isohypses (black lines) at 500-hPa-level and mean sea level pressure (white lines). The color-coding refers to ambient temperatures at the 850-hPa-level and denotes the distribution of warm and cold air masses. The red star denotes the area used for RF1. Plotted with ERA5-data provided by Hersbach et al. (2018).

The vertical profile of different aerosol types is partly affected by the dominating weather pattern. During the ND-MAX campaign, three prevailing air mass periods and corresponding meteorological systems were observed, which are depicted in the following subsections.

3.3.1 Cold air mass period

A cold air mass period affected the Research Flights 1, 2, and 8. The average meteorological conditions were characterized by a center of a low pressure system over Northern Europe, a frontal zone which had already passed the measurement region, and a sector of cold, descending air masses around the flight area that lead to a subsidence of the local tropopause. As an example for the post-frontal pattern, the meteorological conditions of RF1 are described in detail here. The meteorological conditions of RF2, and RF8 are introduced in the appendix (see App. B.2).

RF1 was characterized by a large high-level trough over Northern Europe ranging from Greenland to the Baltic Sea. Located at the south flank of the low-pressure system, the flight region was affected by the advection of moist, and cold air masses from subpolar regions, which is indicated by the northwesterly

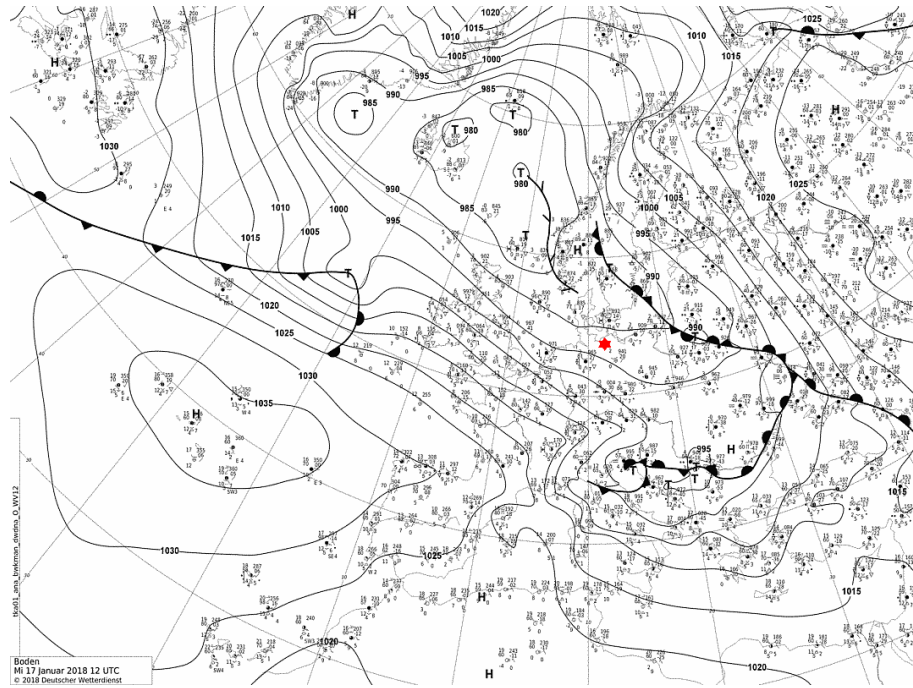


Figure 3.3: Synoptic weather map of German Weather Service (Deutscher Wetterdienst; DWD) of 17th January 2018, 12:00 UTC. The map provides an overview over the pressure systems and corresponding fronts in Europe. Thin black lines depict the location of isobars and pressure systems, 'H' (H: Hoch, engl.: High) and 'T' (T: Tief, engl.: Low) mark the center of high-pressure and low-pressure systems, respectively. Bold lines reveal the position of fronts (semicircles: warm front; triangles: cold front). The red star denotes the area used for RF1. Adapted from wetter3 (2018).

atmospheric circulation along the isohypses (black lines) and isobars (white) in Fig. 3.2. Consequently, the temperatures at 850 hPa-level ranged between -4 and -8 °C.

The region of interest was placed at the back of a small secondary depression over Poland and the appendant front that reached from Norway to the Black Sea (Fig. 3.3). Hence, this region belonged to the cold air sector, which was dominated by a well-mixed boundary layer (BL), low-level tropopause, and a westerly circulation. The wind data of the synoptical weather stations agreed with the air mass circulation typically known for post-frontal weather conditions. Fig. 3.4 shows the vertically-resolved meteorological parameters as well as trace gases and particle number for the first period. The detected wind direction ranged between 260 and 300 °, which could be referred to west to northwest winds and, thus, confirms the wind data of the synoptical stations.

The well-mixed BL was indicated by a nearly constant potential temperature in the lowermost 2 km and above (Fig. 3.4). This was confirmed by the vertical temperature profile that denoted a continuous decrease and no temperature

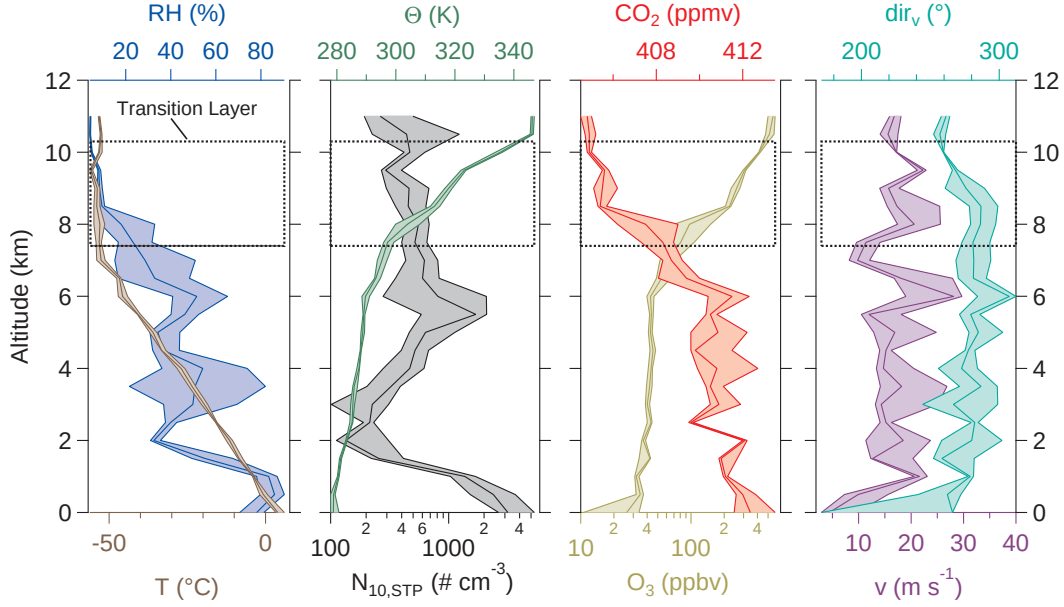


Figure 3.4: Vertical profile of meteorological parameters as measured by the NASA DC-8 (RH: Relative Humidity, T: Temperature, Θ : Potential Temperature, v: Wind Speed, dir_v : Wind Direction) (provided by Melissa Yang-Martin, NSRC), volume mixing ratios of O_3 , and CO_2 (provided by Hans Schlager, DLR), and aerosol particle number concentration ($N_{10,STP}$) (provided by Christiane Voigt, DLR) for cold air mass period during RF1, RF2, and RF8. Median and interquartile range are shown. The black box denotes the Transition Layer.

inversion. Furthermore, the level of CO_2 was only slightly enhanced in the BL (412 ppmv) compared to the free troposphere (FT) (410 ppmv) and the particle number concentration exceeded those of the FT by one order of magnitude (~ 1000 vs $\sim 100 \text{ cm}^{-3}$). The wind speed increased between 500 m and 1 km and implied the entrainment of air masses from above into the BL.

The weakening of the negative temperature gradient at a level of approximately 7 km implied a low-level tropopause. The relative humidity approached a minimum below 10% at an altitude of 8.5 km and the Θ -profile revealed an enhanced rise in potential temperature above 7.5 km. Moreover, the trace gases CO_2 and O_3 also pointed out the transition region from tropospheric conditions towards stratospheric conditions just above 6 km in altitude: CO_2 decreased then from values around 411 ppmv down to values below 405 ppmv, whereas O_3 increased from tropospheric conditions around 40 ppbv to lowermost stratospheric conditions larger than 100 ppbv.

Cloud conditions on RF1 were mainly driven by the secondary cyclone over Poland. The abundance of stratus clouds which were related to the front was replaced by single cumulus clouds rising across the North Sea. This implied an increasing unstable stratification of the troposphere (see Fig. 3.5). However,

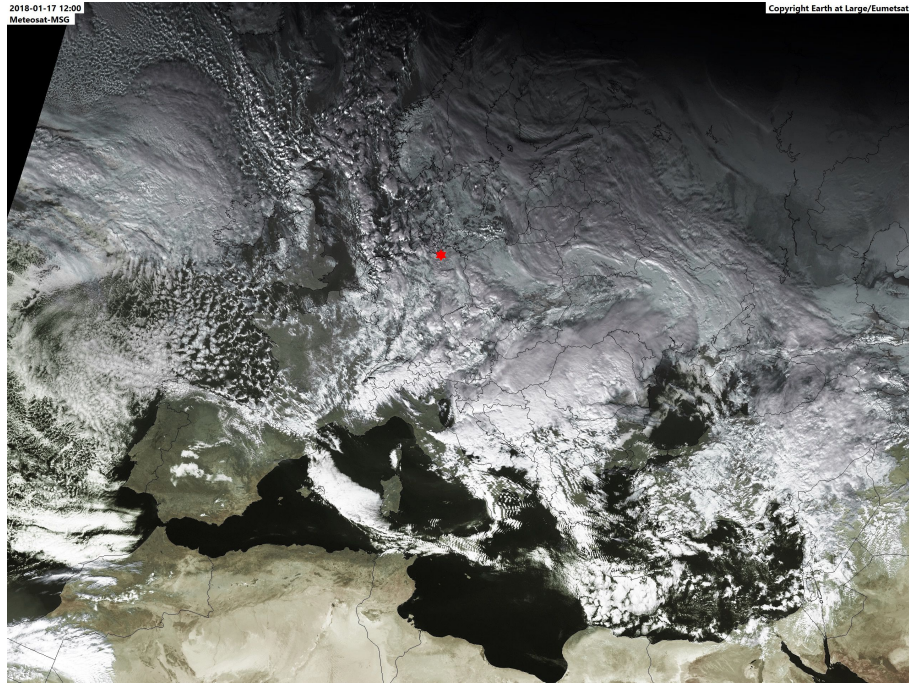


Figure 3.5: Satellite image of EUMETSAT of 17th January 2018, 12:00 UTC, Meteosat Second Generation, VIS-Channel $0.6\ \mu\text{m}$. The image shows the cloud coverage over Europe and the unstable stratification (indicated by convection) in the vicinity of the flight region. The red star denotes the area used for RF1. Adapted from Valk (2018) with permission from EUMETSAT.

there were no thunderstorms active within the flight hours over Central Europe, implying the absence of cumulonimbus-related cirrus, as indicated by Wanke (2024). Although the weather conditions did not favor the formation of cirrus and contrails, a calculation of the Schmidt-Appleman-Temperature (Fig. 3.6) revealed a potential for the formation of contrails. This was probably due to aircraft cruise altitudes close to the tropopause, which were in favor of cold air masses and supersaturation in plume mixing events.

The air mass history was analyzed by using backward trajectories for a time-frame of 10 days along the flight path derived with the HYSPLIT-model (see Sect. 2.7). For each of the trajectories approaching the aircraft, the calculated trajectory points inside the BL were sorted in bins according to the source region and their fraction was plotted in Fig. 3.7. The major contribution of marine air mass origins referred to the East Atlantic throughout the entire troposphere (Fig. 3.7a). Small fractions were attributed to the West Atlantic, and above an altitude level of 7 km, small fractions were traced back to the Pacific. Continental air mass origins were also covered throughout the whole troposphere. The major part could be linked to North America, whereas small fractions were assigned to Canada. Below 3.5 km, the fraction of European air

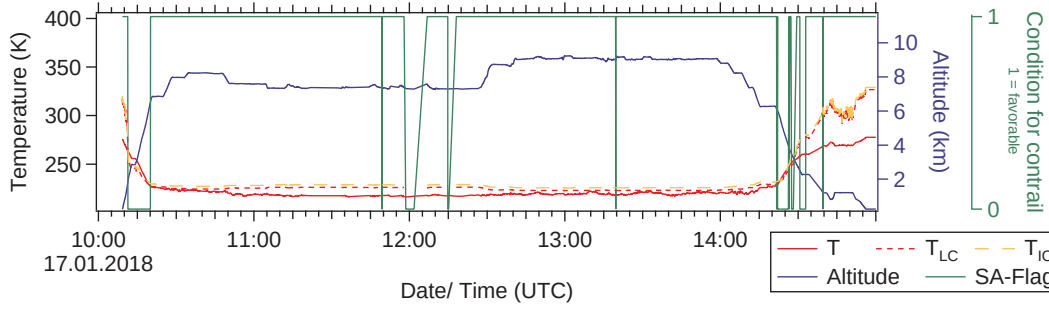


Figure 3.6: Ambient temperature (red), flight level (blue), the Schmidt-Appleman-Temperatures for contrail formation (T_{LC} , red, short-dashed) and persistence (T_{IC} , orange, long-dashed) as a function of time (RF1). The green line marks the legs on which contrails can form and persist, i.e. where both thresholds are underpassed. During RF1, the aircraft passed regions providing appropriate conditions for the formation and persistence of contrails.

masses was continuously rising up to a quarter, implying the impact of the local BL. The influence of ice-covered regions was only noticed during the cold air period: trajectories coming from the Arctic BL were observed between 1.5 and 10 km. Along the entire altitude range, fractions below 5% could be traced back to Greenland, and at 10 km air masses of Alaskan origin were observed.

The large number of trajectories of Canadian origin in the lowermost altitude bin was unexpected. This could be the result of descending air masses driven by the meteorological conditions that promoted a downward mixing into the BL. However, the contribution of 13% of Canadian air masses in the lowermost bin was quite large compared to the Canadian impact at all. This was probably related to the low number of trajectories and according trajectory points at all and has to be considered with caution.

In summary, RF1 was under the influence of a high-level trough over Northern Europe along with a secondary cyclone over Poland. Due to its post-frontal location, cold maritime air masses of Atlantic origin were advected from the northwest (e.g. Arctic, Atlantic, Canada) leading to subsidence and a low-level tropopause. The strong circulation promoted the entrainment of air masses from the FT into the BL resulting in a smooth changeover between both layers. The sky was covered by stratus and cumulus clouds, of which the latter implied an unstable stratification. Despite the lack of cirrus clouds, which actually form under the same atmospheric conditions as contrails, the Schmidt-Appleman-Temperature exhibited appropriate conditions for contrail formation along the flight track. Indeed, contrails were detected along the flight path of RF1. Trajectories of European origin were detected mainly below 4 km, implying

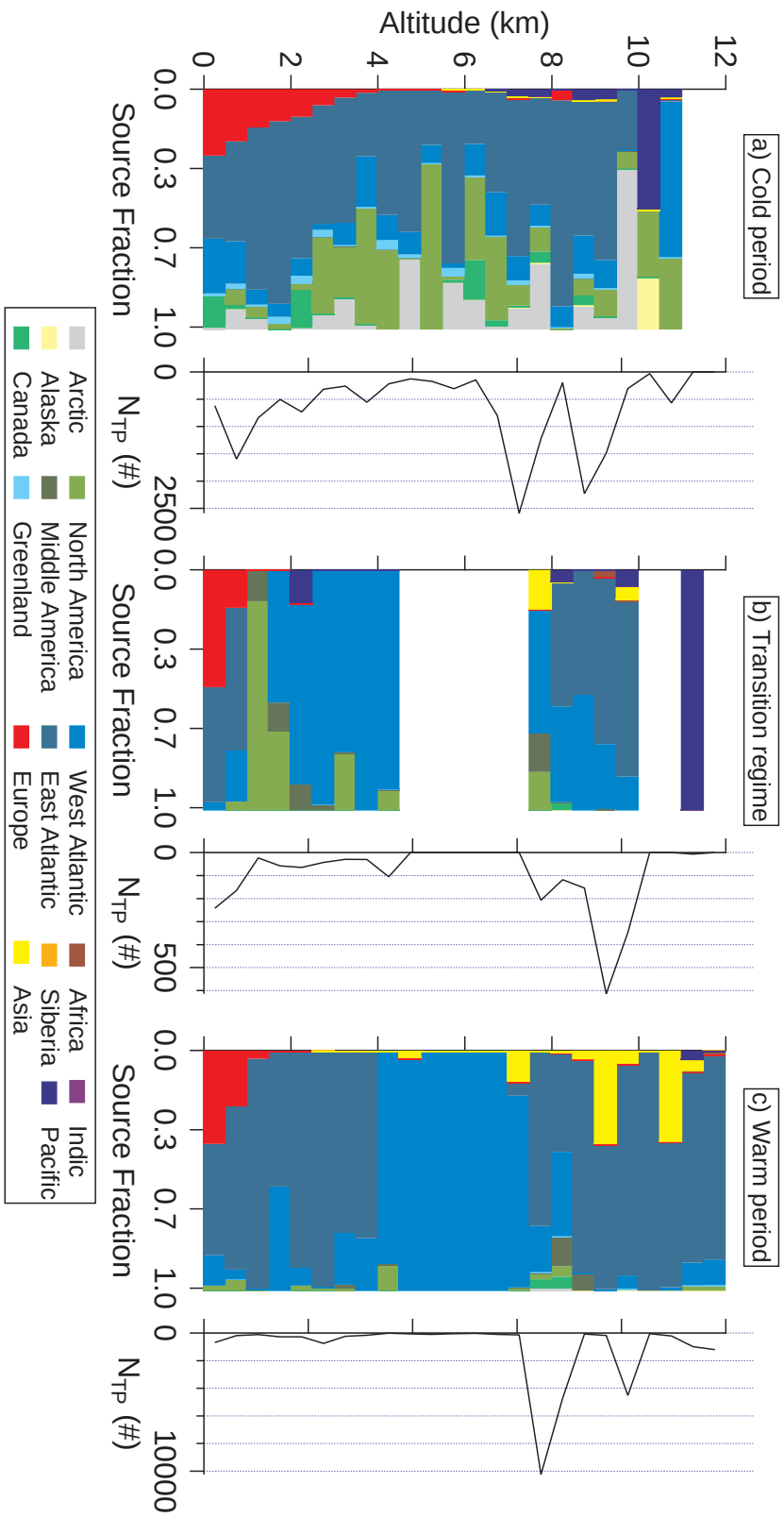


Figure 3.7: Vertical profile of contribution of source regions to flight space area and total number of trajectory points (N_{TP}) for three synoptical weather pattern periods during ND-MAX: cold sector (a), transition regime (b), and warm sector (c). The vertically-binned cumulative contribution is provided as a ratio of the filtered number of trajectory points inside the BL per source region and the number of points for all regions. Further details on the HYSPLIT simulations and the source region definitions are described in Sect. 2.7. The lack of data for (b) between 7.5 km and 7.5 km is a result of low statistics.

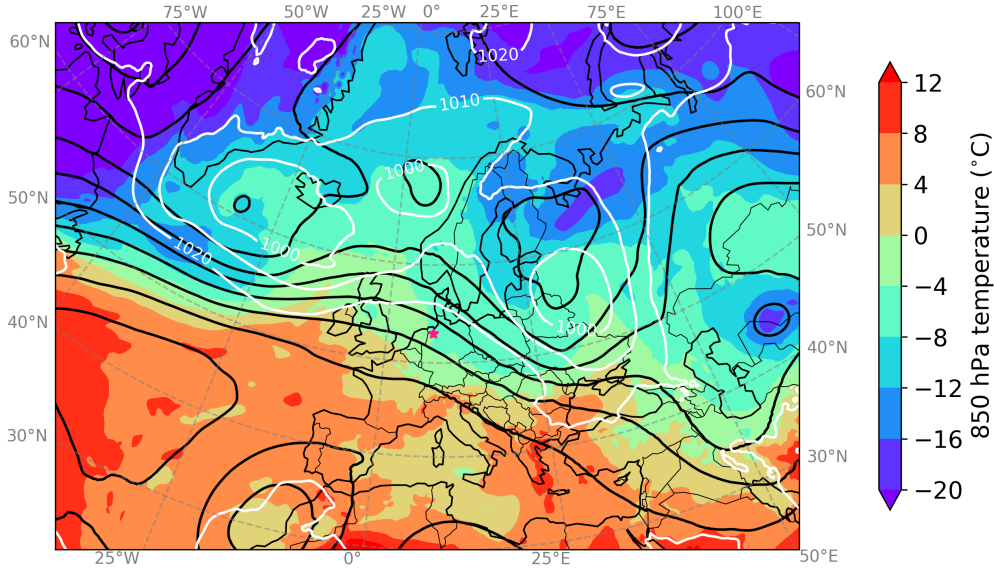


Figure 3.8: Weather map of 30th January 2018, 12:00 UTC as in Fig. 3.2. Plotted with ERA5-data provided by Hersbach et al. (2018).

the impact of the local BL, whereas those of Arctic and American origin were present throughout the atmosphere.

3.3.2 Transition period

RF6 was the only flight which took place in a transition regime that could be attributed neither to a cold nor to a warm period and was located in the changeover sector between both periods (Fig. 3.8). The flight area was surrounded by two high-level troughs determined over the North Atlantic and Eastern Europe. As the isohypsies implied, the area was exposed to a northwesterly circulation under an anticyclonic influence. The temperatures at 850 hPa were in a moderate range between -8 and 0°C .

The ridge of a high-pressure system above the Atlantic Ocean dominated the region of interest. Besides a low-pressure system over Russia and a depression over the North Atlantic Ocean that induced westerlies over Northern Germany, the flight area was under anticyclonic influence (Fig. 3.9). As a result, the warm front crossing Southern Germany from France to Austria had no significant impact on the local weather in terms of precipitation and wind. In contrast, the wind was of low speed and of different directions according to the synoptic stations in the weather map. Nevertheless, the warm front over the Norwegian Sea promoted the ascent of warm and moist air masses over the North Sea and, thus, supported the formation of cirrus and contrails over Northern Germany.

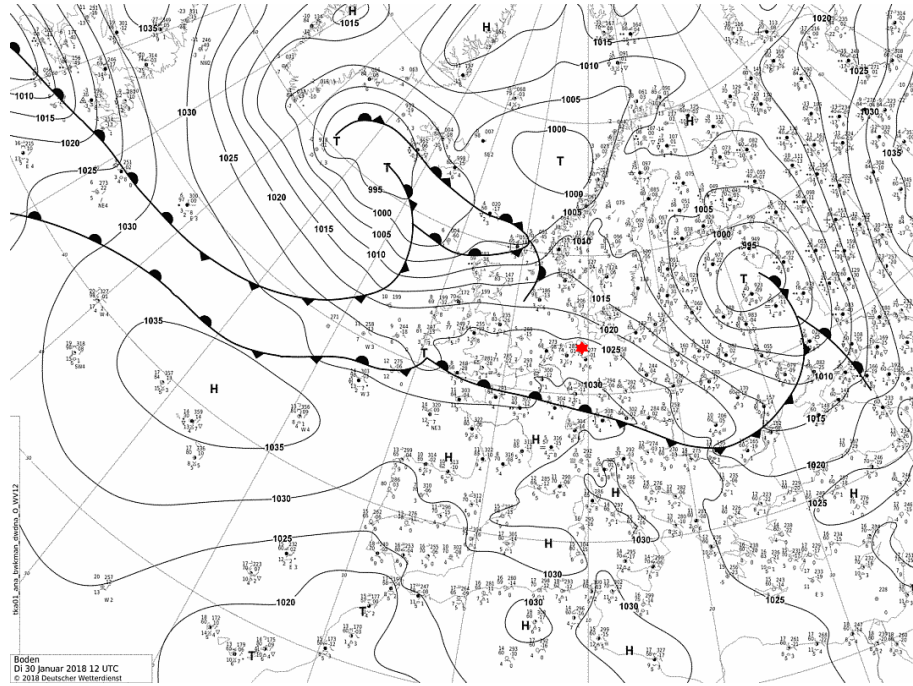


Figure 3.9: Synoptic weather map of German Weather Service (Deutscher Wetterdienst; DWD) of 30th January 2018, 12:00 UTC as in Fig. 3.3. Adapted from wetter3 (2018).

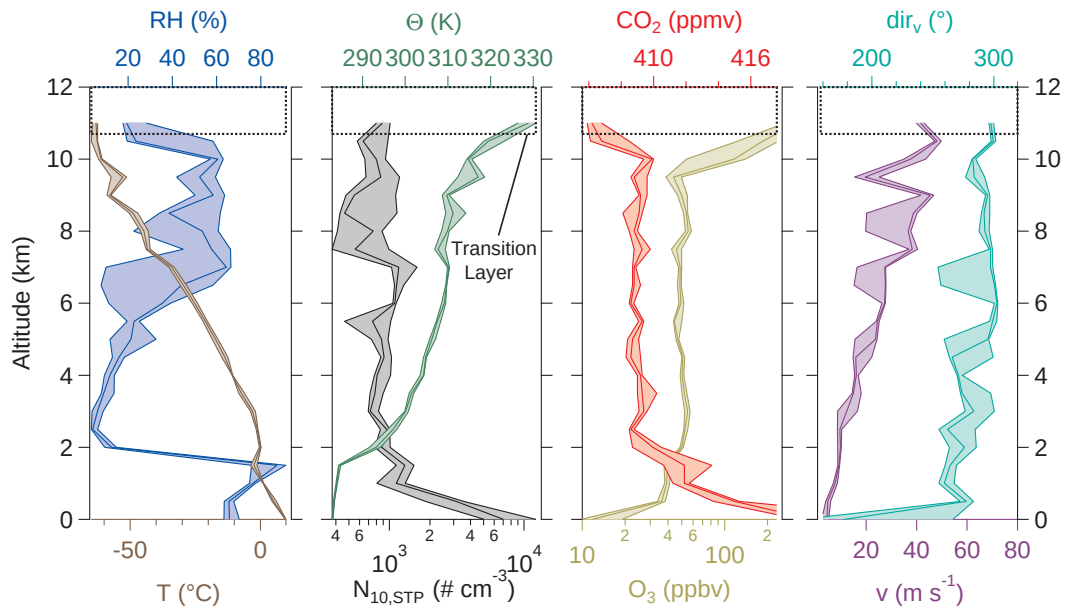


Figure 3.10: Vertical profile of meteorological parameters as measured by the NASA DC-8 (RH: Relative Humidity, T: Temperature, Θ : Potential Temperature, v: Wind Speed, dir_v : Wind Direction) (provided by Melissa Yang-Martin, NSRC), volume mixing ratios of O_3 , and CO_2 (provided by Hans Schlager, DLR), and aerosol particle number concentration ($N_{10,STP}$) (provided by Christiane Voigt, DLR) for transition period during RF6. Median and interquartile range are shown. The black box denotes the Transition Layer.

The transition period revealed characteristics of high-pressure systems during wintertime in Central Europe such as a temperature inversion above 1.5 km and an associated sharp drop in relative humidity (Fig. 3.10). Thus, a layer of stable stratification could form close to the ground as long as the westerlies (dir_v : 260-300° in Fig. 3.10) were weak and no front was approaching. This was confirmed by the wind profile unveiling a weak wind speed below 10 m s⁻¹ inside the BL up to 2.5 km. The aerosol particle number concentration was strongly enhanced inside the BL with values up to 7000 cm⁻³ along with high CO₂ mixing ratios and decreased at higher altitudes down to approximately 1000 cm⁻³.

Moreover, the transition period was characterized by an uplifted tropopause region compared to the cold regime. As the volume mixing ratios of CO₂ and O₃ implied, the turnover from tropospheric to stratospheric features started above 10 km. The ozone level denoted a striking increase from 50 ppbv to more than 200 ppbv, whereas the amount of carbon dioxide dropped from 410 ppmv to 406 ppmv. In addition, the temperature remained constant and the potential temperature revealed a significant enhancement with height above an altitude of 10 km.

Thin high-level clouds dominated the cloud coverage during the anticyclonic conditions on RF6. Along with smaller cumulus clouds over the North Sea, which did not affect the reserved air space, cirrus and cirrostratus clouds were observed on the satellite image (Fig. 3.11). These clouds are common for continental high-pressure weather patterns. However, they are also indicators for the presence of contrails as they form under the same atmospheric conditions. Besides, the Schmidt-Appleman-Temperature revealed suitable conditions for contrail formation as the ambient temperatures provided ideal conditions in case of plume mixing (Fig. 3.12).

The trajectories calculated for RF6 unveiled a large effect of maritime air masses and therein two regimes (Fig 3.7b). The air masses from the East Atlantic were prevailing in an altitude range below 1 km and above 8 km. The range from 1.5 to 8 km was dominated by West Atlantic air masses, except for a data gap between 4.5 and 7.5 km due to low statistics. Besides, small fractions of air masses could be traced back to the Pacific area. Trajectories of continental origin appeared above 7.5 km and were found to be from Asia, Middle, and North America. In contrast, the cold air period was dominated by maritime air masses originating from the East Atlantic. Further points of trajectories detected below 4.5 km were linked to Middle, and North America but their number was limited. Due to the limited statistical representation of these data, they are not meaningful. Compared to the cold air period, the impact of air masses from Middle and North America was limited as their trajectories were not found

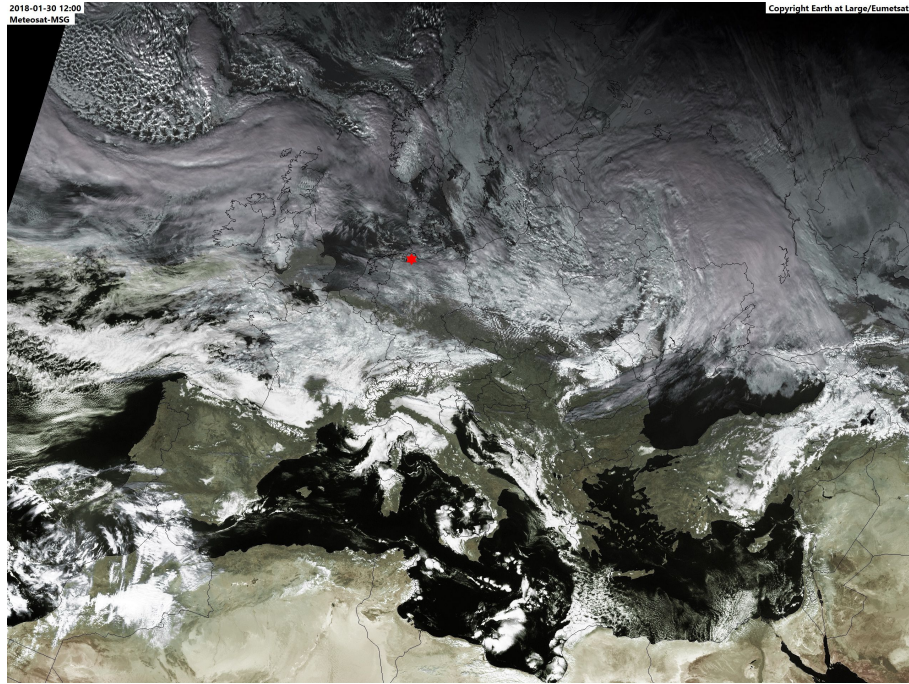


Figure 3.11: Satellite image of EUMETSAT of 30th January 2018, 12:00 UTC, Meteosat Second Generation, VIS-Channel $0.6\ \mu\text{m}$. The image shows the cloud coverage over Europe and the unstable stratification (indicated by convection) in the vicinity of the flight region. The red star denotes the area used for RF6. Adapted from Valk (2018) with permission from EUMETSAT.

throughout the entire atmosphere. The influence of European air masses was only observed up to 1 km, whereas in the cold air period contributions were found up to 3.5 km.

Summarizing, RF6 was affected by a northwesterly circulation under anticyclonic influence. As a result of slow wind speeds, a temperature inversion formed and was detected above 1.5 km suppressing the exchange of air masses between the FT and the BL. Consequently, sharp gradients in relative humidity, aerosol particle number concentration, temperature, and CO_2 were detected. The tropopause level was increased compared to the cold period (see Sect. 3.3.1) and was detected around 10 km as inferred from CO_2 and O_3 . The presence of thin cirrus and cirrostratus along the flight track implied favorable conditions for the formation of contrails, which was confirmed by the Schmidt-Appleman-Temperature and the detection of contrails. Similar to RF1, the air space area was mostly affected by maritime air masses, but of two distinct regimes. Besides the impact of West and East Atlantic region, some trajectories were traced back to Asia, Middle and North America, whereas the Arctic, Alaskan or Greenland influence was not present anymore.

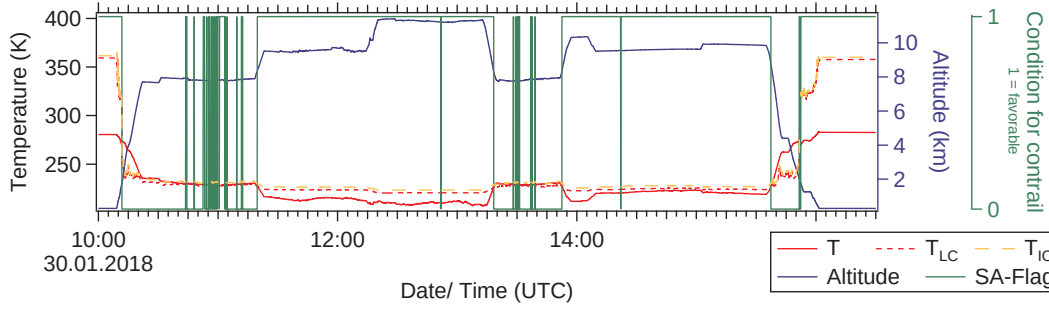


Figure 3.12: Ambient temperature (red), flight level (blue), the Schmidt-Appleman-Temperatures for contrail formation (T_{LC} , red, short-dashed) and persistence (T_{IC} , orange, long-dashed) as a function of time (RF6). The green line marks the legs on which contrails can form and persist, i.e. where both thresholds are underpassed. During RF6, the aircraft passed regions providing appropriate conditions for the formation and persistence of contrails.

3.3.3 Warm air mass period

RF3, 4, 5, and 7 were categorized into the warm air period and pre-frontal meteorological conditions. These conditions were defined by the weakening of a high-level ridge and an approaching trough of the depression located westwards. Furthermore, the advection of warm air led to temperatures above -4°C at 850 hPa, ascending air masses, and a rise of the local tropopause to levels above 10 km. The features of the warm air period are demonstrated using RF3 as an example. The weather conditions of RF4, 5, and 7 are described in the appendix (see App. B.2).

The passage of a ridge over Central Europe and the approach of a trough from the North Atlantic defined the high-level conditions during RF3 (Fig. 3.13). Accordingly, the air space area was affected by the advection of warm and moist air masses from the South Atlantic that replaced the cold air prevailing during RF1 and RF2. The advance of warm and moist air masses was attributed to the warm conveyor belt and promoted the formation of cirrus and contrails. These observations were confirmed by the weather chart in Fig. 3.14, which demonstrates the approach of a severe cyclone over the North Atlantic Ocean and the transport of marine air masses of Atlantic origin by the occlusion and two upstream fronts towards Central Europe. The fronts implied the passage and formation of cirrus clouds and, thus, also contrails along the flight track.

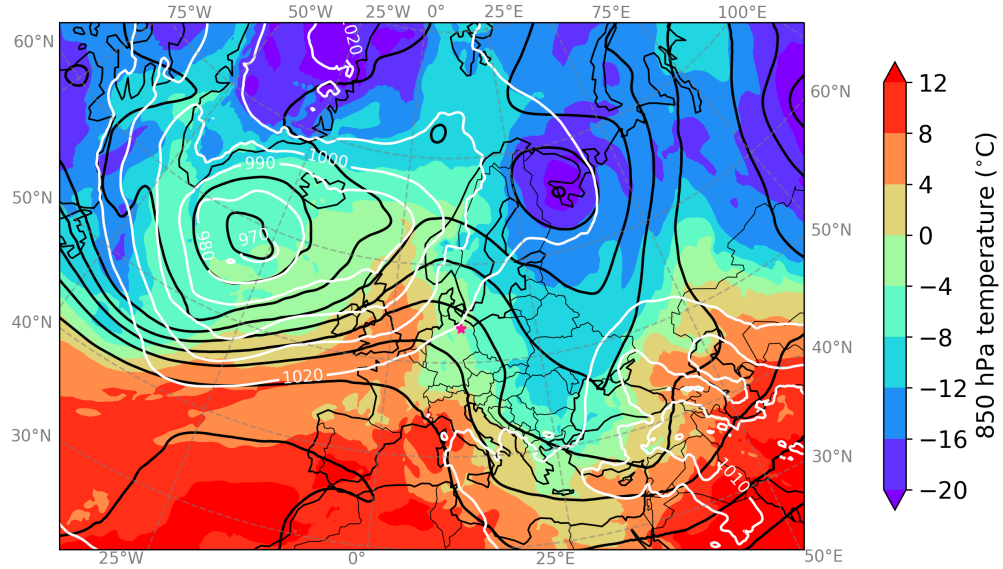


Figure 3.13: Weather map of 23rd January 2018, 12:00 UTC as in Fig. 3.2. Plotted with ERA5-data provided by Hersbach et al. (2018).

Compared to the FT, the relative humidity of up to 85%, aerosol particle number concentration of $\sim 2500 \text{ cm}^{-3}$, and the CO_2 mixing ratio of 415 ppmv were enhanced below 1.5 km, indicating an isolated BL (Fig. 3.15). This is a typical feature of the warm period in a Central European winter. However, the temperature profile depicted a breakup of the temperature inversion as the front approached due to the entrainment of free tropospheric air masses. This was confirmed by the increase in wind speed from $\sim 4 \text{ m s}^{-1}$ to $\sim 20 \text{ m s}^{-1}$ and the wind direction ranging from southwesterlies ($dir_v : 240 - 270^\circ$ in Fig. 3.15) in the BL to northwesterlies ($\sim 280^\circ$) above.

Furthermore, the warm period was characterized by a high-level tropopause above 10 km and the uplift of marine air masses ahead of the frontal zone. Actually, the data recordings reaching up to an altitude of 11.5 km did not show a switch from tropospheric to stratospheric conditions. Nevertheless, the temperature gradient was slightly reduced above 10.5 km and the potential temperature revealed a slight enhancement above 10 km, implying proximity to the tropopause transition layer. This was confirmed by an increasing amount of O_3 above 9.5 km. The uplift of air masses was pointed out by the large amount of humidity up to 60% in the upper troposphere above 8 km and the positive trend of particle number concentration towards higher altitudes from 300 to 2000 cm^{-3} .

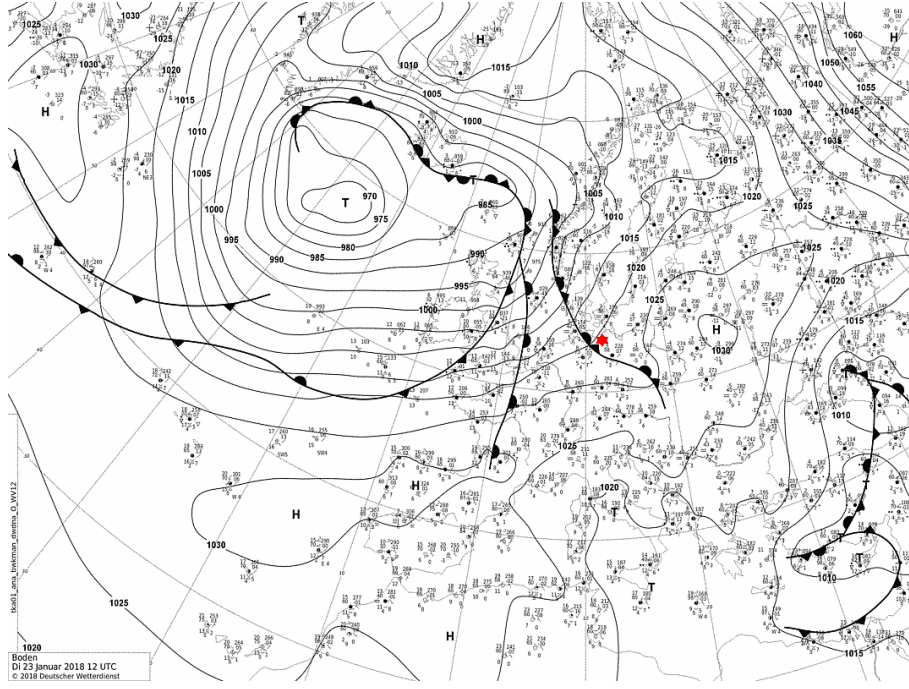


Figure 3.14: Synoptic weather map of German Weather Service (Deutscher Wetterdienst; DWD) of 23rd January 2018, 12:00 UTC as in Fig. 3.3. Adapted from wetter3 (2018).

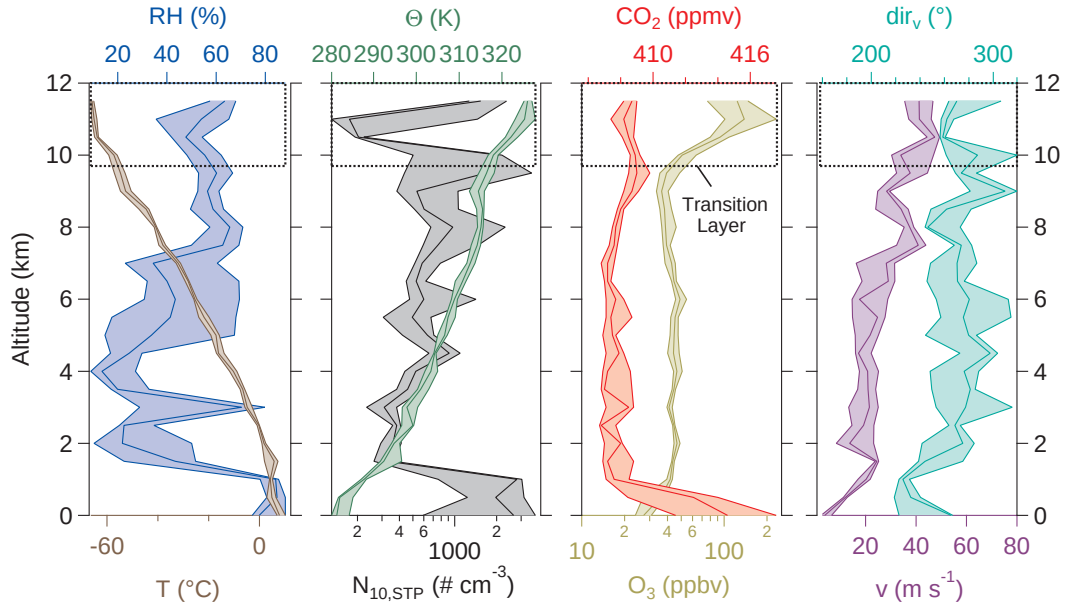


Figure 3.15: Vertical profile of meteorological parameters as measured by the NASA DC-8 (RH: Relative Humidity, T: Temperature, Θ : Potential Temperature, v: Wind Speed, dir_v : Wind Direction) (provided by Melissa Yang-Martin, NSRC), volume mixing ratios of O_3 , and CO_2 (provided by Hans Schlager, DLR), and aerosol particle number concentration ($N_{10,STP}$) (provided by Christiane Voigt, DLR) for warm air periods during RF3, RF4, RF5, and RF7. Median and interquartile range are shown. The black box denotes the Transition Layer.

The trajectory analysis in Fig. 3.7 depicted the predominance of marine air masses advected from the West and East Atlantic Ocean. Up to 4 km and also above 7.5 km, the air masses originated from the East Atlantic, whereas in the section in between air masses from the West Atlantic were dominating. Some of the trajectories starting above 7 km were traced back to Asia but their fraction had to be handled with care. Just a few trajectory points were attributed to those altitude bins in total as the vertical distribution depicted. In contrast, a small fraction was found to be of Middle American, North American, and Canadian origin, and was based on a large number of trajectory points in an altitude range of 7 to 8.5 km. The BL was affected by air masses from Europe, East Atlantic, and to a small degree by air masses from West Atlantic and Middle America, which was not expected. Actually, the warm period was characterized by ascending air masses, i.e. trajectories originating from transatlantic regions were expected to approach the testsite at more elevated altitude levels.

The warm sector exhibited similar features as the transition period regarding the trajectory source analysis: the trajectories in the lowermost troposphere and the upper troposphere were mostly of East Atlantic origin, and those in between were from West Atlantic region. Both periods showed small influences from Asia, Middle, and North America above an altitude level of 7 km. The effect of air masses from Europe were observed in the lowermost 1 km. However, the transition period below 4 km was much more affected by air masses of Middle, and North America than the warm sector. In addition, some trajectory points detected in the transition region could be attributed to a Pacific origin, whereas the warm sector displayed only minor contribution of Pacific air masses.

Cirrus and cumulus clouds dominated the flight space area during the warm period. As depicted by Fig. 3.16, convection appeared along the occlusion front in the flight region, which implied an unstable stratification over Germany. Triggered by the convection, a cluster of high-reaching cumulus clouds formed next to the flight track. Yet, as the lightning archive in Wanke (2024) exhibited, the convection did not lead to thunderstorms and cirrus clouds addicted to its outflow. Besides, the cloud band of the upstream fronts approached slowly from the west including a field of cirrus and cirrostratus that indicated favorable conditions for the formation of contrails. This was confirmed by the comparison of the ambient temperatures along the flight track that did not satisfy the Schmidt-Appleman temperatures for contrail formation and persistence (Fig. 3.17).

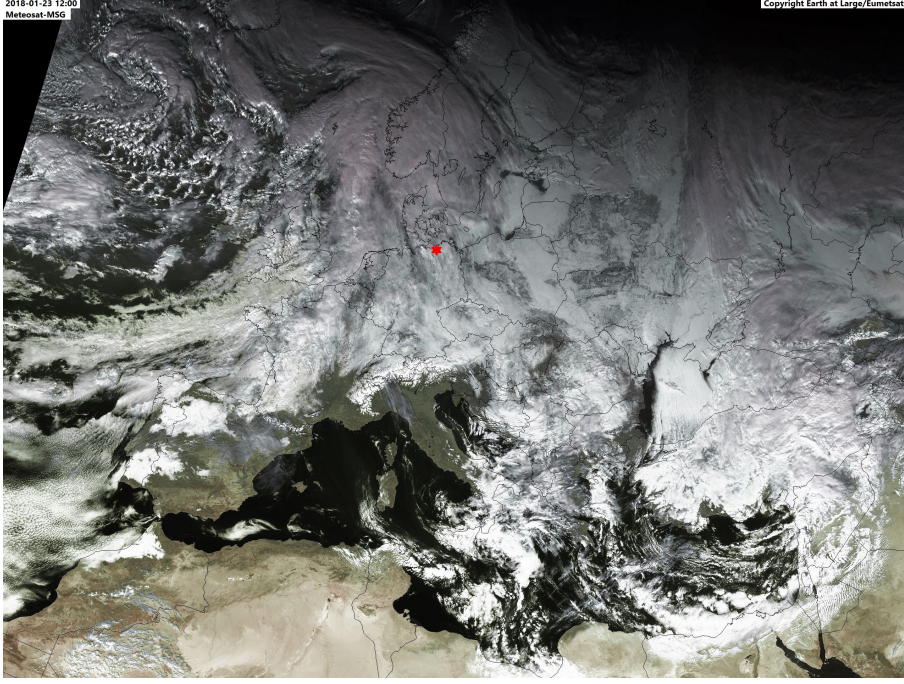


Figure 3.16: Satellite image of EUMETSAT of 23rd January 2018, 12:00 UTC, Meteosat Second Generation, VIS-Channel 0.6 μm . The image shows the cloud coverage over Europe and the unstable stratification (indicated by convection) along the flight region. The red star denotes the area used for RF3. Adapted from Valk (2018) with permission from EUMETSAT.

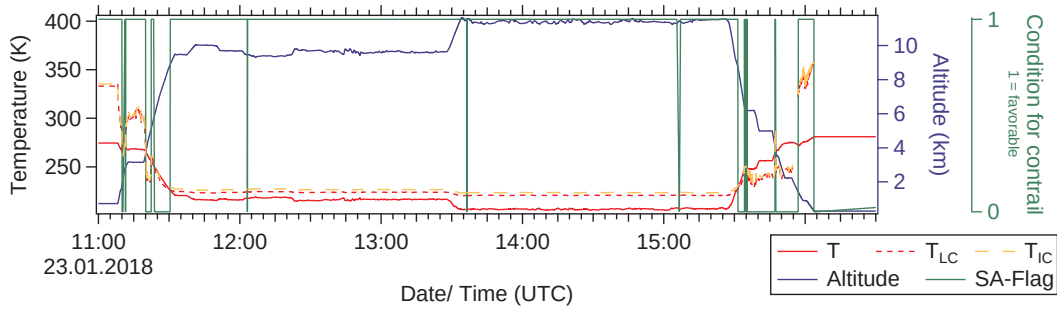


Figure 3.17: Ambient temperature (red), flight level (blue), the Schmidt-Appleman-Temperatures for contrail formation (T_{LC} , red, short-dashed) and persistence (T_{IC} , orange, long-dashed) as a function of time (RF3). The green line marks the legs on which contrails can form and persist, i.e. where both thresholds are underpassed. During RF3, the aircraft passed regions providing appropriate conditions for the formation and persistence of contrails.

To summarize, RF3 was affected by the passage of a high-level ridge over Central Europe and the approach of a trough. Accordingly, the fronts of the advected low-pressure systems transported warm and moist air masses to the area of interest that enhanced the temperatures at the 850-hPa-level and provided

conditions for the formation of cirrus and contrails. The BL was affected by the entrainment of air masses of the FT that broke up the temperature inversion layer. As expected, the tropopause was at a high level above 10 km as inferred from vertical profiles of temperature, potential temperature, and ozone. The air masses detected during the flight were of Atlantic origin to a large extent and dividable into two regimes as for the transition period. Continental influences were detected from Middle and North America beside Canada and Europe. The observed cumulus clouds revealed slight convection, whereas the detected cirrus clouds implied the potential for contrail formation.

RESULTS

This chapter presents the results of the ERICA measurements from the ND-MAX campaign 2018. A statistical overview is provided about the particles and cloud residuals detected from the research flights. Comparisons of aircraft exhaust versus background population and of cirrus versus contrails are provided in order to address the central questions of this thesis. The vertical profiles are used to understand the impact of variable weather patterns and air mass regimes on the occurrence of the individual particle types. Besides, the analysis of backward trajectories based on ERA5-reanalysis data gives insight to the origin of certain particle types. Regarding the aircraft exhaust, several particle types are checked for their relation to the exhaust plume using particle size distributions, distance analysis, and chemical markers within their mean mass spectra. Further, the impact of sustainable alternative jet fuel on the aircraft exhaust is analyzed. Laboratory measurements unveiled the detection of nitrogen oxide signals with ERICA-LAMS as a result of nitrogen and oxygen recombination of former species such as ammonium and sulphur dioxide. Moreover, a potential source was found for cation sulphur signals that were occasionally detected within single-particle mass spectra recorded during the ND-MAX research flights.

4.1 AEROSOL PARTICLE CHEMICAL COMPOSITION IN THE UTLS

This section provides an overview of the particle types detected during the ND-MAX campaign in the midlatitude winter UTLS and investigates their sources and properties in order to characterize their nucleability and contribution to the formation of cirrus and contrails.

4.1.1 *Statistics on particle measurements*

In total, 151.110 particles were successfully ablated and analyzed throughout the ND-MAX campaign. Two thirds of these particles (110.901) were detected during the research flights but only 59.466 particles could be attributed to the test points, i.e. to the periods when the *Flying Laboratory* NASA DC-8 chased the DLR-ATRA or commercial aircraft (see. Sect. 3.1) in order to sample

emission plumes. Of these particles, 5.73 % were sampled by the CVI (see Sect. 2.3.2) when flying inside clouds or contrails with the aim of detecting CPRs. Thus, 94.27 % were covered using the scoop-style aerosol sampling inlet to detect interstitial aerosol particles. All particle types were clustered using the *fuzzy c-means* algorithm described in Sect. 2.2 and then interpreted by the analysis of the characteristic peaks in the mean anion and cation spectrum (see Sect. 2.2.2). Finally, 15 particle types were determined and construed according to markers that have been found in literature. These types are listed in Table 4.1 including their total number and relative contribution, which is also referred to as *PF* (particle fraction, see Sect. 2.2.3). However, when comparing individual events, only a certain subset of particles was taken into account. For example, CVI- and scoop-measurements were compared only within the same test points in order to minimize external influences on the composition, e.g., by different weather patterns and atmospheric regimes.

The midlatitude winter UTLS was dominated by organic particles. 67.8 % of all particles detected with the scoop inlet were attributed to organic material. Among these, the group of biomass burning particles (BB) provided the largest fraction in terms of relative abundance of 37.8 % as Fig. 4.1 reveals. At least one type was traced back to wildfires reported in North America (see Sect. 4.1.6). Another dominant particle type was the internal mixture of processed elemental and organic carbon (ECOC) with a fraction of 24.4 %. Besides, fresh and coated soot had a common fraction of 10.7 % and processed organic carbon (OC) a fraction of 5.6 %. The soot types were traced back to aircraft fuel combustion, whereas the ECOC and processed OC could not be fully attributed to exhaust plumes (see Sect. 4.1.2). Yet, amines, motor oil, and nitrate-rich particles¹ only seemed to play a minor role as they revealed a very low relative abundance of 0.1 %, 0.8 %, and 2.2 %.

However, the latter type was of special interest as it revealed a mean mass spectrum which is similar to a particle type found within the Asian tropopause aerosol layer (ATAL). This type was dominated by a large cation peak on $m/z +30$ (NO) and was frequently detected in the vicinity of enhanced mass concentrations of particulate ammonium and sulphate (Appel et al., 2022). The correlation promoted the assumption of nitrate-rich particles to be produced by a combination of the precursor substances ammonium (NH₄) and sulphuric acid (H₂SO₄) or ammonium sulphate (AS, (NH₄)₂SO₄). In order to analyze the impact of AS on the formation process of nitrate-rich particles, laboratory measurements were conducted (see Sect. 4.2).

¹ Nitrate-rich refers to the individual particle type as in Table 4.1, not to be confused with other particles also containing a nitrate chemical signature in general. These, however, contain other signals besides nitrate.

Table 4.1: Overview of the classified particle types detected by ERICA during the ND-MAX campaign, including their predefined names, interpretation, absolute, and relative abundance in total and for the distinct periods of aircraft chase (test points, TPNs).

Particle type	Interpretation	Total no. of particles (relative contribution in %)	No. of particles detected in TPNs by scoop/ CVI (rel. contribution in %)
CaKNaClMg	Sea spray	6311 (5.69 %)	680/ 749 (1.61/ 23.79 %)
KNaClMet-NOSO	Processed sea spray	795 (0.72 %)	187/ 91 (0.47/ 3.23 %)
AlOrgNO-PhoSOCI	Mineral dust	618 (0.55 %)	226/ 102 (0.57/ 3.14 %)
MetOrgNO-PhoSOCI	Internal mixture of mineral dust, salt, metal	695/2700 (2.43 %)	470/ 308 (1.76/ 12.74 %)
EC	Elemental carbon (EC)/ fresh soot	7296 (6.58 %)	1780/ 96 (6.67/ 3.97 %)
OrgSO	Coated soot	4112 (3.71 %)	1066/ 83 (3.99/ 3.43 %)
OrgNOSO	Internally mixed elemental and organic carbon (ECOC) with nitrate and sulphate	22330 (20.14 %)	6519/98 (24.4/ 0.04 %)
OrgNOSO2	Processed organic carbon (OC)	5489 (4.95 %)	913/ 3 (3.41/ 0.12 %)
KOrgNOSO1	Biomass burning (BB) type 1	15222 (13.73 %)	4409/ 193 (16.51/ 7.98 %)
KOrgNOSO2	Biomass burning (BB) type 2	11643 (10.50 %)	4132/ 234 (15.47/ 9.68 %)
KOrgNOSO3	Biomass burning (BB) type 3	7908 (7.13 %)	1543/ 195 (5.78/ 8.06 %)
Amine	Amine	665 (0.60 %)	17/ 11 (0.06/ 0.5 %)
NOSO	Nitrate-rich	2948 (2.66 %)	582/ 0 (2.18/ 0 %)
NaMgFe	Meteoric material	9579 (8.64 %)	995/ 86 (3.73/ 3.56 %)
MetOrg-PhoSO	Motor oil	703 (0.63 %)	223/ 90 (0.84/ 3.72 %)
Rest	Undefined	12582 (11.35 %)	3349/ 316 (12.54/ 13.07 %)
Total	All particles	110901 (100 %)	26706/ 2418 (91.7/ 8.3 %)

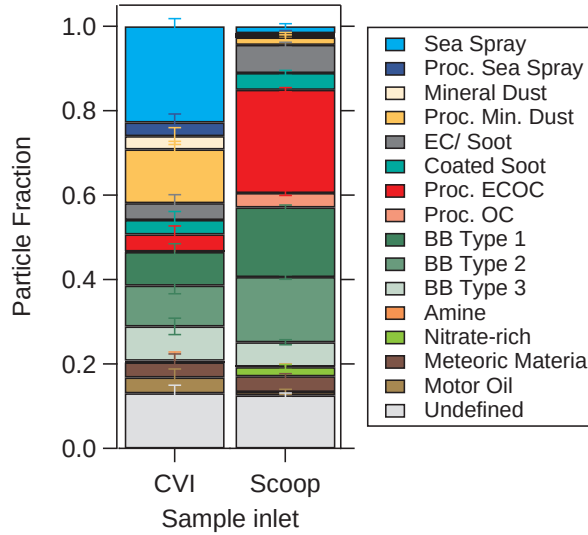


Figure 4.1: Overview of the relative abundance of detected particle types at different sample inlets CVI and scoop during the ND-MAX campaign. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

Apart from the organics, the aerosol chemical composition revealed a contribution from meteoric material with a fraction of 3.7 %. This referred to approximately one sixth of the fraction (of 23.5 %) reported in Schneider et al. (2021) for the complementary transfer flights of ND-MAX that took place in the LMS. The RFs of ND-MAX, however, were majorly conducted within the UT, except for a few periods during the cold period, where the tropopause layer was descended, and the aircraft dived into the LMS. These exceptions are analyzed later on (see Sect. 4.1.3). Further inorganic substances of low relative abundance were sea spray (1.6 %), processed sea spray (0.4 %), mineral dust (0.5 %), and an internal mixture of metals and mineral dust (1.8 %), which was referred to as processed mineral dust.

Sea spray was the most important inorganic particle type contributing to cloud formation in the midlatitude winter UTLS. With a fraction of 22.8 %, sea spray was the dominant CPR besides organic species that led to a total contribution of 30.3 %. Moreover, processed sea spray also contributed to CPRs with an additional fraction of 3.2 % as Fig. 4.1 reveals. Due to its large hygroscopicity, sea spray is a well-suited cloud condensation nuclei (CCN) and implies the CPRs to be of liquid origin (Andreae and Rosenfeld, 2008 and therein).

A large fraction of residuals (15.8 %) was assigned to pure and processed mineral dust. While the pure form of mineral dust unveiled a fraction of 3.1 %, the processed type made up to 12.7 %. As described in Sect. 4.1.4, a higher processing

stage of mineral dust results in a higher probability to act as a CCN. In consequence, the large fraction of processed mineral dust and the low fraction of (pure) mineral dust also indicated the cloud formation via the liquid phase.

Organic species played an important role in CPRs implying that they had a high nucleability. Of all organic residuals, a fraction of 25.7 % was attributed to BB, followed by a fraction of 7.4 % linked to fresh and coated soot residuals, and 4.1 % of processed ECOC. However, amines and processed OC residuals were rarely detected (0.5 % and 0.1 %) and, thus, expected to have a low probability to act as nucleating particles. The *nitrate-rich* type ¹ was not found in the CVI samples.

Motor oil residuals contributed to the formation of clouds with a fraction of 3.7 %. The mean mass spectra of this particle and cloud residual type (A.15) displayed the characteristic signals of C_4H_9 ($m/z +57$), C_6H_{13} ($m/z +85$), $C_6H_7O_4$ ($m/z -143$), and $H(PO_3)_2$ ($m/z -159$) that were traced back to motor oil by Clemen et al. (2024). A further investigation is provided within the comparison of cirrus and condensation trails (see Sect. 4.1.4).

4.1.2 *Exhaust versus Background*

In order to analyze the particle types measured with the scoop inlet that were related to aircraft exhaust, the recorded data points were divided into two phases. The *Exhaust* period was characterized by a large number of aerosol particles and an enhanced concentration of carbon dioxide released by the aircraft turbines, whereas the *Background* period showed no influence of aircraft emissions (see Sect. 2.6.1). The particle number concentration and the level of CO_2 unveiled no spikes of emission plumes. In contrast to the comparison of particle types and their abundances measured at the sample inlets CVI and scoop, all exhaust and background periods are taken into account because of statistic reasons. However, the differences between both periods are analyzed for the impact of variable atmospheric conditions that might affect the abundance of individual particle types.

The differentiation of particle composition between *Exhaust* and *Background* periods with ERICA-LAMS was difficult. The chemical composition in terms of relative abundance of certain particle types detected with the mass spectrometer was very similar for both periods. Not only the number of individual particle types detected in both periods was the same, but also their relative frequency of detection was very similar as Fig. 4.2 depicts. For example, processed ECOC

¹ Particles including nitrate-compounds were still sampled with the CVI and contributed to cloud chemistry.

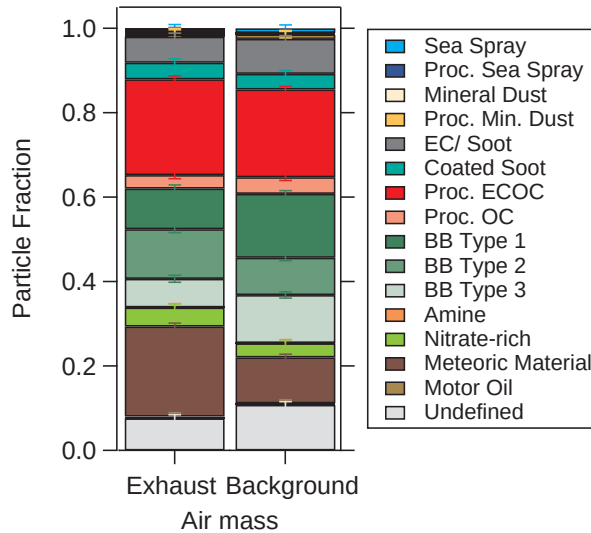


Figure 4.2: Overview of the relative abundance of detected particle types for Exhaust and Background periods during the ND-MAX campaign. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

particles had a fraction of 22.7 % (20.8 %) in the *Exhaust* (*Background*) period, processed OC particles a fraction of 3.2 % (3.9 %). Major differences between both periods were found for the meteoric material (10.5 %) and the BB types 1 (5.5 %) and 3 (4.6 %). Regarding the meteoric material, the differences were traced back to the different prevailing atmospheric regimes for *Exhaust* and *Background* periods. Of all particles detected during the *Exhaust* period, 88.3 % were attributed to the TL¹ and stratosphere, usually accompanied by meteoric material. In contrast, only 71.9 % of the particles measured within the *Background* periods were linked to the TL (see Sect. 2.5) and stratosphere. Thus, a higher detection rate of tropospheric particles led to a lower fraction of meteoric material. The variability of the fraction of BB material was also attributed to variable atmospheric conditions between *Exhaust* and *Background* periods in general. When comparing individual events on a small time scale of approximately five minutes, the abundance of BB particles within the exhaust and the corresponding background period was almost equal (Fig. C.1 in the appendix).

Besides the chemical composition, ERICA-LAMS could not resolve the differences between *Exhaust* and *Background* periods with respect to particle sizes. The size distribution in Fig. 4.3 reveals that the majority of particles for both periods was detected within a mode ranging from 200 to 2000 nm.

¹ Here, the transition layer refers to the Extratropical Transition Layer (ExTL).

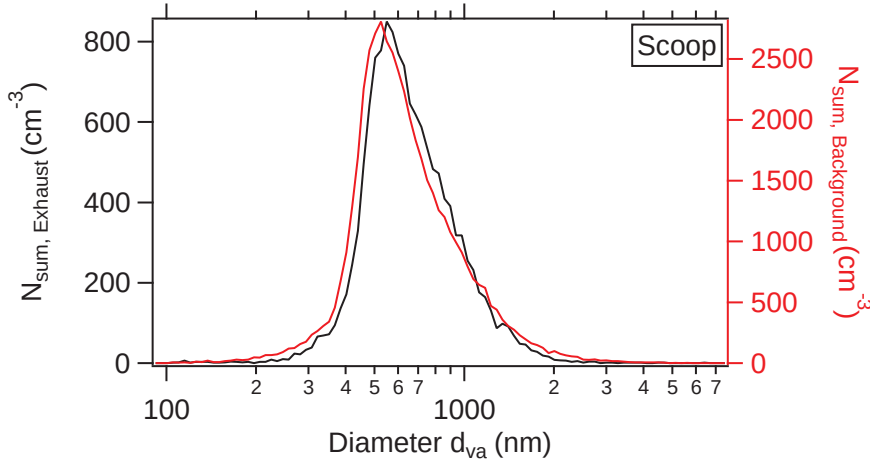


Figure 4.3: Size distribution of particles detected with ERICA-LAMS during ND-MAX separated into Exhaust and Background periods.

Yuan et al. (2022) showed size distributions of black carbon emissions for multiple engine and source types. According to her findings, the maximums of the size distributions range between 45 and 62 nm regarding the mobility diameter. Those correspond to vacuum aerodynamic diameters of 81 and 112 nm, respectively, when assuming the morphology of soot particles to be near-spherical (Wang et al., 2021) and their material density as of 1.8 g cm^{-3} (Taylor et al., 2015).

Small particles such as soot from incomplete combustion were also expected to be emitted by the aircraft turbines of the DLR-ATRA and detected during the *Exhaust* periods of ND-MAX. As the size distribution in Fig. 4.3 displays, there were nearly no particles detected in the size range below 112 nm. However, complementary measurements of other instruments for aerosol detection such as the CPC (see Sect. 2.4.1) and the LAS (see Sect. 2.4.2) measured particles down to 5 and 90 nm in size, implying the presence of small particles in general. Fig. 4.4 reveals the size distribution of particles detected with LAS in a range of 90 and 7500 nm, extended by an additional *Bin0*. For that, the total number concentration of particles detected by the LAS was subtracted from the total number concentration detected by the CPC in order to gain information about the size range of 5 to 90 nm. This covers the size range of emitted soot particles (Moore et al., 2017). The size distributions displayed minor discrepancies between the *Exhaust* and *Background* periods. Both distributions showed a maximum at approximately 90 nm but the number of small particles up to 90 nm was enlarged during the *Exhaust* period, indicating the additional particles related to aircraft exhaust. Furthermore, the distribution of the *Exhaust* particles was slightly shifted towards smaller particles. Both findings confirmed the expectation to detect small-sized aerosol particles of diameters below 112 nm.

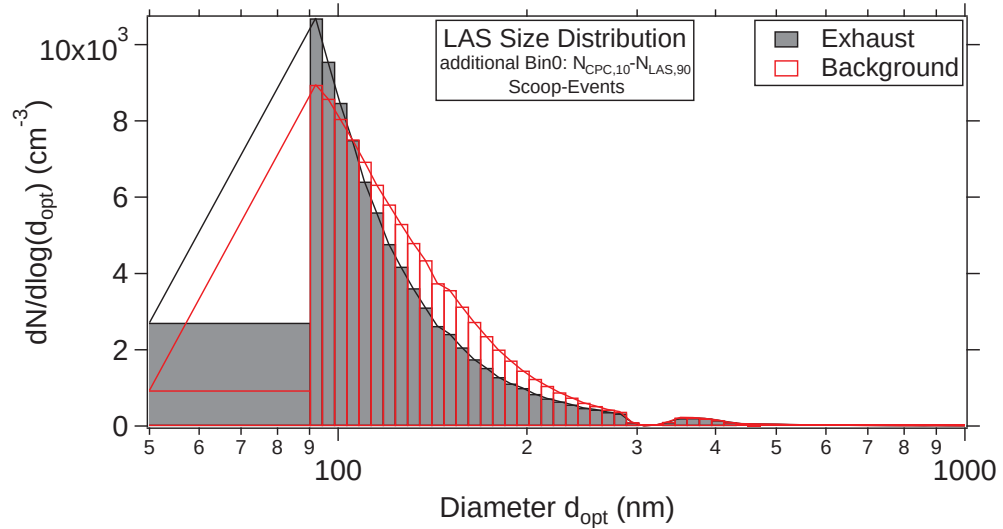


Figure 4.4: Particle size distribution of the Laser Aerosol Spectrometer, extended by an additional *Bin0* facing the number concentration in a size range from 5 to 90 nm. Data provided by Christiane Voigt and Hans Schlager, DLR.

Nevertheless, particles in that size range were not measured by ERICA-LAMS due to a detection limit of the detection units *DU1* and *DU2*. It was found to be 184 nm for *DU1* and 174 nm for *DU2* by Hünig (2021) and is defined as the particle size at which 50 % of the maximum number concentration is still ablated. The minimum size in particle diameters detected during ND-MAX was 92 nm but their overall number (64 in 110901) was neglectable.

In a strict sense, the determined particle diameters of the several instruments are of different definition and actually not directly comparable without regarding their derivation. In ERICA-LAMS, the particle diameter is derived from the velocity that the particle is accelerated to when entering the vacuum chamber. This particle size is referred to as *vacuum aerodynamic diameter* d_{va} (see. Sect. 2.1.3). In contrast, the particle sizes measured with optical counters such as Laser Aerosol Spectrometer are *light-scattering diameters* that depend on the geometric diameter of the particle, wavelength of the source of illumination, index of refraction, and the angle of the scattered light. Their calculation is possible using Mie theory but the solution of light scattering functions is very complex (Mercer et al., 1978). All instruments are calibrated with monodisperse polystyrene aerosol particles of known size and refractive index. Hence, the measured size of ambient aerosols should be interpreted in terms of *equivalent size* under the assumption of a predetermined refractive index, density, and shape that is equal to those properties of the calibration particles. In the framework of this thesis, the vacuum aerodynamic diameter was not converted

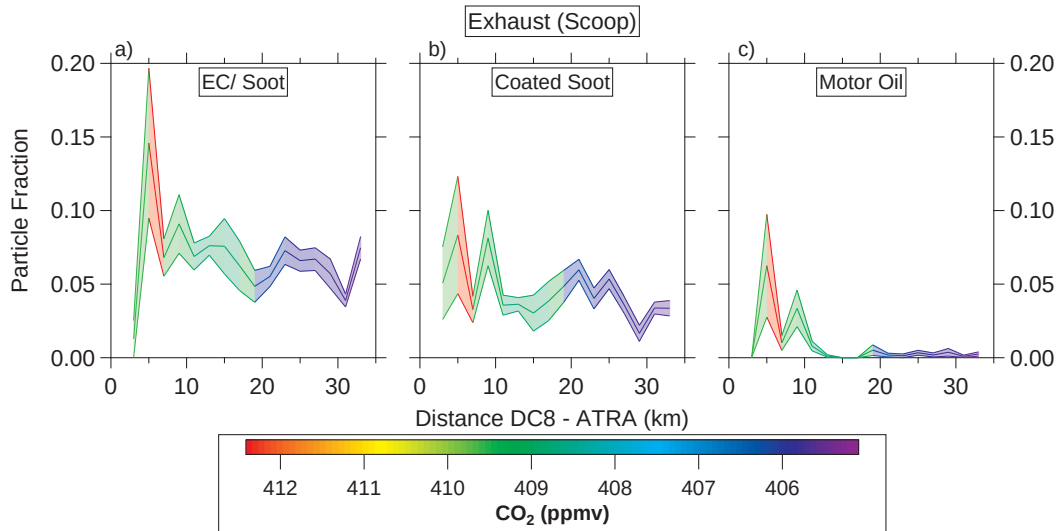


Figure 4.5: Distribution of the relative abundance of exhaust-related a) *EC/ soot*, b) *coated soot*, and c) *motor oil* particles detected by ERICA-LAMS per distance between the exhaust plume generating DLR-ATRA and the *Flying Laboratory* NASA DC-8 during ND-MAX, color-coded with measured volume mixing ratio of CO₂. The shaded area illustrates the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

into a light-scattering diameter but it can be assumed that the difference of both diameters is marginal for the comparison of the detectable size range.

Despite the inability of ERICA-LAMS to detect small-sized exhaust-related particles, three particle types were observed to exhibit an enhanced fraction in a short distance between the NASA DC-8 and the forward flying DLR-ATRA. For a division of the distance between both airplanes into bins of a width of 2 km, the particle types *EC*, *coated soot*, and *motor oil* revealed a decrease in their particle fraction in Fig. 4.5 for an increasing distance. A detailed analysis of EC and coated soot is provided in Sect. 4.1.5. All maximums were detected at a distance of approximately 5 km behind the DLR-ATRA, which was in agreement with the location of the maximum volume mixing ratio of CO₂ of 412.4 ppmv at 5 km. For distances larger than 5 km, the relative abundance of the exhaust-related particle types and the level of CO₂ decreased as more ambient air was mixed into the aircraft exhaust plume. The particle types mentioned above were assumed to be emitted by the aircraft turbines as small particles. As shown in Fig. 4.6, EC, coated soot, and motor oil had an enhanced relative abundance in the size bins below 200 nm, implying that these particles just had grown to sizes that can be detected by ERICA-LAMS. The average time span between the emission of aerosols and their detection was approximately 160 s.

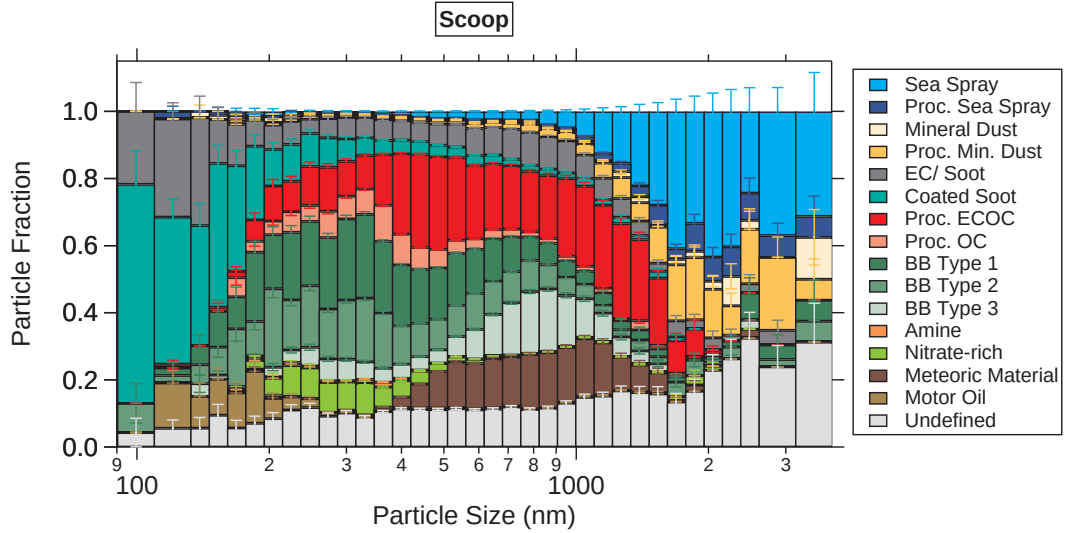


Figure 4.6: Size distribution of the particle types detected with ERICA-LAMS at the scoop aerosol sampling system. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

Besides the particle types of EC, coated soot, and motor oil, three more types seemed to be associated with aircraft exhaust. *Processed organic carbon* (OC), *processed elemental and organic carbon* (ECOC), and *biomass burning* (BB) *type 1* particles were observed to have a larger particle fraction up to a distance of 20 km and a lower fraction for distances above. However, the characteristics of these particle types were different of those mentioned above and not well understood. Processed OC revealed an enhanced fraction of $\sim 10\%$ up to a distance of 15 km before dropping to a low level of $\sim 3\%$. The maximum PF was detected at a distance of ~ 15 km, which differed by 10 km from the maximum of the types presented above (Fig. 4.7). This shift could not be explained by a growth of particles. A comparison of the particle size of that type revealed for a distance range below 10 km and above 15 km a similar size distribution (Fig. C.2 in the appendix). Furthermore, the particle type was majorly detected in a size range of 200 to 800 nm (Fig. 4.6) that was covered by the detection range of ERICA-LAMS. As this type could not be directly attributed to the aircraft exhaust, it was referred to as potential exhaust type. Regarding processed ECOC and BB type 1, both particle types revealed features which disagreed with the idea of an aircraft exhaust origin. For example, the PF of processed ECOC particles raised with increasing distance between the DLR-ATRA and NASA DC-8 when only considering the datapoints detected within the troposphere (Fig. C.3 a) in the appendix). This implies a particle type of ambient air that entrained during the mixing process of the exhaust plume with ambient air masses. In contrast, datapoints detected within the TL and the

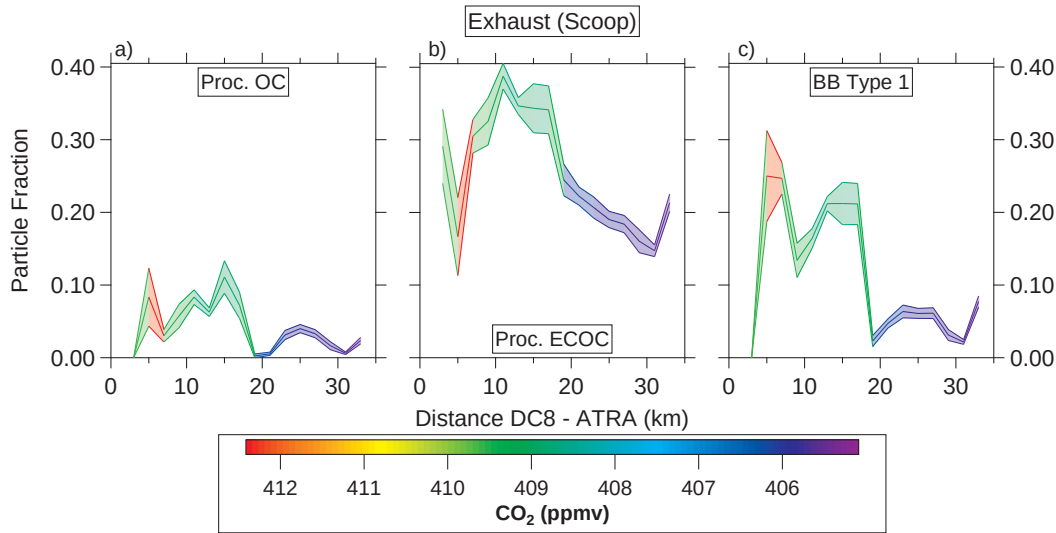


Figure 4.7: Distribution of the relative abundance of potential exhaust particles a) *proc. OC*, b) *proc. ECOC*, and c) *BB type 1* detected by ERICA-LAMS per distance between the exhaust plume generating DLR-ATRA and the *Flying Laboratory* DC-8 during ND-MAX, color-coded with measured volume mixing ratio of CO₂. The shaded area illustrates the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

stratosphere showed a clear drop of *PF* with increasing distance (Fig. C.3 b) in the appendix), giving reason for the assumption of an potential exhaust particle type that had been emitted previously by aircraft turbines. BB type 1 revealed a decreasing *PF* independent of the atmospheric regime and indicated a relation to the aircraft exhaust. However, the mean mass spectrum (Fig. A.11 in the appendix) was typical for a type originating from BB. As this type was assumed to be part of the ambient aerosol background concentration, the enrichment of its fraction for small distances behind the DLR-ATRA remained unclear.

The distance plots reveal a clear enhancement of the *PF* of EC, coated soot, and motor oil particles for a range up to 10 km. Therefore, the exhaust periods were filtered for data points recorded within this aircraft distance in order to obtain information about the abundance of these particle types with respect to individual fuel types. The DLR-ATRA was fueled with four gasoline mixtures of variable aromatic, hydrogen, and naphthalene content (see Sect. 3.2), which are expected to result in alternating soot emissions. Yet, for only three fuel blends appropriate counting statistics were achieved. As the number of datapoints assigned to SAF3 was very limited, they were not taken into account for the analysis.

Indeed, the particle fractions of EC and coated soot differed for several fuel types as depicted in Fig. 4.8 (a). The *PF* of EC was the largest during the use of JetA-

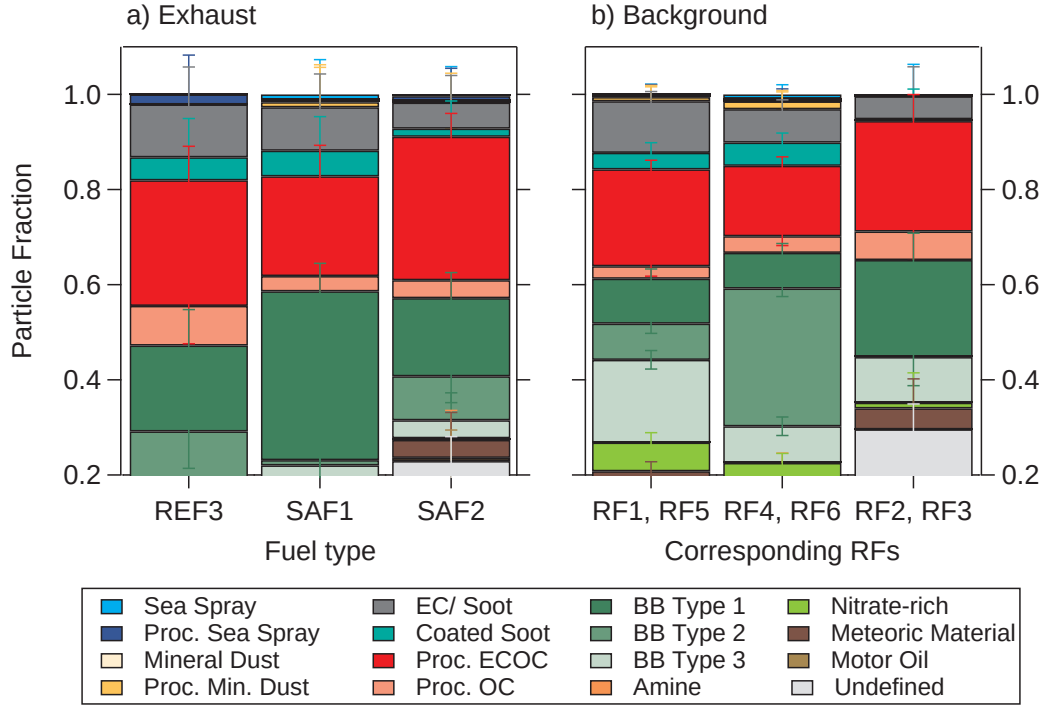


Figure 4.8: Particle types and fraction during exhaust (a) and background (b) periods for several fuel types. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

1 standard kerosene (Ref3, 11.1%), and was reduced for SAF1 (9.1%) and SAF2 (5.5%). The amount of coated soot varied around 5% for Ref3 and SAF1 and was lower for SAF2. Analogously, motor oil particles were less abundant during the use of SAF1 (2.2%) and SAF2 (0.7%) than during flights conducted with Ref3 (2.8%). However, the particle fractions of the corresponding background periods (Fig. 4.8 (b)) displayed similar characteristics for EC, coated soot, and motor oil particles. Besides EC and coated soot, motor oil particles were detected in periods which were actually not directly affected by aircraft exhaust. This is probably a result of the frequently travelled aircraft corridor. Moreover, the reduction in PF could not be attributed to the input of alternative jet fuels and might be affected as well by the background aerosol population. In consequence, the effect of sustainable fuel types on the occurrence of individual particle types detected during ND-MAX was not observable within this dataset.

In conclusion, the size distributions of particles demonstrated the inability of a physical distinction between *Exhaust* and *Background* periods with ERICA-LAMS in relation to particle sizes. Since the detectable size range of the installed detection units was above the size range of small exhaust particles, ERICA-LAMS only covered the range of particles present in both periods.

Consequently, the relative abundance of the certain particle types in both periods was very similar as small exhaust-related particles were not taken into account. In order to detect the small exhaust particles, another instrument needs to be implemented in future aerosol measurements. However, ERICA-LAMS can differentiate very clearly between aircraft exhaust and background on a chemical basis. The size and distance analysis for the relative abundance of the detected particle types in ND-MAX revealed the presence and partial detection of exhaust-related aerosol particles within the detectable particle size range of 174 nm to 3.2 μm . Nevertheless, the majority of these particles was too small for the detection units in ERICA-LAMS and led to a predominance of background particles even during measurements inside exhaust plumes. Three more particle types seemed to be potential aircraft exhaust types but they also exhibited properties that could not be assigned to an exhaust origin. Consequently, the dataset did not provide any information on the impact of sustainable alternative fuels on the chemical composition of aerosol particles in aircraft exhaust plumes. However, the measurements implied that motor oil particles were also present in the absence of fresh aircraft emission plumes.

4.1.3 *Atmospheric vertical profile*

In this section, the vertical profile of the atmosphere is analyzed considering the prevailing weather regimes during ND-MAX, namely the *cold*, *transition*, and *warm period*. The profile was provided by the determination of the relative abundance of individual particle types for certain altitude bins of a width of 500 m. In general, the weather regime had a strong impact on the vertical structure of the atmosphere for the lowermost 12 km and the presence of certain particle types at various altitude levels. This was shown by three distinct particle types.

First, the level of the tropopause layer was affected by the meteorological conditions in the troposphere. As revealed by Fig. 4.9, the fraction of meteoric material detected during the cold period already increased above an altitude level of 7.5 km, whereas for the transition, and warm period, this fraction was only enhanced over 10.5 and 11.5 km, respectively. As this particle type is of extraterrestrial origin (Pruppacher and Klett, 2010; Schneider et al., 2021), its fraction could be used as a tracer for air masses of stratospheric origin. In this case, the particle fraction marked the position of the TL/ ExTL where tropospheric conditions smoothly turned into stratospheric conditions. Fig. 4.10 exhibits the vertical profiles of all RFs considering the particle fraction of meteoric material, and the volume mixing ratio of ozone, which is another marker for stratospheric impact (e.g., Seinfeld and Pandis, 2016 and therein).

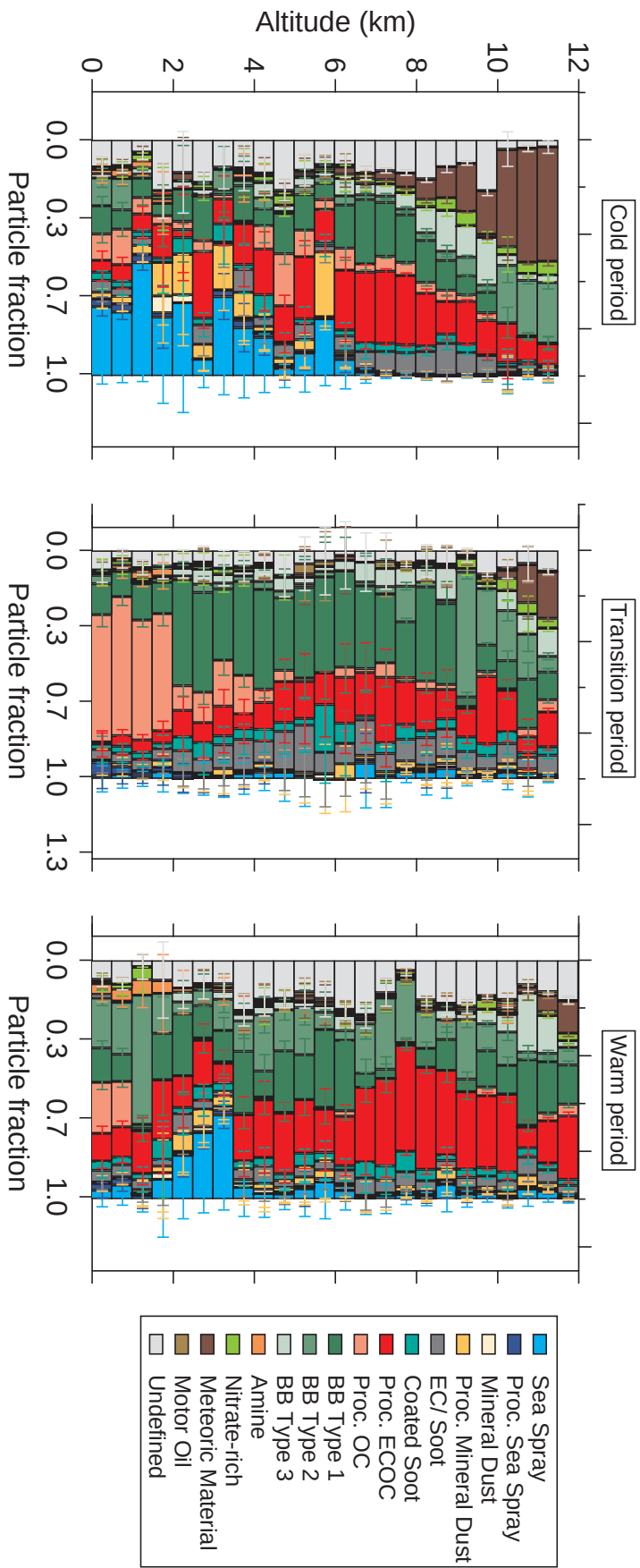


Figure 4.9: Vertical profile of relative particle abundance measured at the scoop inlet for three air mass periods: a) cold, b) transition, and c) warm period. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

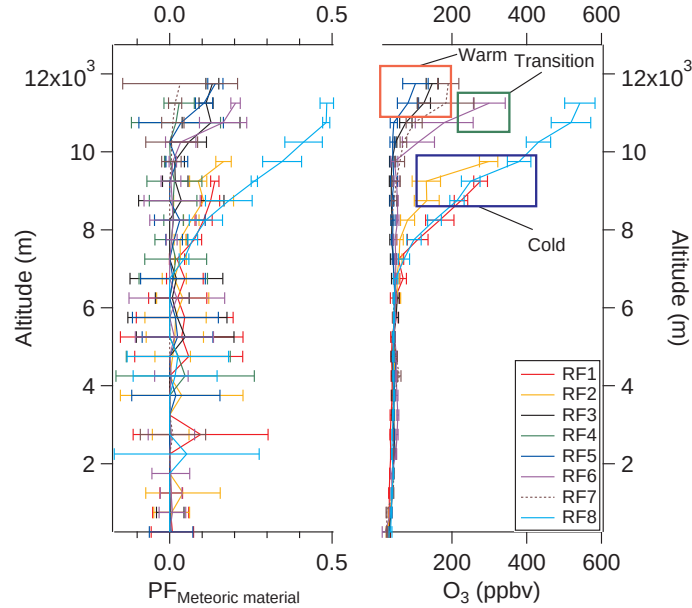


Figure 4.10: Vertical profiles of the fraction of particles containing meteoric material at the scoop inlet, and the volume mixing ratio of ozone measured during ND-MAX. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

Obviously, the particle fraction increased coinciding with the volume mixing ratio of ozone. In detail, three branches for the ozone distribution and also for the particle fraction of meteoric material were observed that could be attributed to the cold, transition, and warm period. Thus, in the cold period, the determined TL (see Sect. A.1) was located at approximately 7.5 km. The low position of the TL was the result of subsiding air masses as described in Sect. 3.3.1. In contrast, the warm period exhibited a higher located TL around 11.5 km, which was due to different air mass densities, and convective processes lifting that layer. The transition period, however, displayed a mixture of characteristics of both the cold and warm period.

Second, the weather pattern impacted the abundance of individual particle types by the advection of air masses of various origins. Fig. 4.9 depicts a large presence of sea spray particles below a level of 6 km for the cold and warm period. Both periods were characterized by the advection of marine air masses (see. Sect. 3.3). During the cold period, air masses were transported from the North Sea and Norwegian Sea towards Germany, whereas in the warm period Germany was affected by zonal winds from the Atlantic. Contrary, the transition region was characterized by a local anticyclonic system and a weak circulation that resulted in small particle fractions of sea spray. Nevertheless, large fractions of sea spray particles were detected besides particles of processed mineral dust,

which are in favor of previous aging processes inside clouds. Thus, a part of the sea spray might have undergone cloud processing before it was detected by ERICA-LAMS.

Third, in contrast to the effect by advection, the weather conditions can also promote weak circulation that result in the local enhancement of the number concentration of individual particle types within a separated BL. A large fraction of processed OC was detected in the lowermost 2 km in the transition period (Fig. 4.9). This particle type appeared less frequently in the BL during the cold and warm periods but was observed throughout the entire vertical profile in the cold period. Moreover, it was detected in the UTLS region during the warm period. The enhancement in the transition region was due to an anticyclonic weather pattern that provided suitable conditions for the separation of the boundary layer. As a consequence of weak pressure gradients and doldrums, a layer of fog and stratiform clouds arises when temperatures decrease below the level of water vapor saturation due to radiative cooling. The layer then acts as a transport barrier and leads to an enrichment of individual particle types of local origin below. Fig. 4.11 displays a vertical profile of the ambient temperature, water vapor mixing ratio, potential temperature, and lapse rate for the transition period. The ambient temperature and the mixing ratio indicated the separation of the lowermost 2 km. The temperature profile revealed an inversion at 2 km and the water vapor mixing ratio exhibited a strong decrease on the same level, implying the separation of air masses attributed to the BL from those of the FT above. This is also shown by the lapse rate, which is a measure of the atmospheric stratification.

An air parcel released at the ground will start to ascend adiabatically and will cool down at a rate of $\sim 0.01 \text{ K m}^{-1}$. As long as the lapse rate of the atmosphere does not exceed this rate, the air parcel will undergo a stronger cooling than the atmosphere. Thus, it will be colder than the ambient air and subsequently descent again to its original level. In consequence, these conditions imply a stable stratification. A positive lapse rate (i.e. an increasing temperature with altitude) as observed at RF6 at a level of $\sim 2 \text{ km}$ (Fig. 4.11) directly implies a temperature inversion and, thus, a suppression of vertical motions. The potential temperature is another measure of stratification and is the temperature a parcel would expect if adiabatically brought to a reference pressure of 1000 hPa. Accordingly, a vertical profile of θ also helps to estimate the atmospheric stratification. If θ increases with altitude as for RF6, the atmosphere is stable. A negative gradient of θ would indicate an unstable stratification.

As the wind circulation is enhanced, e.g., by an upcoming low pressure system, the stratus layer dissipates and a vertical mixing of the BL and the FT reduces

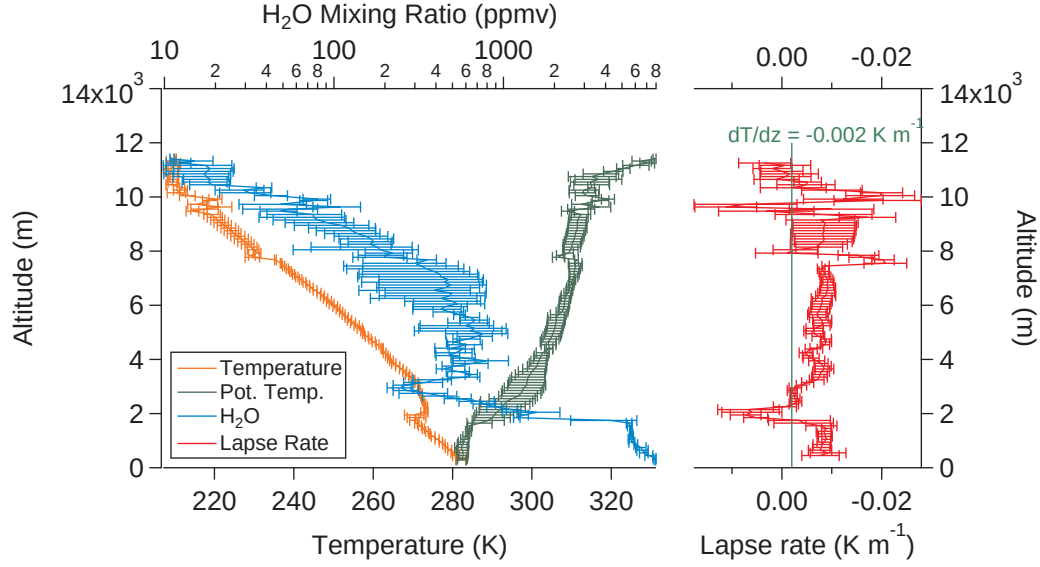


Figure 4.11: Vertical profiles of temperature, θ , water vapor volume mixing ratio, and temperature lapse rate for the transition period (RF6). Plotted are the mean and standard deviation (error bars) per bins of 100 m width.

the gradients, leading to a vertical distribution of the particle types as observed for the cold and warm periods in Fig. 4.9.

The central question of this thesis aims to analyze the particle types that contribute to the formation of cirrus and contrails. So far, this subsection only focused on the vertical profile of interstitial aerosol particles that may be interpreted as potential cloud nuclei. Nevertheless, the contribution of individual particle types can be determined only by viewing in context of the detected cloud residuals.

The vertical profiles of cloud residuals in Fig. 4.12 for the cold and transition period did not cover the entire space between the ground and a level of 12 km. The remaining cloud residuals implied that sea spray played a major role in the UT as it contributed to clouds detected in the midlatitude UTLS region. In detail, sea spray had a relevant fraction of cloud residuals up to 8 km during the cold period, and up to 12 km during the warm period. This implied the presence of sea spray residuals even in regions that exhibited signatures of stratospheric impact. Regarding the transition period, no clear trend was observable as only a small part of the vertical profile was detected in that regime. This was due to a lack of measurements with the CVI-inlet that was only applied in the presence of cloud droplets and ice crystals.

The large discrepancy between the fractions of interstitial sea spray particles and sea spray cloud residuals might have been the consequence of two effects. Firstly, sea spray particles might rather support the formation of hydrometeors

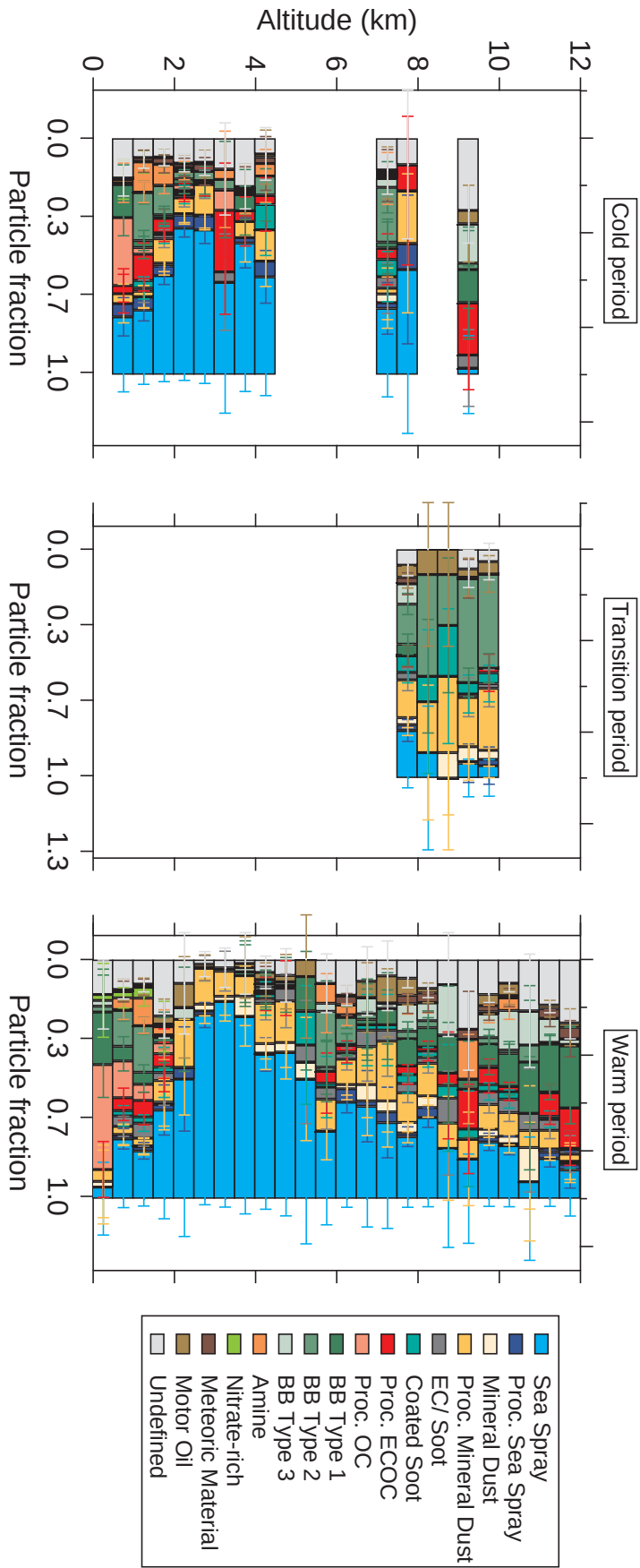


Figure 4.12: Vertical profile of particle fractions of cloud residuals sampled by the CVI inlet for three air mass periods: a) cold, b) transition, and c) warm period. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

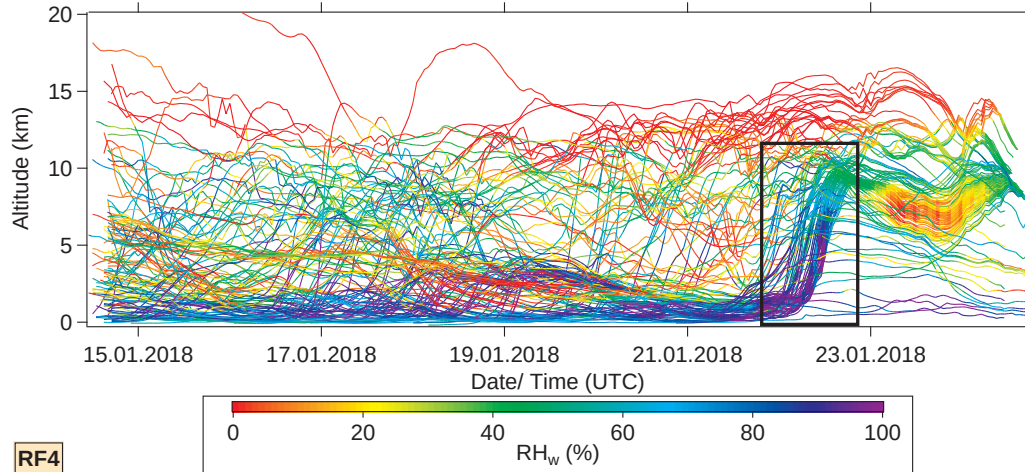


Figure 4.13: Vertical cross section of backward trajectories simulated with HYSPLIT for RF4, color-coded with relative humidity (RH_w). A large number of trajectories is ascending on 22nd January, indicating an uplift of well-humidified ($RH_w > \sim 60\%$) air masses by a warm conveyor belt connected to a low pressure system. The black box marks the ascent period.

than organic particles such as BB type 1 or processed ECOC and, thus, might be more frequently detected by the CVI. Besides their function as CCNs, sea spray aerosols also contribute to the formation of ice crystals (e.g. DeMott et al., 2016; Quinn et al., 2017). In consequence, the fraction of cloud residuals consisting of sea spray might exceed the fraction of organic material. Secondly, the sea spray particles were involved in the cloud formation at low altitude levels where they appeared more frequently. These were transported to higher levels by warm cloud convection, where they were measured inside clouds and contrails then. The vertical cross section of backward trajectories (Fig. 4.13) indicated the uplifting of air masses due to warm conveyor belts connected to low-pressure systems. Similar events were also observed for RF5 (Fig. C.8 in the appendix) and RF7 (Fig. C.10 in the appendix).

Summarizing, the weather patterns had a significant impact on the vertical profile of the atmosphere and, thus, the abundance of individual particle types in several ways. Sea spray particles have been enriched by the advection of marine air masses, and organic particles of local origin were accumulated during periods of weak circulation. The UTLS region was affected by the sequence of high-level troughs and ridges that supported the ascent and descent of air masses from the jet stream and resulted in a variable level of the tropopause layer. Warm conveyor belts played a major role as they contributed to cloud convection, and thus, transported cloud particles such as sea spray or processed mineral dust of ground sources high up into the UTLS region.

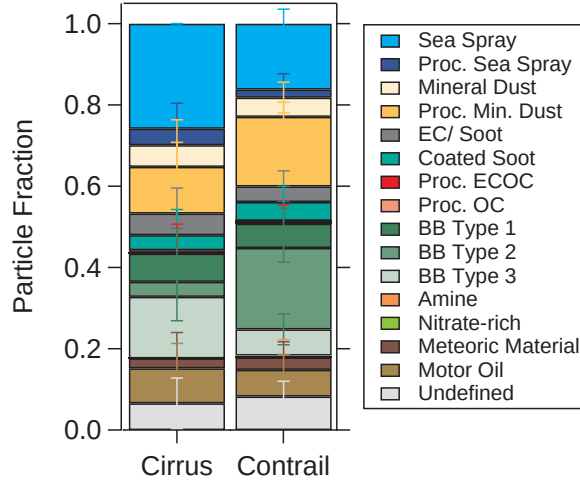


Figure 4.14: Overview of the relative abundance of detected cloud residual types for cirrus and contrail periods during the ND-MAX campaign. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

4.1.4 *Cirrus versus Contrail*

This section focuses on the particle types that contributed to the *cirrus* and *contrail* formation. For that, the cloud residuals detected by the CVI-inlet were divided into two phases. The *cirrus* period was characterized by an enhanced number of aerosol (see Sect. 2.6) and ice particles. Besides, a temperature criterion ($T < -38^{\circ}\text{C}$) was introduced to ensure the analysis of ice-clouds. The *contrail* period was defined by the same boundary conditions as the *cirrus* period with the exception of carbon dioxide. Here, the volume mixing ratio of CO_2 had to be increased in order to distinguish the anthropogenic induced *contrail* from the naturally formed *cirrus*. Only cirrus and contrail measurements were taken into account that referred to the same RFs in order to make both periods comparable.

Cirrus

For cirrus clouds, sea spray was found to be the most abundant inorganic residual type as Fig. 4.14 displays. With a fraction of 25.8% in its relatively pure form and a fraction of 4.1% in a processed state, the contribution of sea spray (29.9%) even exceeded that of the BB residuals (25.8%). As sea spray is well-known to be an ideal CCN (O'Dowd et al., 1997; Pierce and Adams, 2006), the cirrus clouds were assumed to be of liquid origin. Accordingly, pure

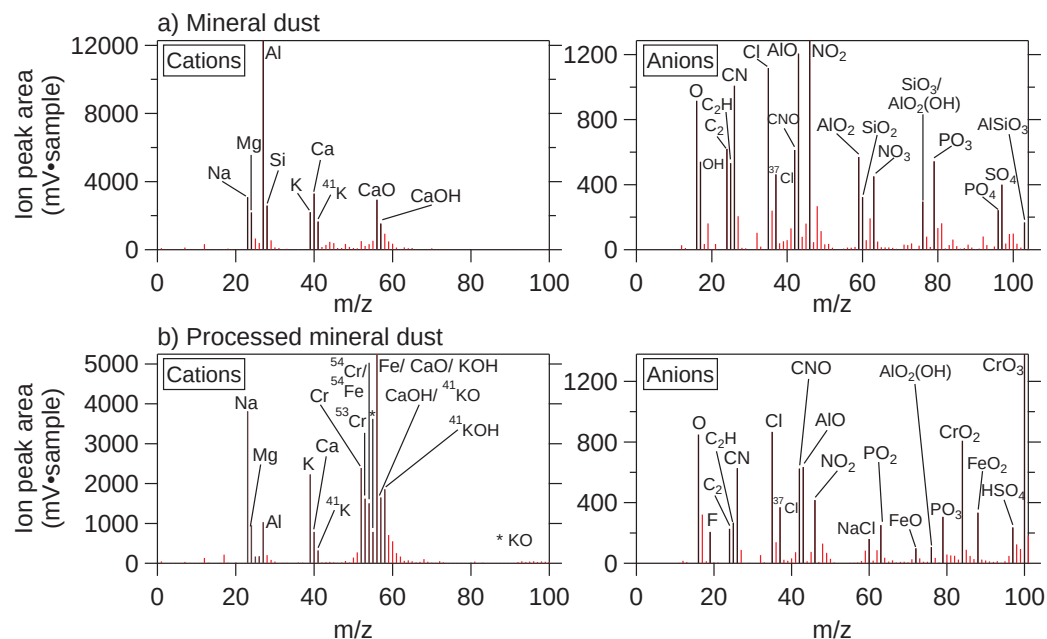


Figure 4.15: Mean mass spectrum of cations and anions for a) mineral dust and b) processed mineral dust detected during the ND-MAX campaign.

mineral dust residuals showed a lower relative abundance in the cirrus CPRs than internally mixed residuals of mineral dust, and thus indicated the cloud formation via liquid phase. First of all, mineral dust had a low relative abundance of 5.3%. Thus, it played a minor role in the formation of cirrus residuals that were detected. This agreed with the insolubility and hydrophobicity in its pure form (Richardson et al., 2007). In contrast, mineral dust is known for its high activity as INP (Richardson et al., 2007; Hoose et al., 2008; Barahona et al., 2010). Consequently, its fraction should have been larger in case of ice phase processes. Second, the processed mineral dust revealed a fraction of 11.5%, which was larger than that of pure mineral dust. Furthermore, its mean mass spectrum contained chemical signatures of sea spray, sulphate, and chrome in addition to dust markers such as sodium, magnesium, aluminum, and silicon as displayed in Fig. 4.15. The presence of soluble material such as NaCl or H₂SO₄ enhances the fraction of mineral dust that acts as a CCN by creating a soluble and hygroscopic particle coating (Levin et al., 2005; Kelly et al., 2007; Karydis et al., 2011). According to Archuleta et al. (2005), the processing also reduces the potential for ice formation. As a result, the low relative abundance of mineral dust in its pure form and the larger fraction of mixed mineral dust implied the cirrus formation based on CCNs. Even though chrome signals were dominant in the mean mass spectra of processed mineral dust, their effect on the nucleability seemed to be limited. However, the chrome components were assumed to be of aircraft origin. Over the last decades, aircraft turbines were

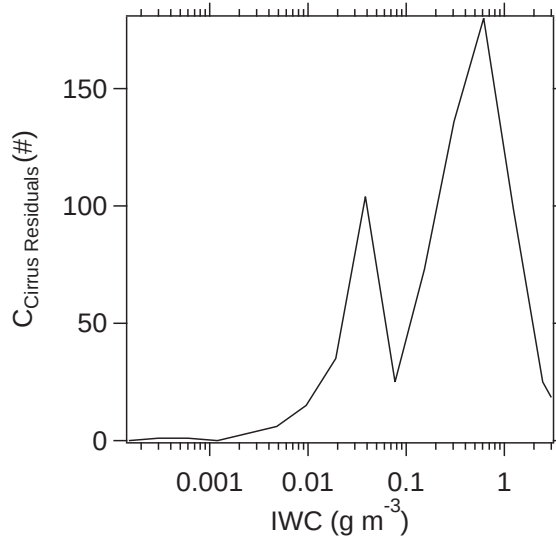


Figure 4.16: Overview of the relationship between cirrus residuals (absolute counts) and the associated ice water content (IWC) during the ND-MAX campaign. Data provided by Anderson et al., 2018, NASA.

protected against corrosion by chromate conversion coating and the usage of primers that contain chromate pigments (Peltier and Thierry, 2022).

According to Krämer et al. (2020), the origin of cirrus clouds can be traced back by the analysis of their ice water content (IWC). Cirrus clouds which exhibit a large IWC in excess of 0.0001 g m^{-3} form at lower altitude levels in the presence of a large amount of water vapor with subsequent lifting to higher altitudes. In contrast, in-situ origin cirrus form at high altitude levels in an environment providing less amount of water vapor. Consequently, these cirrus clouds only reach a maximum of 0.001 g m^{-3} in IWC . In order to analyze the formation process of the detected cirrus clouds, the cirrus residuals were assigned to the IWC detected with the Cloud Imaging Probe (see Sect. 2.4.7). Fig. 4.16 displays the distribution of cirrus residuals as a function of IWC , which was divided into logarithmic bins. Two modes were observed within a range of 0.001 g m^{-3} and 3 g m^{-3} that could be attributed to liquid origin and agreed with the conclusions of the chemical composition. Thus, the cirrus clouds detected during ND-MAX were formed at lower altitude levels under conditions that triggered a condensation process. Especially during the warm period (see Sect. 3.3.3), favorable conditions such as warm advection and convection were observed that support the formation of cirrus. The transport of water vapor to the UT was demonstrated within the simulated backward trajectories of air masses (Fig. 4.13) that resulted in an enhanced relative humidity in an altitude range of approximately 5 to 10 km. Therefore, the cirrus clouds tended to form in a warmed and well-humidified ($RH_w > \sim 60\%$) environment via the liquid

phase before lifted up towards high altitudes where they could freeze as ambient temperatures below -38°C were reached.

Regarding the organics, the BB residuals played an important role in cirrus clouds ($PF = 25.8\%$ in Fig. 4.14). Among them, the BB type 3 residuals made the largest contribution of up to 15.2% . A large number of BB particles acted as CCNs due to their internal mixture of soluble material. Moreover, their nucleability is enhanced as they increase in size and adsorb more soluble chemical species (Andreae and Rosenfeld, 2008 and references therein). In contrast, processed ECOC residuals were rarely detected (0.8%) and further types such as processed OC, nitrate-rich residuals, and amines were not detected during cirrus events. Still, chemical signatures of nitrate were also present in the other particle types mentioned above. Soot and coated soot revealed a fraction of 5.3% and 3.7% , respectively.

Another organic key contributor of cirrus cloud residuals was motor oil with a fraction of 8.6% . This was a large fraction for a series of periods that was actually characterized by undisturbed atmospheric conditions. The background conditions in terms of volume mixing ratio of carbon dioxide and particle number concentration were indicative for the absence of aircraft exhaust as mentioned in Sect. 4.1.2. Hence, the algorithm of differentiation between cirrus and contrail cirrus might need to be improved. Although CO_2 is a long-lived tracer appropriate for distinguishing between exhaust and background periods, further tracers such as soot particle numbers could help to verify the occurrence of contrails (Bräuer et al., 2021b; Voigt et al., 2021). Nevertheless, the presence of motor oil residuals inside cirrus clouds was not necessarily an outcome of an erroneous attribution. As the flight pattern in Fig. 3.1 shows, the flight track consisted of horizontal loops, implying that the same airspace area was passed many times during a flight. Accordingly, the detected motor oil residuals might partly result from a previous cycle. Fig. 4.17 reveals that motor oil residuals were not only detected in the size range up to 300 nm that corresponded to freshly formed motor oil residuals, but also in a range from 450 to 1000 nm that might occur due to previous chase loops. However, the recorded data did not show a trend towards larger residual sizes for an enhanced number of loops. This is a topic for future research campaigns. Yet, the number of cloud residuals is low and low statistics are challenging.

Besides, Clemen et al. (2024) also described the detection of motor oil residuals primarily in cirrus. It is assumed that the majority of motor oil residuals is too small in size when being detected within a contrail by laser ablation mass spectrometry. However, these residuals might grow with time by the adsorption of material of ambient aerosols and remain in the atmosphere. In consequence, the particles may undergo the transformation of a contrail into a cirrus, and

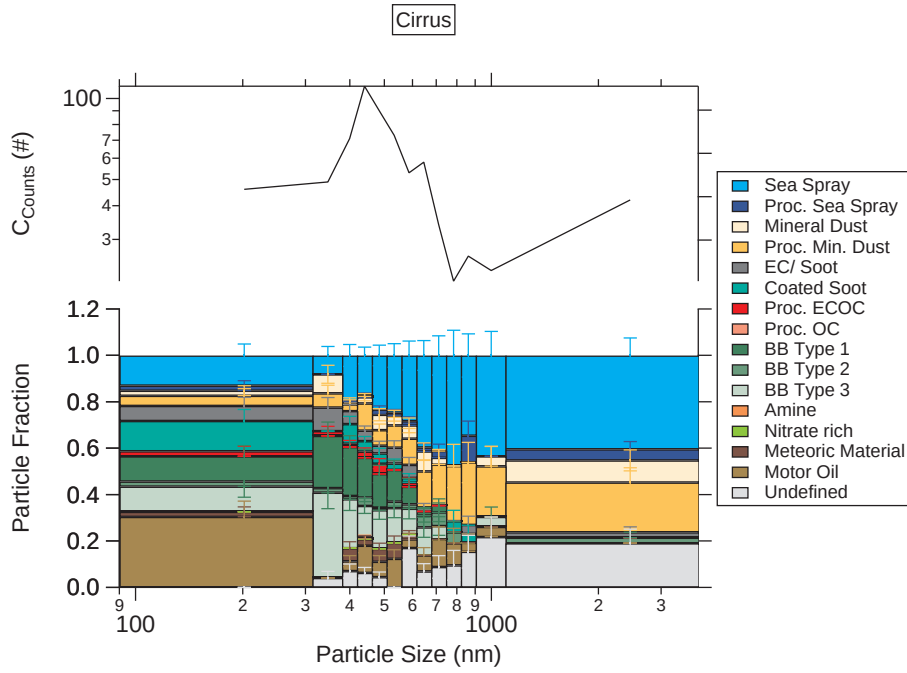


Figure 4.17: Size distribution of the cloud residual types detected with ERICA-LAMS during cirrus events. Data filtered for comparable periods of cirrus and contrail. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

thus, are later on detected as part of cirrus clouds. These assumptions are drawn with some speculation and need more instrumental research to gain insight in the life cycle of contrails, their conversion into contrail cirrus, and the aerosol particle types involved in these processes.

Contrails

Contrails can grow on the same particle types as cirrus clouds. This is shown on the right-hand side of Fig. 4.14. Despite the variable contribution of the individual particle types, the species involved in contrail formation were largely the same as those involved in cirrus formation. BB particles had a major impact on contrails (32.4%), but this time BB type 2 was the dominant residual type (20.0%). Motor oil residuals were also found in contrail periods (6.6%), whereas amines, and processed ECOC were rarely detected (0.5 % and 0.8 %). Equally to their contribution to cirrus clouds, processed OC, and nitrate-rich particles were not detected during contrail periods. Processed mineral dust dominated the fraction of inorganic types in contrails. With a fraction of 17.1 %, it was larger than the contribution of sea spray of 16.2 %. Taking into account the processed mineral dust and processed sea spray, the fractions rose to 21.9 % and

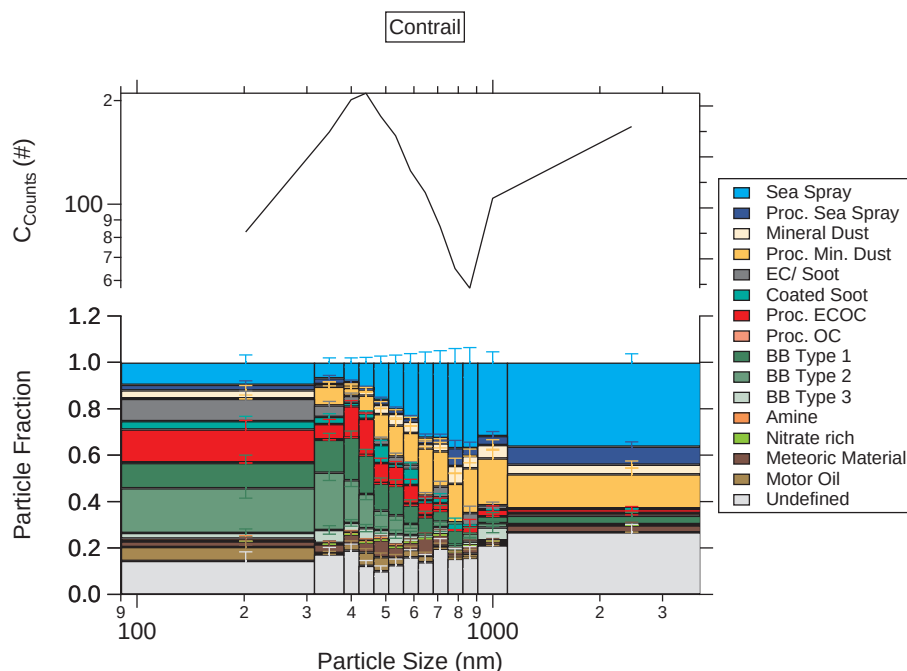


Figure 4.18: Size distribution of the cloud residual types detected with ERICA-LAMS during contrail events. Data filtered for comparable periods of cirrus and contrail. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

18.2 %, respectively. The contribution of sea spray was larger for cirrus clouds than for contrails, implying that the cirrus clouds formed at lower altitudes, where the occurrence of sea spray was enhanced. These cirrus were subsequently lifted up to the UTLS region, whereas contrails were formed at cruise altitudes which were typically located in the UTLS region.

The organic material largely contributed to the small-sized ice particle residuals of cirrus and contrails while the inorganic types of sea spray and mineral dust as well as their processed versions dominated the large-sized residuals (Fig. 4.17 and Fig. 4.18). While the organic particle types of BB, motor oil, soot, and coated soot were predominant in a size range up to ~ 400 nm, the primary inorganic aerosol particles were frequently present for particle diameters above 800 nm. Thus, regarding the size distribution both ice cloud types revealed similar characteristics, implying that the individual residual types detected here contribute to and are processed within cirrus and contrails in the same way.

In general, the chemical composition of contrails and cirrus was very similar, implying that the relevance of fuel type characteristics for the contrail chemical properties is small. In contrast, the contribution of the individual particle types to contrail formation rather seemed to be driven by the aerosol background concentration in the UTLS than by aircraft exhaust particles of fuel combustion

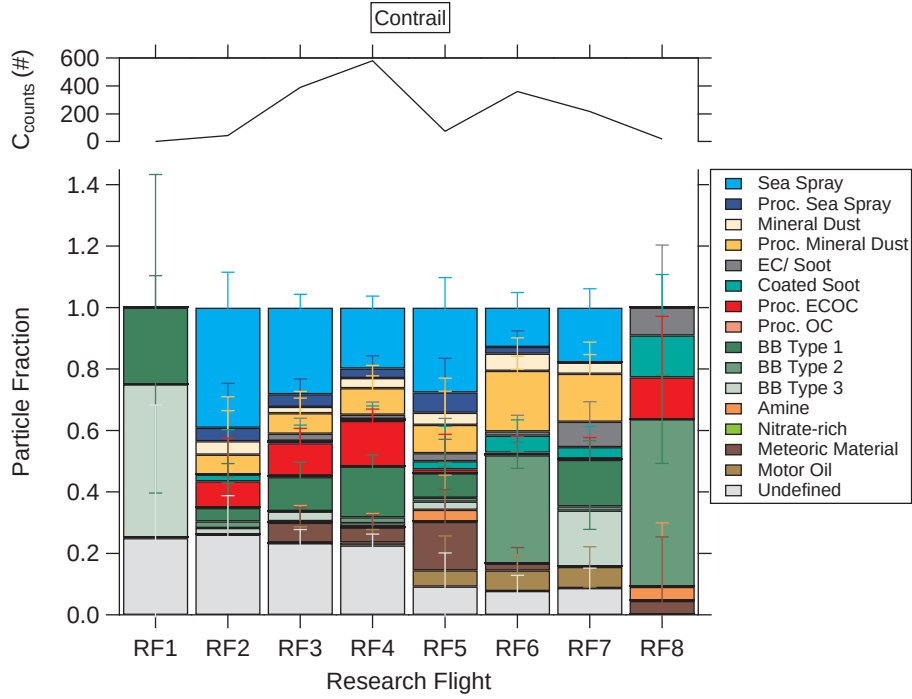


Figure 4.19: Overview of the relative abundance of detected contrail residual types for the individual RFs of the ND-MAX campaign. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

(Fig. 4.19). The chemical composition of contrails demonstrated a large variation of PF of the individual particle types for every single RF, although some of these flights referred to the same fuel types. For example, the blend of SAF1 was conducted on RF4 and RF6 but the chemical composition of ice residuals detected on these flights was largely different. On the other hand, RF3 and RF4 illustrated a similar chemical signature despite the application of two different blends of biofuel (SAF2 and SAF1). Hence, the impact of variable fuel types on the chemical composition of contrail ice residuals was not observed with the adopted technologies. Ergo, the chemical signature must have been mostly determined by the ambient aerosol. A comparison with reference data was impossible because the low number of cirrus data points did not allow for an analysis for each research flight.

The coexisting soot and ice particle measurements of Bräuer et al. (2021b) and Voigt et al. (2021), however, revealed a significant reduction of soot and ice particle numbers for the different SAFs compared to Ref3. In consequence, the physical properties of contrails, and thus, their climate impact was affected by the chemical composition of fuel blends. The discrepancy towards the findings presented in this thesis resulted from the variable particle size ranges that were

taken into account. While the number of ice crystals in Bräuer et al. (2021b) was derived from recordings of the soot particle number, the number of ice cloud residuals presented here was detected with ERICA-LAMS. Moreover, in Bräuer et al. (2021b), the reduction of the ice crystal number was based on the apparent ice emission index, which accounts for contrail aging and dilution processes. These processes and corrections were not considered for the measurements with ERICA-LAMS. Future contrail measurements are necessary to overcome the gap between both approaches.

The large error bars in Fig. 4.14 implied the large uncertainty of cirrus and contrail measurements due to low binomial counting statistics. Further uncertainties like the uncertainty of the ablation process or the uncertainty in the clustering algorithm are hard to quantify and not included here. The counting statistics are the result of several factors. The fraction of cloudy areas that were passed during the flights limits the number of detected residuals as well as the In total, 244 particles were attributed to cirrus periods and 654 particles to contrail periods. This was a consequence of several factors. First, the number of contrail events was limited to the phases during which the NASA DC-8 caught the DLR-ATRA contrail. Second, the campaign did not focus on cirrus events, i.e. they were measured by accident. Third, the events had to be corrected for switching processes regarding the sample inlet line in order to maintain separate aerosol particle and cloud residual data. Fourth, the number of ambient ice crystals in cirrus, and thus residuals, was limited. Mace et al. (2001) and Kärcher and Ström (2003) reported ice crystal concentrations of the order of 0.1 cm^{-3} to 10 cm^{-3} in cirrus clouds. Finally, the cirrus and contrail events which were considered had to be reduced due to reasons of comparability. Only cirrus and contrail events were incorporated that were measured during the same flights, which was true for RF5, RF6, and RF7. A comparison based on the same test points was found to be inappropriate due to a very small number of assigned particles.

Summarizing, sea spray and mineral dust were the dominant inorganic species contributing to the formation of cirrus and contrails in the midlatitude winter UTLS. Sea spray rather contributed in its pure form, whereas mineral dust was rather present in a processed form supporting the formation of cirrus and contrails via the liquid phase. Meteoric material played a minor role in the detected ice cloud residuals. Besides, soot and coated soot made up to 10% in particle fraction. Organic particles had a fraction of more than 30% and were predominated by BB types. In contrast, processed ECOC, OC, amines, and nitrate-rich particles did not seem to play a major role in the formation of cirrus or contrails. Further, contrails can grow on the same particles as cirrus clouds. At least in the size range detected by ERICA-LAMS, both types of

ice-clouds unveiled a similar chemical composition. Organic particle residuals dominated the size range up to 400 nm and primary inorganic material largely contributed to residuals larger than 800 nm in diameter. Further, the formation of contrail ice crystals was rather driven by the abundant background aerosol particles than by aircraft exhaust particles.

4.1.5 Detailed analysis of carbon-containing clusters

The particle types *EC* and *OrgSO* revealed a relation to aircraft exhaust plumes as their particle fractions were enhanced within a distance of 10 km and dropped with increasing distance between the forward flying DLR-ATRA and the chasing NASA DC-8. In consequence, these particle types were assumed to be soot. Additionally, the particle type *OrgNOSO2* seemed to be affected by aircraft exhaust, indicated by an enhanced *PF* for a distance up to 15 km. Within this subsection, the assumption is further investigated.

There were several factors indicating the attribution of these particle types to the aircraft exhaust. First of all, the mean mass spectrum of EC (Fig. 4.20 a)) consisted of a series of carbon cluster ion peaks (C_n^+ and C_n^-) in mass spectra of both polarities. These markers are typical for elemental carbon and have been determined by many single-particle instruments before (e.g., Noble and Prather, 1996; Spencer and Prather, 2006; Toner et al., 2006; Moffet and Prather, 2009; Pratt et al., 2009). Second, cluster ions of EC are attributed to the soot core of particles (Shields et al., 2007). As EC mostly consists of sp^2 hybridized bonds like graphite, it refers to soot (Prather, 2012). Third, its particle fraction was enhanced within a distance of 10 km behind the DLR-ATRA. Carbonaceous material such as soot particles is emitted due to incomplete combustion of fuel hydrocarbon compounds by the aircraft engines (e.g., Voigt et al., 2021 and therein). Fourth, the size distribution of aerosol particles demonstrated a rising *PF* of EC towards diameters below 200 nm (Fig. 4.6), implying the emission of small-sized soot particles by aircraft turbines that just had grown to particle sizes detectable with ERICA-LAMS. Additionally, the mass spectra revealed the presence of hydrocarbon cluster ions (C_nH^+ and C_nH^-). Here, the HC-ions were also attributed to aircraft fuel but, in general, the number of potential sources for HC-chains is quite large. This particle type was detected throughout the vertical scan of the atmospheric profile and also in the absence of exhaust characteristics. Thus, it was also part of the atmospheric background and might be traced back to other sources as well. In consequence, the particles could not be only assigned to aviation soot but may also originate from the BL sources such as fossil fuel combustion or BB, indicated by the large potassium signal on $m/z +39/41$ (Pratt et al., 2009; Voigt et al., 2017).

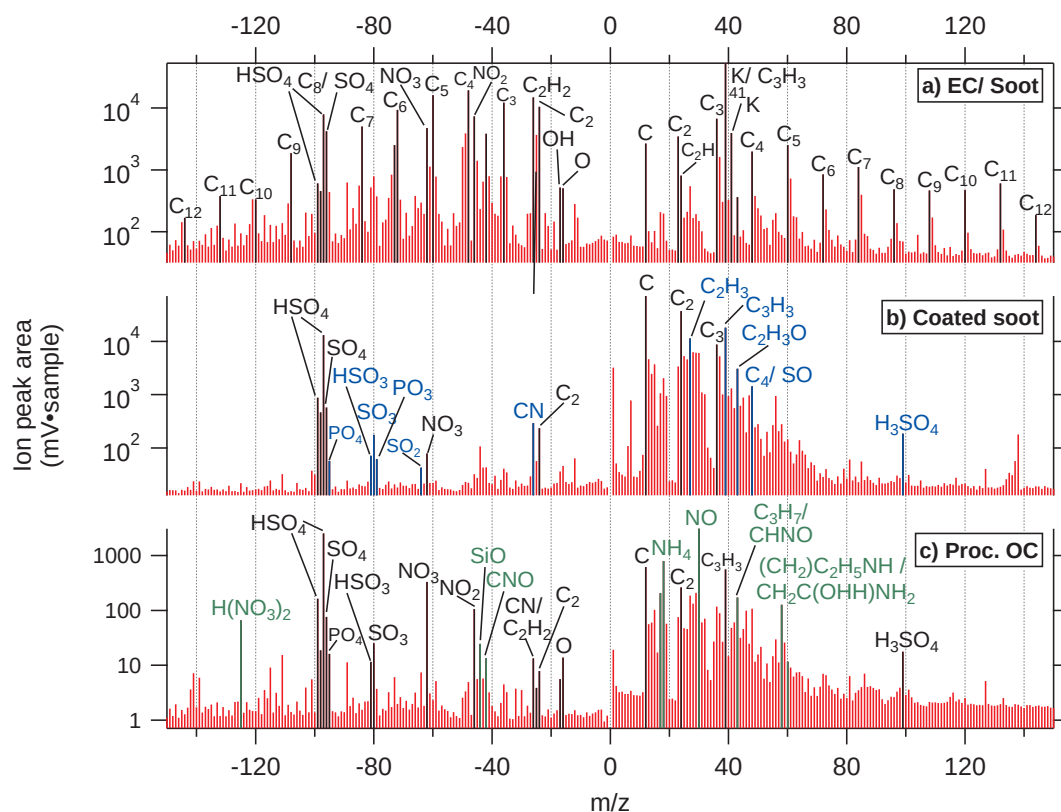


Figure 4.20: Mean bipolar mass spectrum of soot (EC, a), OrgSO (coated soot, b), and OrgNOSO2 (processed OC, c) particles detected during ND-MAX. The blue (green) ion signal peaks highlight the characteristic markers of coated soot (processed OC).

The mean mass spectrum of *OrgSO* (Fig. 4.20 b)) highlighted a signature of carbon cluster ions (m/z +12, +24, +36, and +48) and organic ions (m/z +27, +37, +39, and +43) in the cation spectrum. The carbon cluster ion peaks (C_n^+) in the cation spectrum indicated a soot particle type comparable to EC although their number was limited. Moreover, carbonaceous compounds of m/z -12, -24, -26 were obtained in the anion spectrum besides constituents of phosphate (m/z -79 and -95) and sulphate (e.g., m/z -80, -81, and -97) that were contained in aircraft fuels (Spila et al., 1999; Unger, 2011; Dessens et al., 2014; Gertopski et al., 2019). The ion peaks of processed OC (Fig. 4.20 c)) on m/z +27 (CNH^+ , $C_2H_3^+$), +37 (C_3H^+), +39 ($C_3H_3^+$), and +43 ($C_3H_7^+$, $C_2H_3O^+$) might originate from fuel. For EC particles coated with unleaded fuel vapor, Spencer and Prather (2006) mentioned these markers and those of m/z +51 ($C_4H_3^+$) and +63 ($C_5H_3^+$) that were not detected here. Alike the EC type, *OrgSO* was mainly detected within 10 km behind the DLR-ATRA in a size range mostly below 250 nm, also indicating a particle type that had just been released and was small-sized during the detection with ERICA-LAMS.

Under the assumption of an exhaust-related particle type, which was just a few minutes old, the additional species were rather adsorbed at the particle surface of this type than being mixed into the particle volume. Thus, the type was referred to as *coated soot*.

OrgNOSO2 (Fig. 4.20 c)) was mainly characterized by large ion signals of nitrogen, sulphur, ammonium, and carbonaceous material. Again, markers of EC (m/z +12, +24) and OC (m/z +27, +29, +39, +43) were detected but not to the extent that this type was definitely consisting of a soot core. In addition, large signals of nitrogen (m/z +30) and ammonium (m/z +17, +18) implied a coating of the unknown core with additional material such as ammonium nitrate. The anion spectrum revealed few organic signals and was mostly covered by nitrogen (m/z -46, -62, -125) and sulphur compounds (m/z -80, -81, -96, -97, -99, -177, -195, -197). Referring to the low number of carbon cluster ions and the footprint of OC, the type was interpreted as *processed organic carbon*. As this particle type was more abundant within a distance of 15 km behind the DLR-ATRA than above, it seemed to be related to aircraft exhaust (see Sect. 4.1.2). Nevertheless, the analysis of the vertical profiles of the atmosphere exhibited this particle type as highly abundant inside the BL as well for the transition period (see Sect. 4.1.3), implying a potential source on the ground. In consequence, this type did not originate exclusively from aircraft exhaust. However, the aircraft exhaust seemed to impact the abundance of that particle type during airborne measurements. The size distribution revealed a size range of 200 to 800 nm with higher values than for EC and coated soot. Ergo, this particle type did not result from freshly emitted particulate matter. In contrast, gaseous substances might have condensed onto the particle surface after the passage of the aircraft. Still, more airborne measurements are necessary to analyze the impact of aircraft exhaust on background particles.

In summary, EC and coated soot particles were attributable to aircraft exhaust. The mean mass spectra illustrated a soot core for both types, that could be assigned to incomplete aircraft fuel combustion. However, the vertical profile of the atmosphere showed that a fraction of these soot types was attributed to background aerosol and, thus, might result from various sources such as fossil fuel combustion and BB in the BL. The particle size and distance analysis indicated a relation to the aircraft exhaust plume. In contrast, the largest amount of processed OC particles was detected in the BL during the transition period. Further, the particle size was shifted towards larger diameters not implying freshly emitted soot particles. In consequence, the increased *PF* of OC within 15 km behind the DLR-ATRA was probably the result of aircraft-related gaseous substances that condensed onto the particles. However, this hypothesis needs to be proven by further measurements.

4.1.6 *Relevance of air mass origin*

The origin of air masses recorded during the airborne measurements of ND-MAX was analyzed using the HYSPLIT model by NOAA. A simulation of backward trajectories along the flight track was conducted with the use of GDAS data of a horizontal resolution of $0.5^\circ \times 0.5^\circ$ (see Sect. 2.7). In a second step, the trajectories were filtered for those starting within 50 m above the ground, and those that never traced back to the BL. In addition, trajectories were cut that remained within the BL for more than 12 hours. These trajectories were neglected for further analysis.

The flight corridor was mainly affected by westerlies and air masses coming from transatlantic western territories (Fig. 4.21). The majority of air masses was advected from western regions such as North America over even Asia, except for a few trajectories of RF5 and RF6. These trajectories were traced back to Saharan Region via the Azore's high. Besides, some of the trajectories started in Africa or at the Arabian peninsula and propagated eastwards across Asia, the Pacific region, and the American continent before approaching the Atlantic and finally Central Europe. Still, the largest number of trajectories were traced back to the Atlantic, Middle and North America.

Despite the impact of the Azore's anticyclone on the trajectory paths, the overall analysis did not reveal a direct effect of the regional weather pattern on the trajectory tracks. Days of similar weather pattern (see Sect. 3.3) were not characterized by similar trajectory pattern. For example, RF3, RF4, RF5, and RF7 were attributed to a warm period, which was characterized by the advection of moderate-temperature air masses from the Atlantic ocean. However, the trajectories calculated for the four RFs demonstrated variable properties. RF3 and RF4 followed a zonal circulation that was partly driven by the northern polar jetstream as indicated by the long distance wave structure (Fig. C.14 and C.15 in the appendix), whereas RF5 (Fig. C.16 in the appendix) was mainly driven by a meridional circulation. Additionally, the Azore's high had a large impact on the trajectory paths of RF5. In contrast, RF3 was not affected by the Azore's high. The trajectories calculated for RF7 (Fig. 4.22) were traced back in a wavy structure that combined elements of a zonal and meridional circulation. Thus, the regional weather pattern did not impact the propagation of trajectories within their area of influence, and thus, the advection of air masses from western source regions.

The air masses detected during the ND-MAX RFs were mainly attributed to the Atlantic region (Fig. 4.23). Further, of all continents North America had the largest contribution to air masses probed along the flight paths. Regarding the entire set of trajectories simulated for ND-MAX, 74% of the trajectory

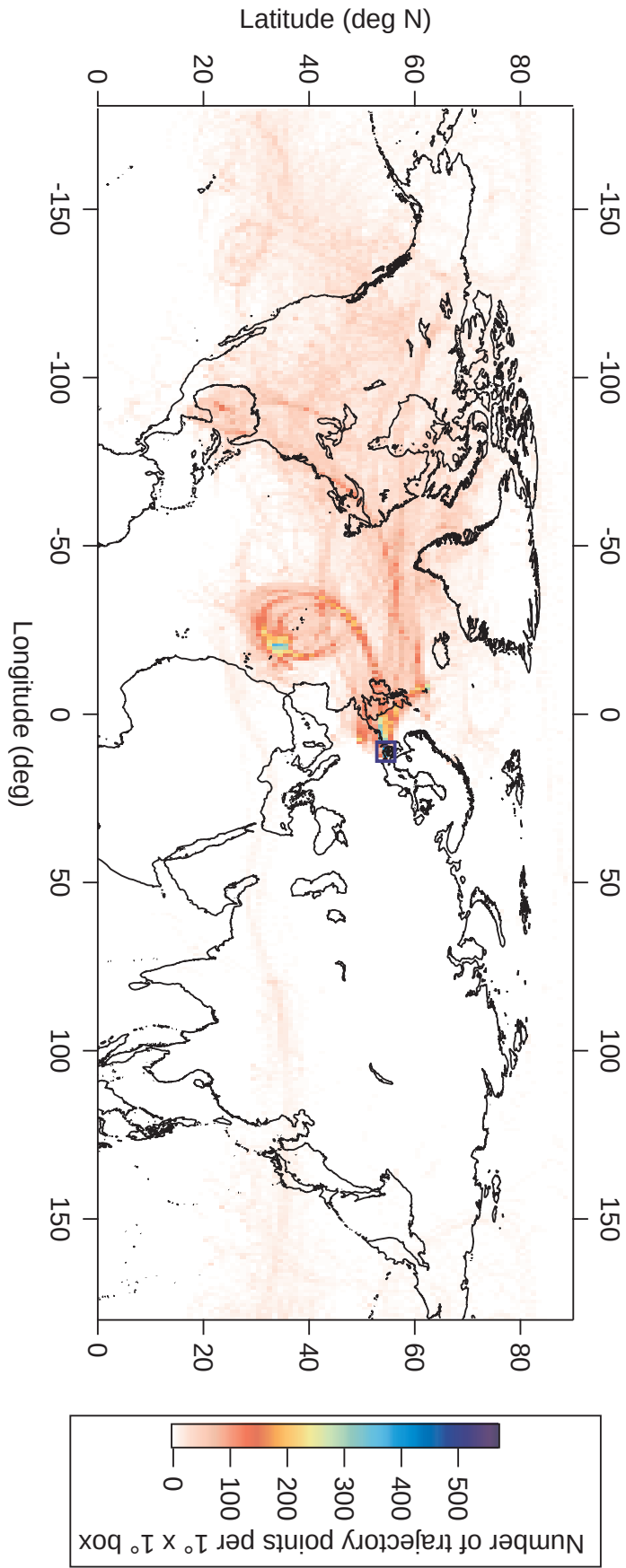


Figure 4.21: Distribution of the trajectory points of all trajectories simulated with the HYSPLIT trajectory model per grid boxes of $1^\circ \times 1^\circ$. The trajectories of all RfFs within January 17th and February 1st 2018 are included. The blue rectangle marks the flight region during ND-MAX.

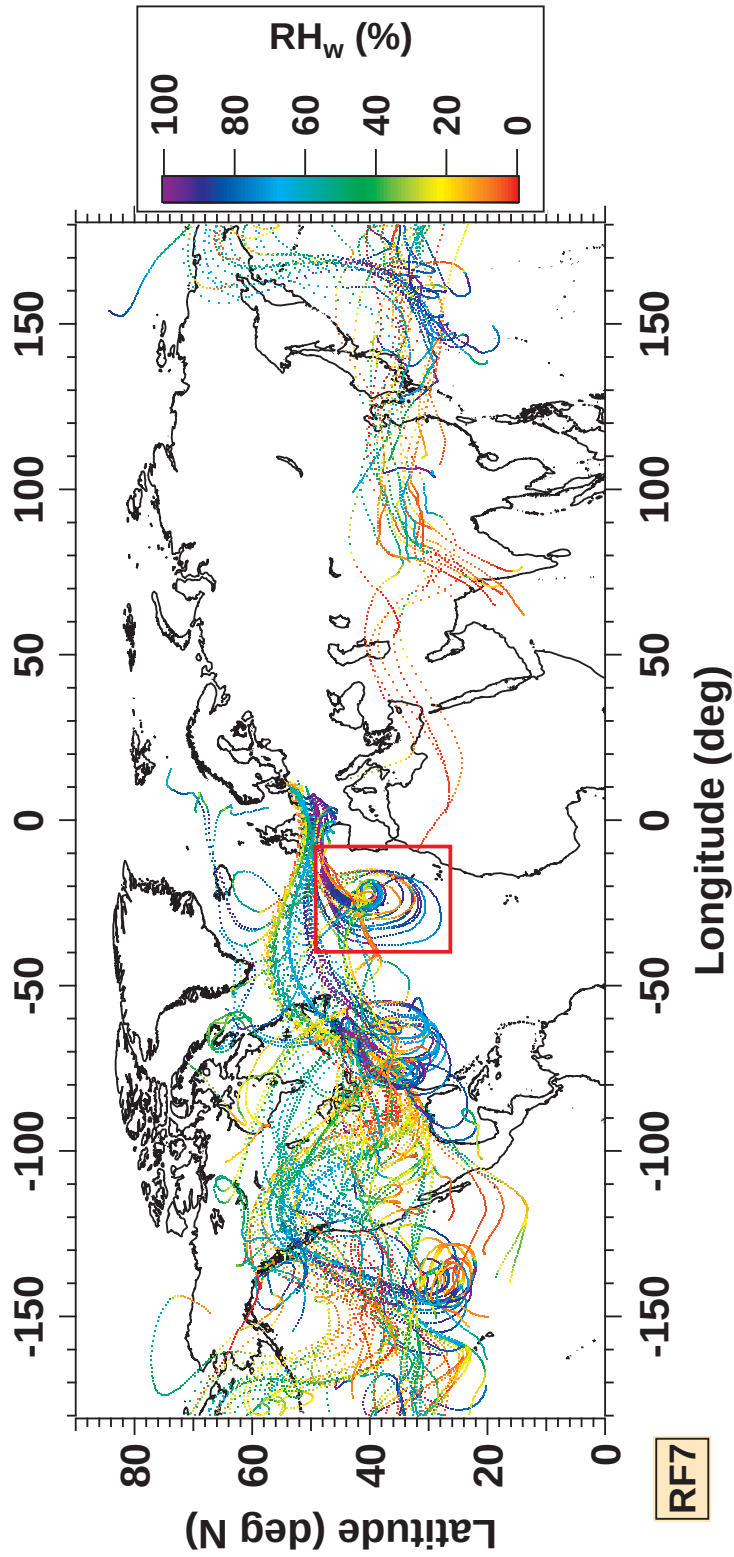


Figure 4.22: Overview of the backward trajectories simulated for RF7, color-coded with the relative humidity (RH_w) as an indicator for the altitude level. The red rectangular depicts the Azore's high, which is present for RF4 to RF7 and impacts the presence of mineral dust and processed mineral dust particles along the flight track.

points inside the BL ($C_{BL\ Traj. Points}$ in Fig. 4.23) were assigned to the West or East Atlantic region. This might explain the detection of sea spray residuals throughout the entire campaign. However, the occurrence of sea spray did not coincide with the contribution of Atlantic source regions (not shown). A larger contribution of Atlantic source regions did not necessarily result in larger particle fractions of sea spray. Besides, 18% of all trajectories were traced back to the North American continent including Alaska, Canada and the United States. In contrast, air masses of European origin only reached a fraction of 3.4%. Other continental regions made up to 1.3% (Middle America) and 1.1% (Asia), whereas the contribution of Africa, Siberia, and India was less than 0.1%, respectively. For Africa, this value was very small and unexpected because of the close proximity to Europe. Besides the propagation of trajectories around the entire planet, few trajectories were traced back along the Azore's high into the Saharan region.

The potential source regions did not seem to impact the occurrence of individual particle types, except for one BB type. For example, of the Atlantic contribution, the eastern part was more dominant than the western part. In seven of eight RFs, more trajectories extended backwards to the East Atlantic than to the West Atlantic, and in one of these flights (RF3) the West Atlantic did not even contribute at all to the air masses detected along the flight track. In contrast, RF4 was dominated by trajectories coming from the western part (54%). However, this scenario did not affect the abundance of any particle or residual type (Fig. C.19). Analogously, RF1 and RF2 demonstrated a significant nordic influence including air masses from Alaska (18.0% and 27.8%, respectively) and Greenland (3.0% and 1.5%). Still, none of the particle types could be attributed to any of these trajectory source regions. With the exception of one particle type (BB type 1), the correlation analysis of the individual particle types and source regions did not provide any evidence about the particles' origin (not shown).

However, BB type 1 could be linked to North America. As Fig. 4.24 a) depicts, the particle fraction of BB type 1 increased when the number of trajectories approaching from North America was enhanced. In fact, 3257 wildfires were reported by the US National Interagency Fire Center for January 2018 (NOAA-NCEI, 2018). Regarding the period from 2001 to 2020, this was the second largest number of fires burning 71,189 acres ($\approx 288.1\text{ km}^2$) (NOAA-NCEI, 2018). The BB particles might be related to these wildfires. However, BB particles also appear next to residential heating, agricultural burning, and other forms of biofuel combustion (Mardi et al., 2021 and therein), and the particulate matter is also detected in winterime (e.g., Schroder et al., 2018). Despite the impact of

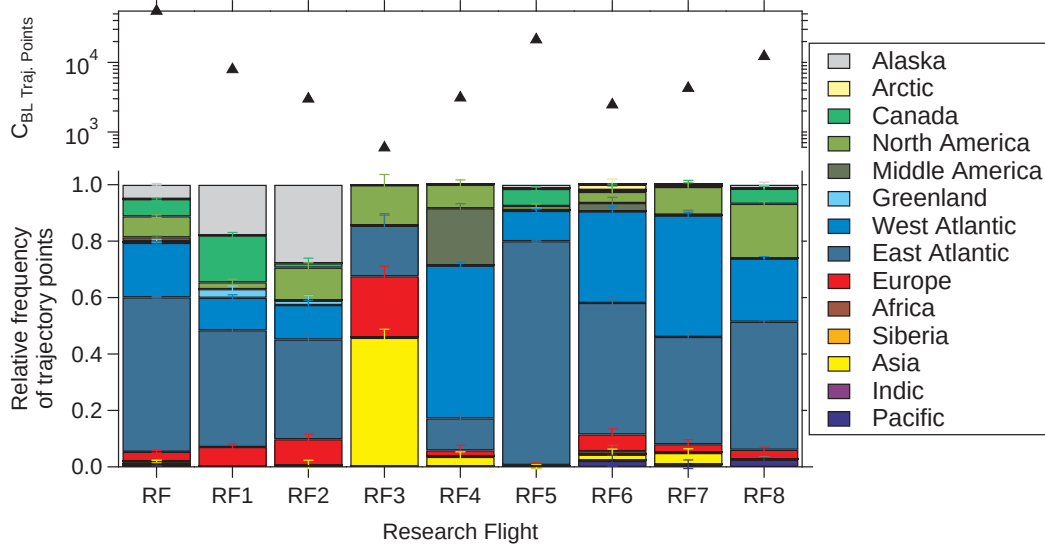


Figure 4.23: Total number of trajectory points inside the BL ($C_{BL,Traj.Points}$) and relative contribution of source regions to the air masses detected along the individual flight tracks of ND-MAX.

North American air masses, two more types of BB detected within the set of RFs were not assigned to that region (not shown).

Processed mineral dust was traced back to Saharan origin. The particle fraction did not correlate with the relative frequency of trajectory points from Africa. Nevertheless, this particle type was mainly detected within RF4 and RF7 (Fig. 4.24 b), i.e. in the vicinity of the Azore's high (red rectangle in Fig. 4.22). Even though the contribution of Africa was very limited, the trajectories passing the anticyclone were tangent to the tropical Atlantic region, which is predestined for the transport of Saharan dust plumes towards Central America even in wintertime (Gläser et al., 2015; Gutleben et al., 2022). In consequence, an air parcel that passes the Azore's high may be exposed to a dust plume originating from North Africa, and thus might lead to a transport of small amounts of mineral dust as observed within the ND-MAX RFs.

Accordingly, the mineral dust recorded during ND-MAX seemed to be released in the Saharan desert. The fraction of particles and cloud residuals of this type (Fig. C.4) also revealed an increased fraction within RF5 and RF7. Yet, the particle fraction detected in the presence of the Azore's high (RF4) was smaller than the fraction detected in the absence of the Azore's high, implying that the abundance of mineral dust was driven by other factors as well. In addition, the cloud residuals revealed an enhancement during RF1, which disagreed with the idea of African origin since there were no trajectories detected that originated from Africa or passed the Azore's high. Still, the error bars indicated the large

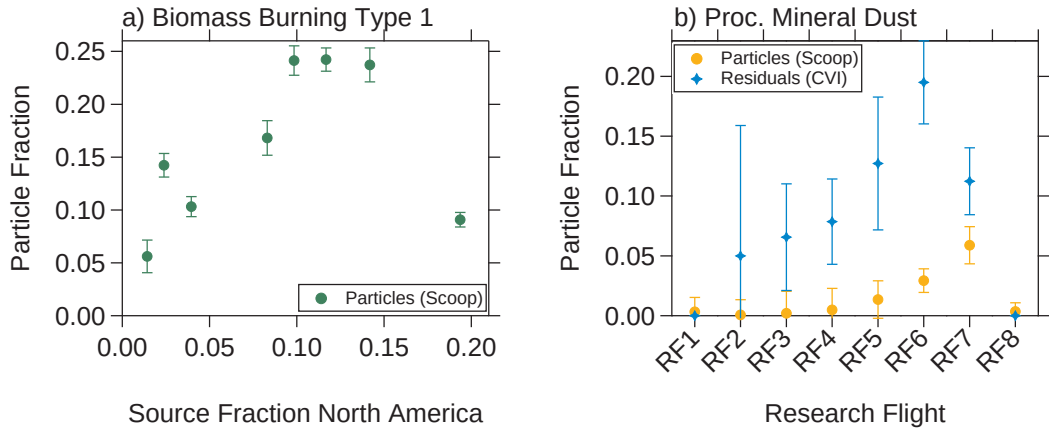


Figure 4.24: Abundance of BB type 1 for a variable contribution of North America as source region (a). Abundance of proc. mineral dust particles (orange) and cloud residuals (blue) for the individual RFs (b) during ND-MAX. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see. App. A.3).

uncertainty of the residual fraction during RF1. Therefore, the assignment of mineral dust to the Saharan desert was not clear. In this context, a larger number of particles would have been beneficial to improve the statistics and to clarify the relation.

In summary, the flight corridor was mainly affected by trajectories approaching from the west, indicating westerlies and the advection of air masses from the Atlantic and North American continent. In detail, the East Atlantic region was the major player throughout the entire campaign when disregarding RF3 and RF4. A relation between the trajectory pattern and the local weather regime was not observed. However, the Azore's high had a strong impact on the propagation of air mass trajectories, and also seemed to affect the amount of processed mineral dust along the flight tracks. This particle type was assigned to the Saharan source region in spite of a missing correlation between its abundance and the contribution of the Sahara to the probed air masses. Further, the non-processed mineral dust type indicated the same origin, but was not verified due to a lack of reliable statistics. Besides, BB type I particles were attributed to air masses coming from North America, which was in agreement with reports of wildfires provided by the US National Interagency Fire Center. This particle type was the only one that could be assigned based on a correlation of its particle fraction and the fraction of a potential source region. Apart from that, the potential source regions did not seem to impact the occurrence of individual cloud residuals or particle types.

Table 4.2: Overview of measurements of ammonium sulphate, hydrochloric, and sulphuric acid.

Chemical constituents¹	d_{mob}^a (nm)	Δt^b (min)	N_{CPC}^c (cm^{-3})	N_{LAMS}^d (cm^{-3})	C_{Shots}^e (s^{-1})	C_{MS}^f (s^{-1})	DE^g (%)	HR^h (%)
61 mg $(\text{NH}_4)_2\text{SO}_4$ + 12 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	200 350	33.5 9	45822.93 5242.39	256.53 152.69	17189 4833	2033 1936	0.6 2.9	1.2 4.0
30 mg $(\text{NH}_4)_2\text{SO}_4$ + 6.7 mg $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	200 350	20 7	21040.69 2148.73	120.98 65.66	10926 3709	2119 2132	0.6 3.1	1.9 5.7
0.76 g of a mixture ² of (HCl + H_2SO_4)	200	31	124909.03	5367.84	12490	1520	4.3	1.2

¹ solved in 80 ml deionized water² mixture consists of 1.31 g HCl (25%) and 0.82 g H_2SO_4 (95%)^a particle size as mobility diameter^b measurement period^c average particle number concentration detected by GRIMM CPC (Sect. 2.4.1)^d average particle number concentration detected by ERICA-LAMS (Sect. 2.1)^e number of shots of the ablation laser in ERICA-LAMS^f number of detected mass spectra in ERICA-LAMS^g detection efficiency with respect to the coincidence values of ERICA-LAMS^h hit rate

4.2 SOURCE OF NITROGEN OXIDE SIGNALS

Ion peak signals of nitrogen oxides are widely detected in single-particle mass spectra recorded with ERICA-LAMS. Especially, the ion signal on $m/z +30$ implies the appearance of nitrogen monoxide (NO) in the cation spectrum, whereas $m/z -46$ and -62 indicate NO_2 and NO_3 in the anion spectrum, respectively. Measurements during the ND-MAX campaign revealed the presence of a particle type which was dominated by peaks of NO_x . A similar particle type was detected within the Asian summer monsoon anticyclone (AMA) together with enhanced mass fractions of particulate ammonia and sulphate (Appel et al., 2022). This leads to the assumption that ion peak signals of NO_x might be the result of a secondary formation process during a combination of two non- NO_x species such as ammonia and sulphur dioxide. Laboratory measurements with ERICA-LAMS were performed, remembering that the detected NO_x signals are the result of two possible effects. First, the detected particle consists of nitrogen oxide constituents that are fragmented and ionized during the ablation process. This has been thought to be the predominant way of generating NO-related ions. Second, the particle does not consist of NO_x compounds but contains precursor substances such as ammonium and oxygen that may interact during the ablation process and result in signals of NO, NO_2 , or NO_3 , respectively.

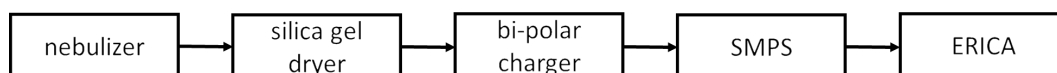


Figure 4.25: Scheme of the instrumental setup for characterization measurements. The SMPS (Scanning Mobility Particle Sizer) comprises the GRIMM DMA (Model No. 5.5-900) and CPC (Model No. 5.400). The instrumental setup is comparable to the measurement setup described in Hünig (2021).

Measurements of ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) and a carrier substance were conducted in order to analyze the detection of NO-related signals in the absence of NO compounds. The carrier substance was necessary since the optical system in ERICA-LAMS was not capable of detecting pure ammonium sulphate (AS) particles. The ionization of pure AS particles requires a very high laser power of $>1600 \text{ MW cm}^{-2}$ for an ablation laser wavelength of 248 nm (Thomson et al., 1997). As the ablation laser of ERICA operated with a less energetic wavelength of 266 nm, the provided energy power of 1360 MW cm^{-2} did not suffice to form ions of AS (Hünig, 2021). The carrier substance had to fulfill two requirements. On the one hand, it should not include components of nitrogen oxides, which create additional peaks of NO. Also, substances providing organic material with a mass-to-charge ratio of 30 should not be included. On the other hand, it should not contain components of extremely high ionization efficiency such as potassium, which generate very high peaks. This would result in matrix effects since strong ion signal peaks of substances of low ionization energy suppress low-level peaks related to nitrogen. Thus, two aqueous solutions of AS were prepared using Iron(II) sulphate heptahydrate ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$) and Tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$), respectively. Further details are provided in Table 4.2.

For the measurements conducted within this framework, the instrumental setup was installed once in the laboratory and remained unchanged throughout the series of measurements. The particle droplets were generated in a nebulizer system by spreading the solution using compressed air (Fig. 4.25). In a second step, the beam of particle droplets was exposed to a diffusion dryer in order to remove the water from the individual particles. Next, the dried particles were guided to a bipolar charger, which provided a natural distribution of electrical charges to the polydisperse aerosol particle population. Inside the differential mobility analyzer (DMA) (Model No. 5.5-900 by GRIMM Aerosol Technik GmbH Co. KG), the particles were filtered for a preset electrical mobility. The classifier was set to an appropriate voltage to extract the particles of a certain particle size d_{mob} that is related to the electrical mobility and the number of charges per particle. Thus, the particle size can be inferred from the electrical mobility. Finally, the population of monodisperse aerosol particles was guided

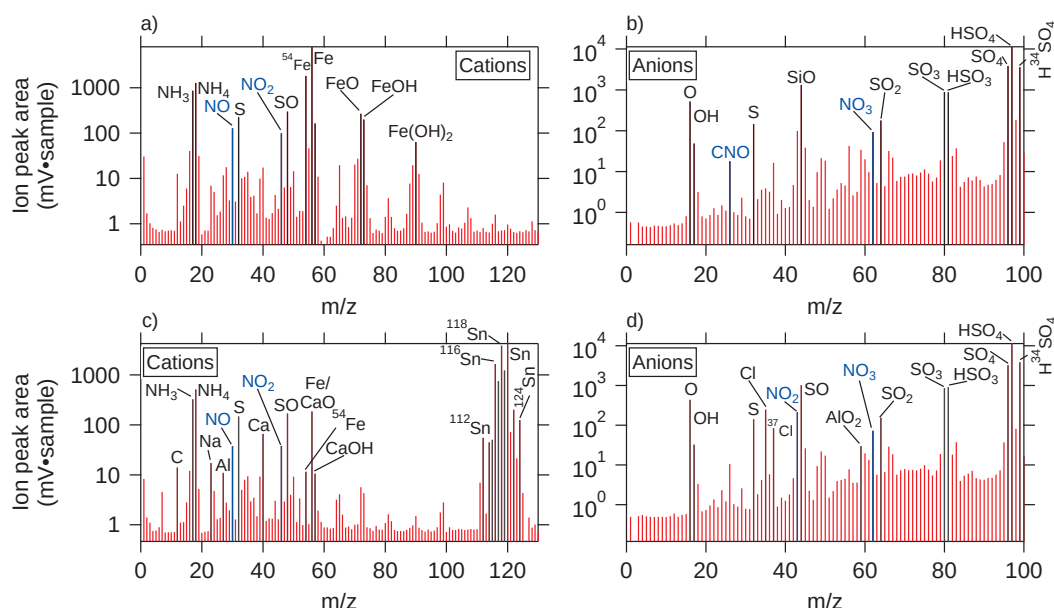


Figure 4.26: Mean mass spectrum of cations and anions of AS with FeSO_4 (a,b) and AS with SnCl_2 (c,d) showing signals of nitrogen oxides at m/z +30, +46, -26, -46, and -62.

to the CPC (Model No. 5.400 by GRIMM Aerosol Technik GmbH Co. KG) and to ERICA, where it was introduced via the CPI-system. The measurement period was chosen according to the number of recorded mass spectra. In order to obtain a solid statistical foundation, approximately 2000 spectra were recorded for each pre-defined particle size.

The mean mass spectra of mixtures of AS with FeSO_4 or SnCl_2 , respectively, revealed that signal ion peaks of nitrogen oxides were detected even in the absence of NO_x compounds in the chemical substances (Fig. 4.26). Regarding the mixture of AS with FeSO_4 , the ion marker peak on m/z +30 and +46 exhibited the presence of nitrogen monoxide and nitrogen dioxide, respectively. These markers were confirmed by characteristic markers in the anion spectrum of m/z -26 (CNO) and m/z -62 (NO_3), of which the first implied a contamination of the setup by organic material, which could not fully be excluded but on the other hand demonstrates the sensitivity of ERICA-LAMS. Analogously, the mean mass spectra of AS+ SnCl_2 depicted the presence of NO, NO_2 , and NO_3 . In consequence, nitrogen oxides probably formed during the ablation process of single particles as long as precursors such as nitrogen and oxygen were present. The results suggested that individual particle types showing signals of nitrogen oxides in their mass spectra do not necessarily consist of nitrogen oxides but may contain nitrogen compounds such as ammonia. However, the signal peaks of nitrogen oxides detected within this characterization were always smaller

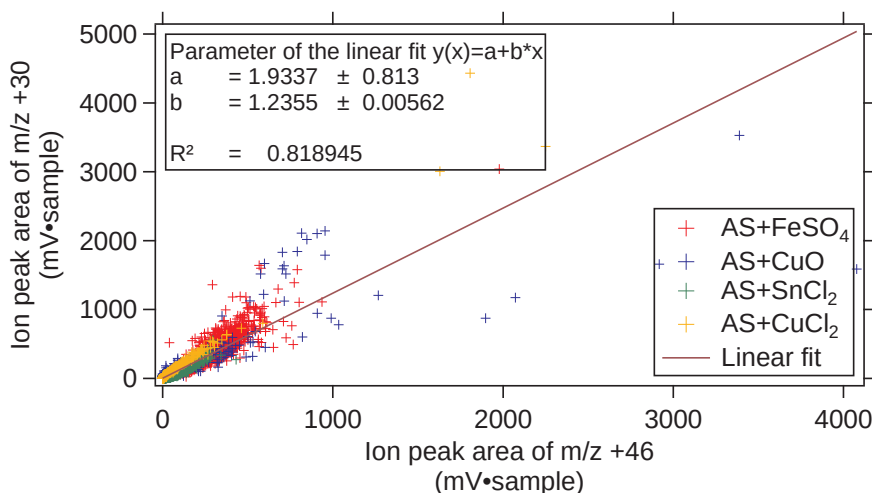


Figure 4.27: Distribution of nitrogen ion peak signals for measurements of $(\text{NH}_4)_2\text{SO}_4$ with FeSO_4 (red), CuO (blue), SnCl_2 (green), and CuCl_2 (orange).

than peaks of ammonium. Therefore, strong ion signals of nitrogen oxides were still attributed to NO compounds bound in the aerosol particle. This series of measurements was conducted twice in order to exclude artificial NO_x -signals due to a potential contamination of the measurement setup. Therefore, the nebulizer, diffusion dryer, DMA, and the CPI-system of ERICA were dismantled and cleaned separately. Still, a contamination could not fully be excluded due to potential debonding of particles inside the DMA. As a consequence, the nitrate-rich particles detected during the RFs of ND-MAX and within the AMA during the StratoClim campaign were not attributed to a combination of non- NO_x precursors within the ablation process.

In the presence of AS and the absence of nitrogen oxides, ions of nitrogen oxides were formed in an averaged ratio as shown in Fig. 4.27. The measurements of AS with several other chemical compounds were taken into account for the mean ratio of the signal ion peaks of m/z +30 and +46. A linear fit was used to examine the relationship between both ion signals. However, for signal intensities larger than 1000 mV•sample, the cloud of data points broadened. Thus, a nonlinear correlation for the higher ion signals might be possible as well.

4.3 SOURCE OF SULPHATE CATION SIGNALS

The analysis of the individual particle types detected during ND-MAX revealed one cluster of strong sulphur signals in the cation spectrum. As sulphur signals were majorly detected within the anion spectrum on m/z ratios of -64 (SO_2),

-80 (SO_3), -81 (HSO_3), -96 (SO_4), -97 (HSO_4), and -99 (H^{34}SO_4), the cluster of ECOC was of special interest. As depicted in Fig. A.18, sulphur signals were also detected in the cation spectrum on mass-to-charge ratios of m/z +32 (S), +48 (SO), and +99 (H_3SO_4). Laboratory measurements of hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) were conducted in order to find the origin of cation sulphur signals. The instrumental setup of Fig. 4.25 was reused.

Cation sulphur signals were detected by ERICA-LAMS for sulphuric- and hydrochloric acid measurements, but only in the context of contaminating substances such as AS. Fig. 4.28 reveals the mean cation (a) and anion (b) spectrum of HCl and H_2SO_4 -particles. The cation spectrum included ion signals of sulphur compounds on m/z +32, +48, and +99. In addition, signals of sulphur dioxide (m/z +64) and sulphuric acid (m/z +98) were detected. The anion spectrum reveals sulphur signals which were detected in many other particles types of ND-MAX as well, and thus, did not seem to be specific. Besides the compounds mentioned above, individual signals were obtained on m/z -115 ($\text{HSO}_4(\text{H}_2\text{O})$), -177/179 (HSO_4SO_3), and -195/197/199 ($\text{H}(\text{HSO}_4)_2$). Regarding non-sulphur material, the cation spectrum depicts the presence of hydrogen (m/z +1), ammonium (m/z +18), carbon (m/z +12, +24, +36), nitrogen oxides (m/z +30 and +46), and copper (m/z +63/65), which imply another contamination of the setup. As already stated by Thomson et al. (1997), the detection of pure sulphuric acid requires a large ablation laser beam power to form ions that can be detected by single-particle mass spectrometer. Power values of $> 1600 \text{ MW cm}^{-2}$ were necessary at a wavelength of 248 nm to ionize contaminated sulphuric acid (Thomson et al., 1997), whereas ions of pure H_2SO_4 droplets were not obtainable for such a wavelength. Therefore, the low number of mass spectra (87) detected during the measurements confirmed the findings of Thomson et al. (1997). Using a wavelength of 266 nm for the ablation laser in ERICA-LAMS, particles of pure sulphuric acid were not obtainable by the laser beam photons. Yet, the additional material in terms of contamination supported the detection of H_2SO_4 particles. The cation sulphur signals were not attributable to sulphuric acid but the strong signal of ammonia indicated that positive sulphur ions might form in the presence of AS.

As a consequence of the low number of recorded spectra, measurements of AS with Copper(II) oxide were performed using the same instrumental setup. The particles detected within these measurements exhibited similar characteristics as those of H_2SO_4 and HCl. The mean mass spectra (Fig. 4.28 c, d) provide characteristic peaks that mostly agree with those of H_2SO_4 and HCl. Except for the signal of sulphuric acid (m/z +98), the same cation sulphur signals were detected. Even the mean anion spectrum shows the same characteristics. The detection of non-sulphate material included the same substances as those

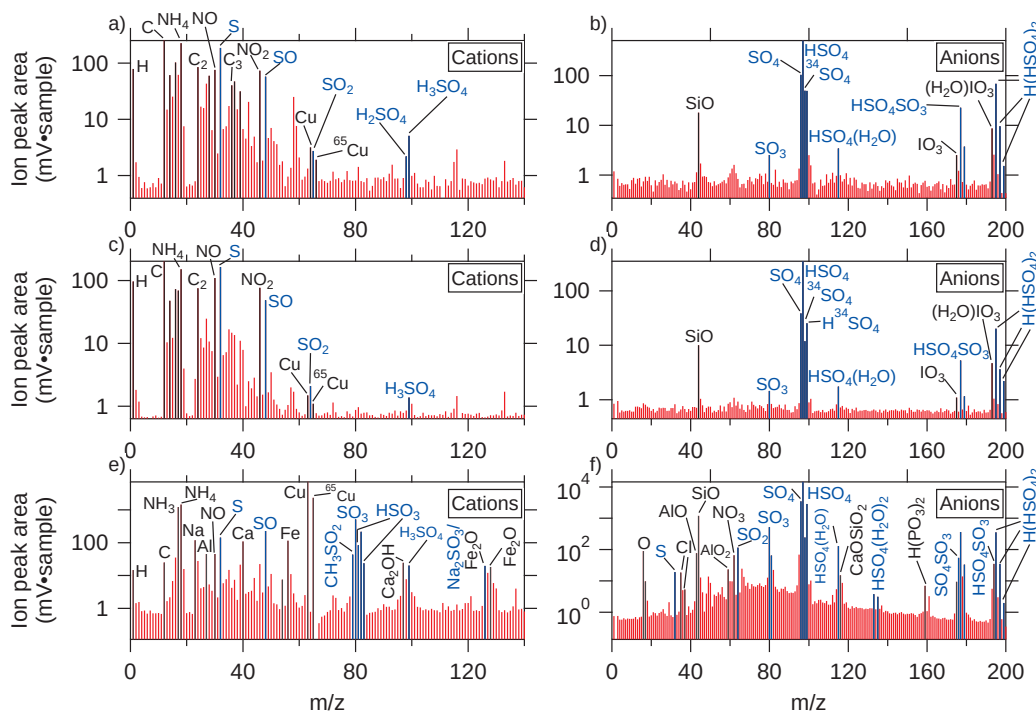


Figure 4.28: Mean mass spectrum of cations and anions of a mixture of sulphuric acid (H_2SO_4) with hydrochloric acid (HCl) (a,b), and mixtures of AS with CuO (c,d) and AS with CuCl_2 (e,f) showing cation signals on m/z +32, +48, and +99 and anion signals of sulphur on m/z -80, -81, -96, -97, -98, -99, -115, -177, -195, -197, and -199.

measured before. Ion signals of hydrogen, ammonium, carbon, and copper were observed in the cation spectrum. The presence of nitrogen oxides confirmed the assumption of the previous measurements of AS with FeSO_4 or SnCl_2 , respectively (see Sect. 4.2), that also depicted the formation of NO-containing ions in the vicinity of nitrogen compounds during a lack of nitrogen oxides.

The similarity of both particle types of AS with CuO and of contaminated H_2SO_4 with HCl might be the result of a low solubility of Copper(II) oxide. During the dissolution process of AS and CuO , the latter mostly failed to dissolve within the solvent. This was observed during the mixing process of the solution and was also implied by the low ion peaks of copper (m/z +63/65) in the cation spectrum. Since refractory material such as metal compounds is of low ionization energy (Reilly et al., 2000), its ions are predestined for a charge transfer that results in strong ion signals in the single-particle mass spectrum. Therefore, a very low copper content in the mixture could be assumed from the detection of low copper signals. In consequence, a mixture of Copper(II) chloride, AS and deionized water was set up to overcome the issues of dissolution.

The measurements of AS and CuCl_2 could reproduce the cation sulphur signals detected in the previous laboratory experiments. In addition to the sulphur signals mentioned above, peaks on m/z +79 and +126 were recorded that might be assigned to CH_3SO_2 (Galloway et al., 2009), and Na_2SO_3 when summing up the single molecule masses. Besides, iron compounds were detected based on the mass-to-charge ratios of m/z +54/56 (Fe) and +127 (Fe_2OH) that also implied the presence of Fe_2O ions on m/z +126 (Maunit et al., 1996). Consequently, the ion peak on m/z +126 could not uniquely be assigned to Na_2SO_3 ions. Further ion signals of hydrogen, ammonium, and copper were obviously related to the initial substances AS and CuCl_2 . Additionally, ion peaks of sodium (m/z +23), aluminium (m/z +27), and calcium (m/z +40 and +97) were observed and agreed with anion signals on m/z -43 (AlO), -59 (AlO_2), -116 (CaOSiO_2). Nevertheless, the origin of these substances remained unclear as they were not recorded during previous measurements and no adaptations were made to the instrumental setup except for the replacement of the solutions.

In conclusion, the cation sulphur signals detected within the ND-MAX particle type *ECOC* were obtained again by measurements of AS in mixture with several chemical compounds such as Copper(II) dioxide, Copper(II) chloride, Iron(II) sulphate heptahydrate, and Tin(II) chloride dihydrate. Thus, the positive ion signals of sulphur compounds were traced back to AS. Even though the first series of measurements based on sulphuric and hydrochloric acid, impurities of ammonium, nitrogen oxides, and a low amount of carbon were detected, which were actually in favor of AS (see Sect. 4.2). Therefore, the detection of cation sulphur signals was rather an effect of the contamination with AS than a result of sulphuric acid. The series of measurements which based on AS and CuO or CuCl_2 , respectively, demonstrated similar characteristics in the cation spectrum. Furthermore, all measurements were characterized by mean anion spectra predominated by sulphur compounds and an ion peak signal of silicon monoxide, which was related to the silica gel used in the diffusion dryer to dehumidify the generated aerosol particles coming from the nebulizer. The laboratory measurements supported the idea that AS led to cation sulphur signals. However, there was no assurance that the cation sulphur peaks detected within the ND-MAX campaign were induced by AS. More measurements are required to identify the potential sources of cation sulphur signals in single-particle mass spectra. Further research campaigns will have to help to identify the contribution of ambient AS to aerosol particles in the UTLS region.

CONCLUSIONS AND OUTLOOK

This thesis focused on the chemical composition of aerosol particles in the wintertime UTLS region over Germany. Airborne measurements were conducted in two restricted airspace areas over Northern Germany within the ND-MAX campaign aboard the NASA DC-8 operating at various distances behind the forward flying DLR-ATRA and public aircraft. The measurements were analyzed for aerosol particles and cloud residuals in the presence and absence of aircraft exhaust, cirrus, and contrails in order to improve the knowledge about the chemical composition of aerosol particles in the UT and LMS over Central Europe during wintertime. The hybrid mass spectrometer ERICA was applied to determine the individual particle types by laser-ablation single-particle mass spectrometry (ERICA-LAMS) that contribute to the aerosol population and catalyze the cirrus and contrail formation at mid-latitudes. The following part summarizes the key results of this study and addresses the questions posed in Sect. 1.2. In addition, ideas will be provided for future studies and upcoming campaigns, derived from the limitations of this study.

Chemical composition of wintertime UTLS-region over Northern Germany

As a result of this study, 15 individual particle types were identified and interpreted based on their chemical composition, particle size, and temporal presence. Organic particles dominated the midlatitude winter UTLS region over Northern Germany and were consisting of BB, processed ECOC, EC, coated soot, and processed OC. Amines, motor oil, and nitrate-rich particles were detected but not very often. The inorganic fraction was composed of meteoric material, sea spray, and mineral dust. Of the 15 types, only 12 acted evidently as cloud-nucleating particles. The largest fractions of CPRs were attributed to sea spray and processed mineral dust, indicating their large potential to act as CN. In contrast, biogenic particles, such as processed ECOC, processed OC, and the nitrate-rich type, had only a small contribution to the cloud droplets and ice crystals detected during ND-MAX. Besides BB particles, however, motor oil was found to be in favor of nucleating hydrometeors and was more frequently detected in cirrus than in contrails.

Exhaust plumes versus atmospheric background

This study has shown that the aircraft exhaust plumes and the atmospheric background over Northern Germany were characterized by a similar chemical composition. Within the detection range of ERICA-LAMS of 174 to 3173 nm, the individual particle types and their contribution were alike for both periods. Small-sized particles of exhaust below 90 nm were not detected by the DUs of ERICA but were still present and recorded by the reference instrument. Yet, the particle types of EC, coated soot, and motor oil have been attributed to aircraft exhaust based on the particle size inspection and a distance analysis of *PF* with respect to the chased DLR-ATRA. Three more particle types seemed to be potential exhaust types but they also unveiled nontypical properties. The impact of sustainable fuels on the chemical composition of exhaust-related particles was not observed within this dataset.

Vertical structure of atmospheric profiles

The effect of three different weather patterns on the vertical atmospheric profile has been studied within this framework. The abundance of sea spray particles was attributed to the advection of marine air masses in the presence of low-pressure systems, and the accumulation of OC particles correlated with the formation of an isolated BL due to a weak vertical mixing process. Cloud-nucleating particles such as sea spray and processed mineral dust were transported from ground sources high up into the UTLS region via convection and warm conveyor belts. High-level troughs and ridges affected the UTLS region by promoting the ascent and descent of air masses, and thus the level of the tropopause layer. This layer and the adjacent troposphere and stratosphere could be identified using several tracers (e.g. ozone and water vapor) and confirmed by ERA5 data.

Cirrus versus contrail

The comparison of both events has revealed that contrails can grow on the same particle types as cirrus clouds. The contrail ice crystal composition is rather affected by the background aerosol population than by aircraft exhaust within the size limits of the ERICA-LAMS. In the midlatitude winter UTLS region, sea spray and processed mineral dust were the main inorganic contributors and imply the formation of both ice cloud types via the liquid phase. Besides, BB particle residuals were frequently detected and their contribution among

cirrus and contrails was highly variable. EC, coated soot and motor oil partly contributed to the formation of hydrometeors, implying that these compounds remain in the atmosphere, at least for the lifetime of cirrus clouds. The amount of motor oil residuals was larger in cirrus than in contrails, indicating that these particles need to grow before being successfully detected.

Air mass origin

The results of the HYSPLIT analysis illustrate the impact of the strong global western circulation during the campaign phase. The majority of trajectories approached the flight paths from the west, indicating the advection of air masses from the Atlantic and North American continent. The East Atlantic was found to be the most important source region except for RF3 and RF4. A large fraction of trajectories was traced back to West Atlantic, Canada, North America, and Alaska. A significant number of trajectories passed the Azore's high within RF4 and RF7, coinciding with an enhanced fraction of processed mineral dust detected during these flights. As a consequence, this particle type was attributed to the Sahara region although a correlation analysis of the particle fraction and the contribution of the Sahara region could not confirm a direct relationship between them. Except for the Azore's high, the trajectory paths were unaffected by local weather pattern. Only BB type I could be attributed to North America based on a comparison of particle fraction and source fraction for the individual RFs. This coincides with reports of a large number of wildfire events during the campaign.

Laboratory measurements

The laboratory measurements of AS and FeSO_4 or SnCl_2 , respectively, unveiled the detection of low signal peaks of nitrogen oxides in the absence of NO_x compounds. The NO_x signals were markedly lower than marker peaks of ammonium. However, large NO_x peaks are still attributed to NO_x compounds. Ergo, the nitrate-rich particle types detected during ND-MAX and the StratoClim campaign are not attributed to a recombination process of the NO_x precursors. Further, recordings of a mixture of AS with CuO_2 or CuCl_2 , respectively, lead to cation sulphur signals as they were previously found in the mass spectra of ECOC particles of ND-MAX. These measurements evidently provide a potential source of cation sulphur signals. Yet, there is no assurance about AS causing the signals during the airborne measurements of ND-MAX. This conclusion needs to be supported by future experiments.

Outlook

The impact of aircraft exhaust on the population of the detected aerosol particles was very small in the size range of ERICA-LAMS, indicating one limitation of the presented measurements. The lower detection limit inhibits the sampling of exhaust-related particles below 174 nm. In consequence, small particles of fuel combustion were underrepresented and did not allow for the analysis of an impact on the aerosol population and their contribution to contrail formation. In order to overcome these issues, the DUs need to be improved for particle sizes below 100 nm.

The application of several SAF types unveiled no differences in particle chemical composition towards the use of Jet A-1 standard kerosene within this size range. A sampling of undiluted exhaust plumes might increase the chance to identify individual particle types that could be attributed to the single fuel types. In addition to the RFs, ground measurements in the exhaust plumes of the aircraft engines were conducted during ND-MAX but were not considered within this framework. This dataset might help to emphasize the identified exhaust-related particle types and to further differentiate among them. Moreover, laboratory measurements of several aircraft fuel types are necessary to identify the characteristic ion marker peaks of these particles. The addition of atmospheric sulphur and nitrogen compounds within laboratory measurements might help to identify particle coatings and processing. Such measurements were conducted at the AIDA (Aerosol Interaction and Dynamics in the Atmosphere) chamber facility of the Karlsruhe Institute of Technology and need to be analyzed for further airborne campaigns.

A wide range of individual particle types was detected during the ND-MAX campaign. The characterization of these types requires much effort when considering their chemical composition. For future campaigns, chemical transport models such as CLaMS should be adopted to gain insight into the potential chemical contributors that affect the aerosol formation and alteration in the probed air masses. Moreover, these models provide additional information on the potential emittents and source regions.

The analysis of backward trajectories highlighted the potential source regions of air masses probed along the flight track. However, only two particle types were traced back to individual source regions. The HYSPLIT model revealed difficulties as some trajectories irregularly traced back to higher altitude levels even though air masses were coming from low-level altitudes. Thus, the trajectory analysis should be repeated using another tool like the Lagrangian Analysis Tool (Lagranto) to calculate air mass trajectories.

The analysis of cloud residuals detected at the CVI revealed limited counting statistics due to a low number concentration of cloud residuals and short sample periods of cirrus and contrail events. For upcoming aircraft experiments, the flight planning need to enlarge the legs of cloud events in order to obtain a solid statistical foundation. Further, a larger number of cloud residuals increase the chance to discover more individual particle types that act as potential cloud or ice nuclei.

Finally, the observation of small NO-related peaks in single-particle mass spectra may be due to a recombination of species not containing NO-compounds but precursor substances such as nitrogen and oxygen in $(\text{NH}_4)_2\text{SO}_4$. This needs to be considered and proven by additional laboratory experiments. The nitrate-rich particle types detected during ND-MAX and StratoClim, however, are not attributed to a recombination process within the particle ablation. Further, the detection of cation sulphur signals in single-particle mass spectra was traced back to AS for laboratory measurements. Future measurements of ambient air should cover the detection of AS to analyze its impact on cation sulphur peaks in the mass spectra.

APPENDIX: SUPPLEMENTARY INFORMATION FOR CHAPTER 2

A.1 TROPOPAUSE DERIVATION

This section provides the vertical distribution of the ozone volume mixing ratio versus the potential temperature θ . As described in Sect. 2.5, the location of the TL was inferred from the ozone profile regarding the amount and its fluctuation which were given by the statistical parameters mean, median, absolute and relative standard deviation, and the interquartile range (25-75%). Besides, the ozone distribution was proven by verified reanalysis data from ERA5 which confirmed the location of the TL. Furthermore, the missing ozone data for RF4 were replaced by the water vapor mixing ratio. Again, the ERA5 reanalysis data of ozone agreed on the location of the TL inferred from water vapor. Consequently, the TL was defined according to the thresholds of θ inferred from the profiles (Fig. A.1 - A.6) provided below.

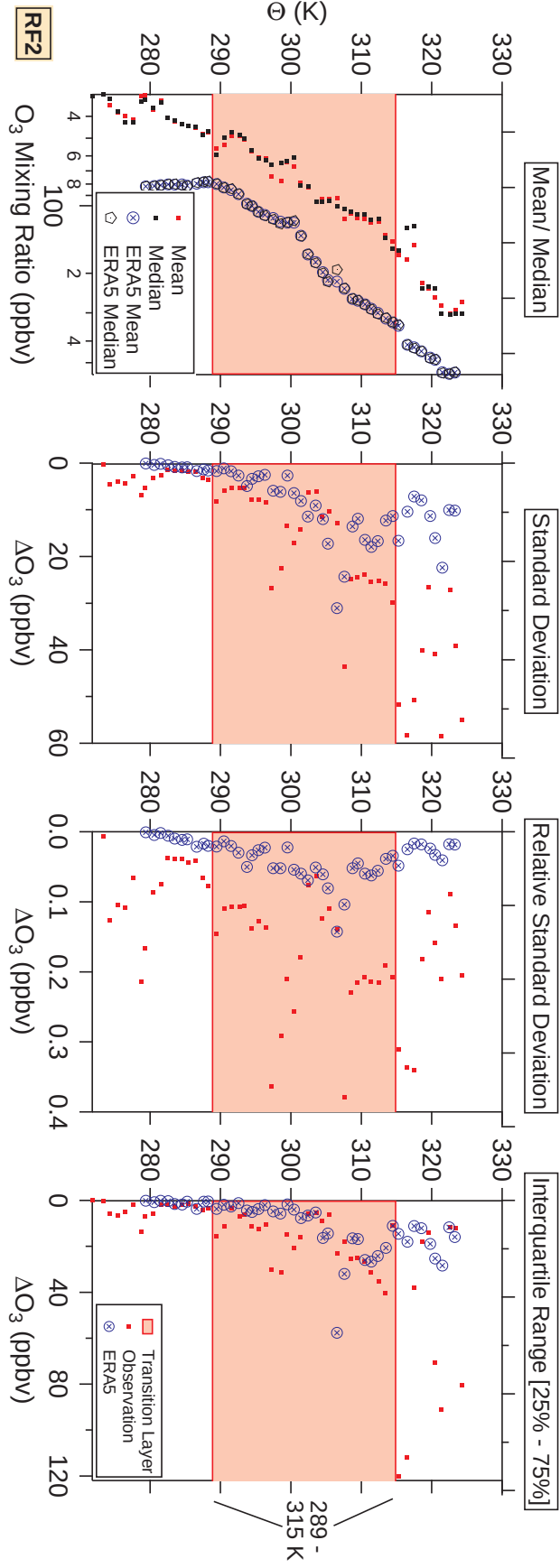


Figure A.1: Vertical profile of the statistic parameters mean, median, absolute and relative standard deviation, and the interquartile range of the O_3 volume mixing ratio during RF2. Red and black dots depict observational data, blue and grey circles denote ERA5 reanalysis data provided by Hersbach et al. (2018) interpolated on the flight track. The reddish area represents the 3.9 km thick transition layer between 289 and 315 K in potential temperature.

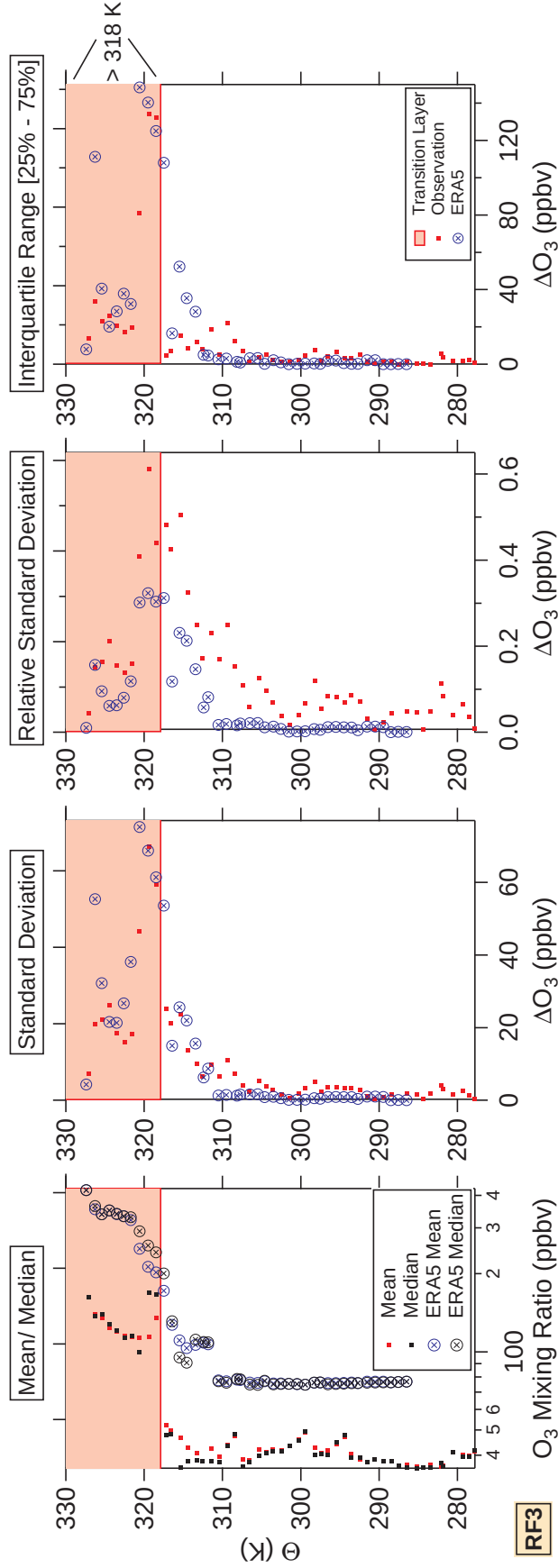


Figure A.2: Vertical profile of the statistic parameters mean, median, absolute and relative standard deviation, and the interquartile range of the O_3 volume mixing ratio during RF3. Red and black dots depict observational data, blue and grey circles denote ERA5 reanalysis data provided by Hersbach et al. (2018) interpolated on the flight track. The reddish area marks the transition layer, located above 318 K potential temperature or 10.8 km.

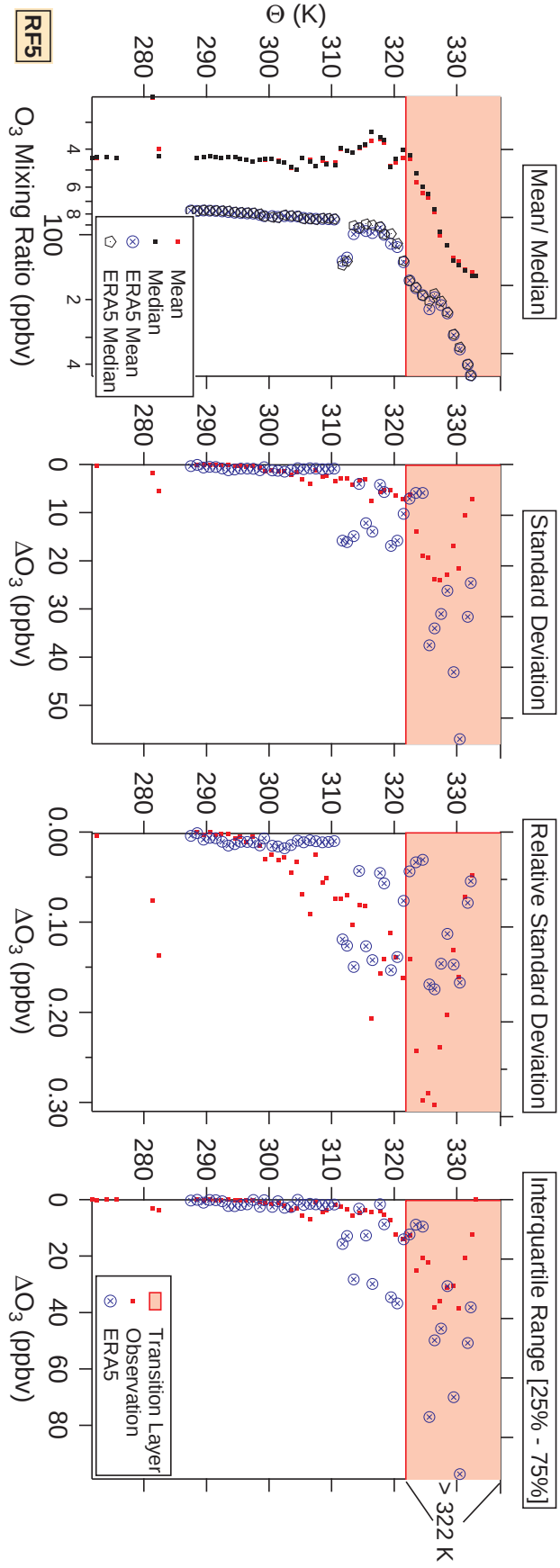


Figure A.3: Vertical profile of the statistic parameters mean, median, absolute and relative standard deviation, and the interquartile range of the O_3 volume mixing ratio during RF5. Red and black dots depict observational data, blue and grey circles denote ERA5 reanalysis data provided by Hersbach et al. (2018) interpolated on the flight track. The reddish area marks the transition layer, located above 322 K potential temperature or 11.1 km.

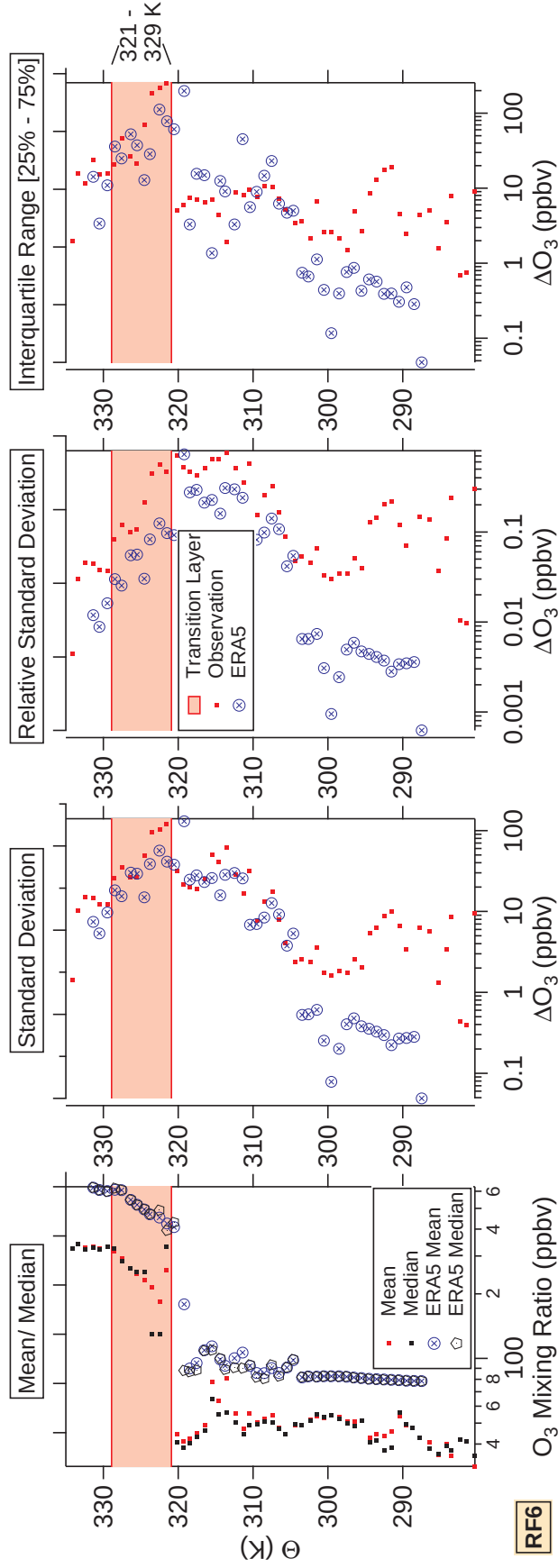


Figure A.4: Vertical profile of the statistic parameters mean, median, absolute and relative standard deviation, and the interquartile range of the O_3 volume mixing ratio during RF6. Red and black dots depict observational data, blue and grey circles denote ERA5 reanalysis data provided by Hersbach et al. (2018) interpolated on the flight track. The reddish area represents the 0.6 km thick transition layer between 321 and 329 K in potential temperature.

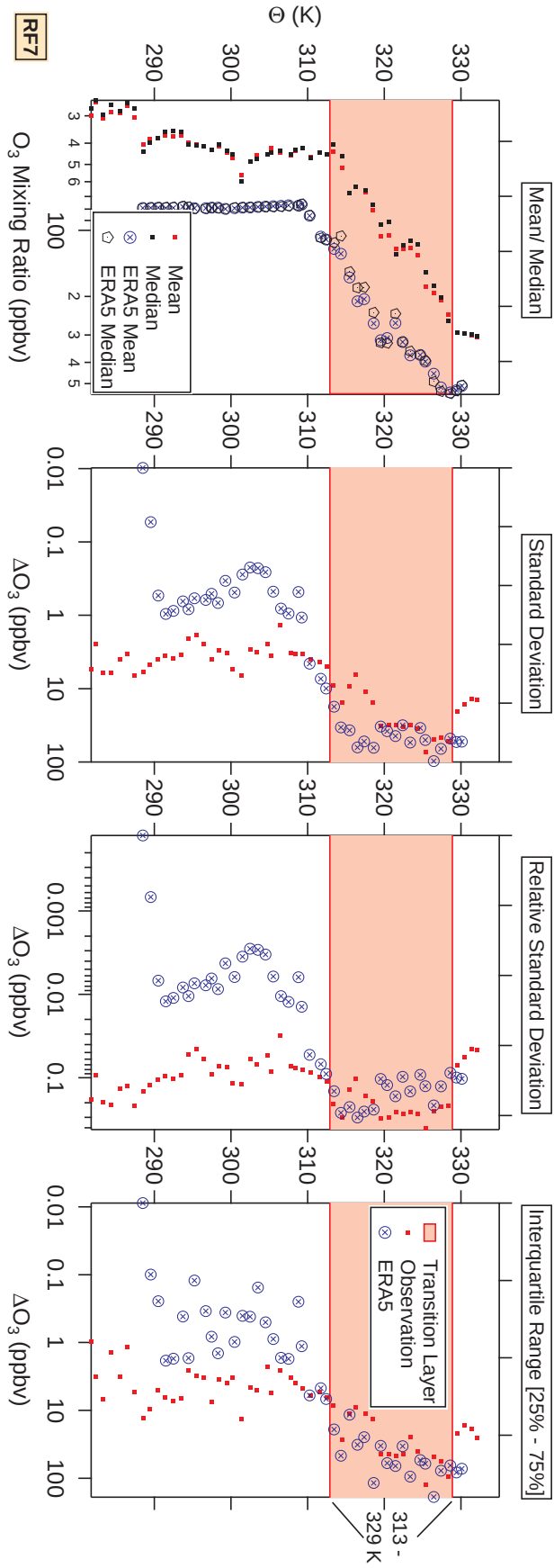


Figure A.5: Vertical profile of the statistic parameters mean, median, absolute and relative standard deviation, and the interquartile range of the O_3 volume mixing ratio during RF7. Red and black dots depict observational data, blue and grey circles denote ERA5 reanalysis data provided by Hersbach et al. (2018) interpolated on the flight track. The reddish area represents the 1.3 km thick transition layer between 313 and 329 K in potential temperature.

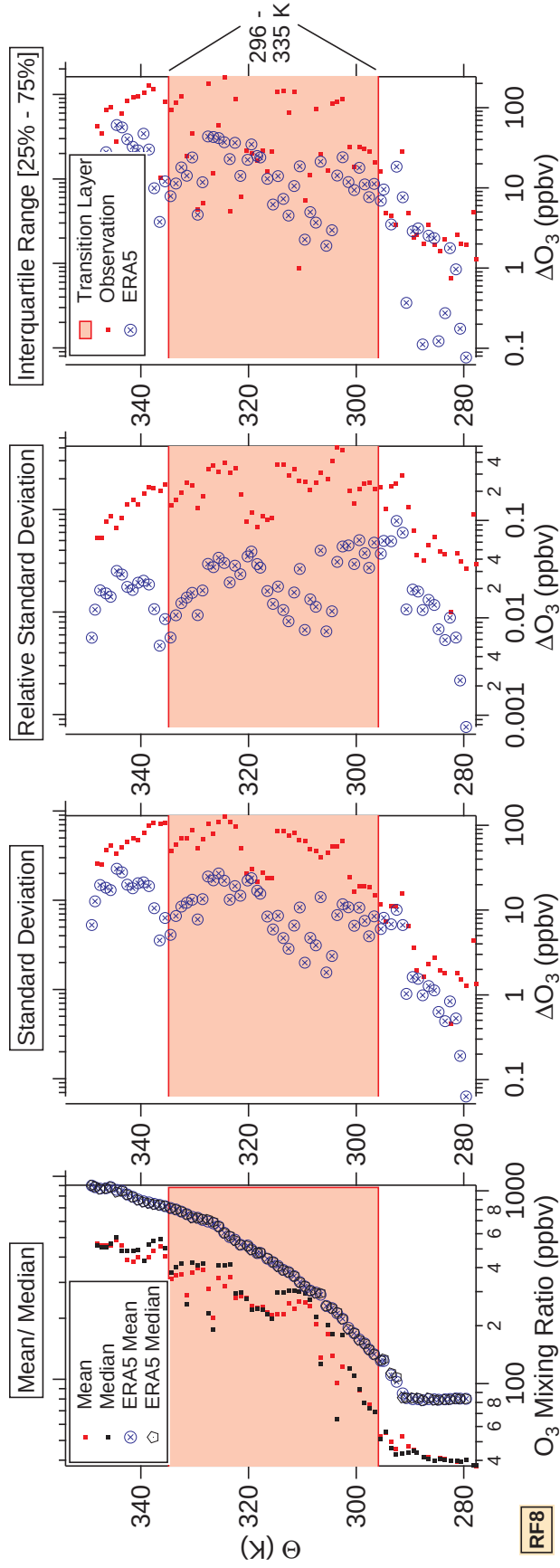


Figure A.6: Vertical profile of the statistic parameters mean, median, absolute and relative standard deviation, and the interquartile range of the O_3 volume mixing ratio during RF8. Red and black dots depict observational data, blue and grey circles denote ERA5 reanalysis provided by Hersbach et al. (2018) interpolated on the flight track. The reddish area represents the 2.9 km thick transition layer between 296 and 335 K in potential temperature.

A.2 MASS SPECTRA OF ND-MAX PARTICLE TYPES

This section describes the classification of particle types as introduced in Sect. 2.2.2. The mass spectra of the particle types detected during ND-MAX are analyzed for their major peaks regarding the cation and anion spectrum. Once the peaks were inferred with the help of a fragmentation table based on literature, the particle types were interpreted with the aid of several studies of single particle mass spectrometry. The particles are described according to the list of detected particles provided in Table 2.2.

According to the list provided in Table 2.2, the second particle type is *CaK-NaClMg*, which has a chemical signature typically known for *sea spray*. The ion signal peaks in Fig. A.7 are typical cation markers of sodium ($m/z +23$), magnesium ($m/z +24/25/26$), potassium ($m/z +39/41$), calcium ($m/z +40$), and chemical compounds of them. The anion spectrum is dominated by chloride ($m/z -35/37$), salt ion clusters ($m/z -93/95$), and nitrate ($m/z -46$ and -62) of which the last is an indicator of aging (Prather et al., 2013; Collins et al., 2014; Su et al., 2023).

The cation and anion spectrum of *elemental carbon* (EC) consist of a series of carbon cluster ions (C_n^+ and C_n^-) that are typical indicators of elemental carbon (Moffet and Prather, 2009; Pratt et al., 2009) and are also attributed to soot cores (Shields et al., 2007). The additional peaks of organics ($m/z +25$, $+37$, $+39$, -26 , and -42), nitrate ($m/z -46$ and -62), and sulphate ($m/z -97$) in Fig. A.8 imply the aging process of these particles. This particle type was shown to have a decreasing fraction with the distance between the NASA DC-8 and the DLR-ATRA (see Sect. 4.1.2). Therefore, this particle type is assumed to be of aircraft engine origin. As carbonaceous soot particles are emitted due to incomplete combustion of fuel hydrocarbon compounds by the aircraft engines (e.g. Voigt et al., 2021 and therein), the EC is assumed to be soot, and, thus, is referred to as *EC/ soot* within the framework of this thesis. A more detailed analysis of this particle type is provided in Sect. 4.1.5.

Beside an ammonium peak ($m/z +18$), the *hydrocarbons* type exhibits a chemical signature based on hydrocarbon fragments ($m/z +58$ and $+59$) (Fig. A.9). The main peak on $m/z +58$ is a marker of diethylamine (Pratt and Prather, 2010), the signals on $m/z +30$ and $+72$ may refer to the methanamine radical CH_2NH_2^+ and the carbonaceous compound $\text{C}_3\text{H}_7\text{NH}(\text{CH}_2)^+$ which are constituents of dipropylamine according to Angelino et al. (2001). As mentioned by Healy et al. (2015), $(\text{CH}_3)_3\text{N}$ ($m/z +59$) is a marker ion for trimethylamine. Consequently, this type is referred to as *amines*. The anion spectrum is very noisy and contains weak signals of nitrate and sulphate.

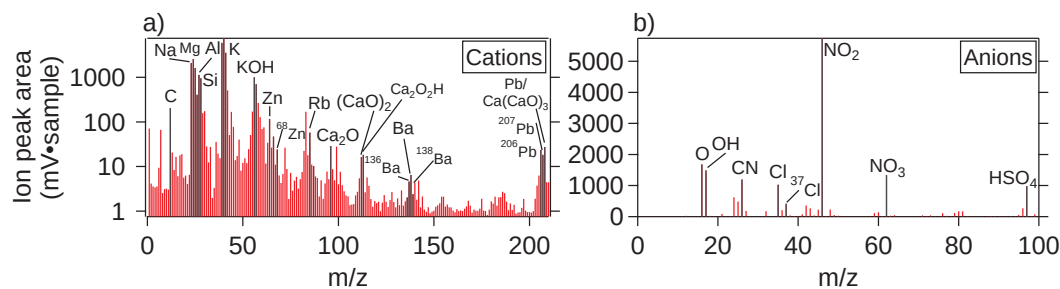


Figure A.10: Mean mass spectrum of cations (a) and anions (b) of the particle type *processed sea spray* detected during ND-MAX.

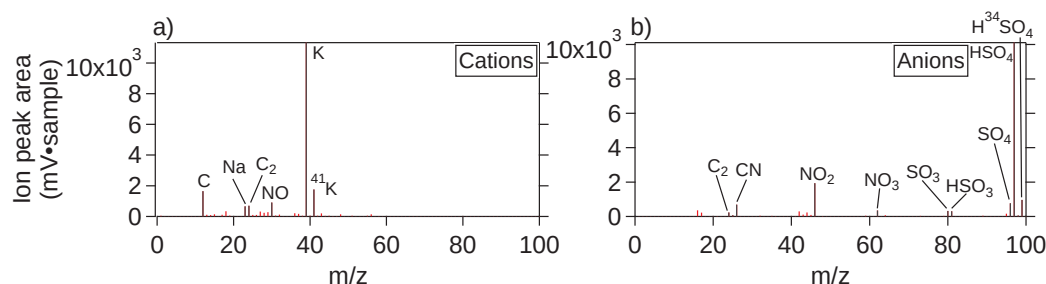


Figure A.11: Mean mass spectrum of cations (a) and anions (b) of the particle type *biomass burning type 1* detected during ND-MAX.

spectrum of both polarities is characteristic for sea spray particles although some of the assigned particles might originate from soil dust (Cornwell et al., 2020).

KOrgNOSO is the name of three clusters that show similar mean spectra for cations and anions. All of them are dominated by (and named accordingly) the potassium signature on $m/z +39/41$ in the cation spectrum and anion signals of nitrate ($m/z -46$, and -62) and sulphate ($m/z -81$ and $-97/-99$) as depicted in Fig. A.11. Minor cation signals refer to carbon ($m/z +12$ and $+24$) and sodium ($m/z +23$) which suggest a biomass burning origin (Pratt et al., 2009; Pratt and Prather, 2010). Consequently, this particle type is interpreted as *biomass burning type*. The differences between the three types are based on their chemical signatures, the signal intensities of the anions, and the particle size. In Fig. A.12, *KOrgNOSO2* contains additional anion signals of silicates ($m/z -60$ and -76), and phosphate ($m/z -79$), that were not found for the first type. Furthermore, the signal intensity of anion signals is decreased by two orders of magnitude. However, the particles are detected in the same size range as for *KOrgNOSO1*, mainly within 150 nm and 850 nm (Fig. 4.6). In contrast, the third type *KOrgNOSO3* rather consists of particles ranging from 500 nm to

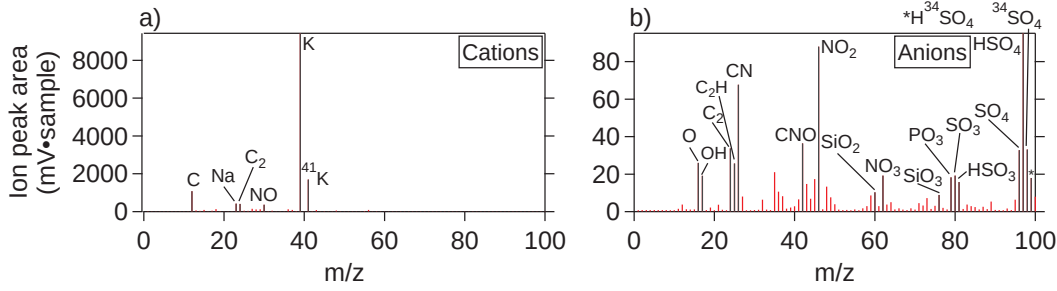


Figure A.12: Mean mass spectrum of cations (a) and anions (b) of the particle type *biomass burning type 2* detected during ND-MAX.

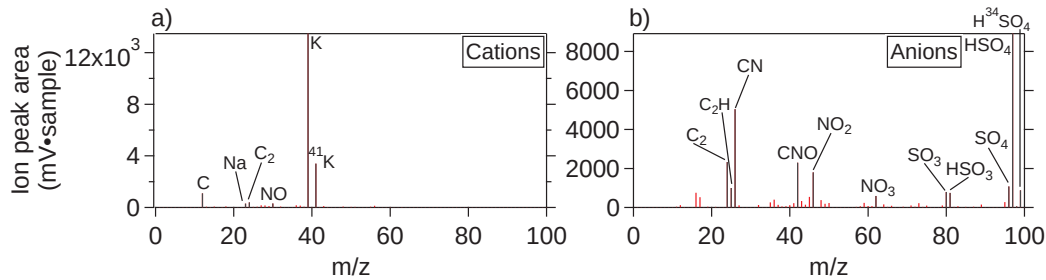


Figure A.13: Mean mass spectrum of cations (a) and anions (b) of the particle type *biomass burning type 3* detected during ND-MAX.

1200 nm as depicted in Fig. 4.6. Apart from that, the mean spectra (Fig. A.13) are very similar to those of *KOrgNOSO1*.

Following the *AlOrgNOPhoSOCl* type in Sect. 2.2.2 interpreted as *mineral dust*, a second particle type reveals similar characteristics but also includes strong signatures of chrome. Furthermore, fragments of fluor and chloride are detected, indicating a mixture with sea spray. In Fig. A.14, the cation spectrum of this type shows ion peaks of sodium ($m/z +23$), magnesium ($m/z +24/25/26$), aluminium ($m/z +27$), potassium ($m/z +39/41$), calcium ($m/z +40$), and iron ($m/z +54/56$) which are alike the ion peak markers of mineral dust. In contrast, signal peaks of chrome ions ($m/z +52/53/54$) are detected and confirmed by the mass-to-charge ratios $m/z -84$ and -100 in the anion spectrum. Since chrome has been used in the last decades to protect aircraft turbines against corrosion (see Sect. 4.1.1), its origin is assumed to be from aerospace travel. The signals of negative ions include those of silicon as indicative for mineral dust, and those of phosphate, nitrate, and sulphate alike the mineral dust type implying a processing of the particle type. In addition, the peaks of fluor and chloride suggest a mixture of mineral dust with sea spray, probably due to processing inside cloud droplets. Therefore, the particle type is interpreted as *processed mineral dust*.

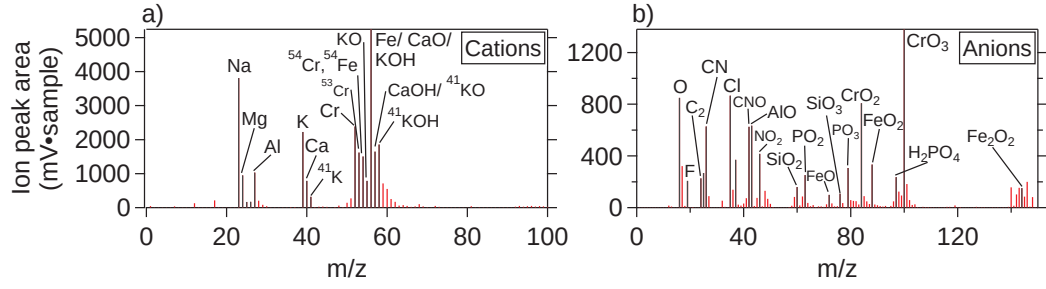


Figure A.14: Mean mass spectrum of cations (a) and anions (b) of the particle type *processed mineral dust* detected during ND-MAX.

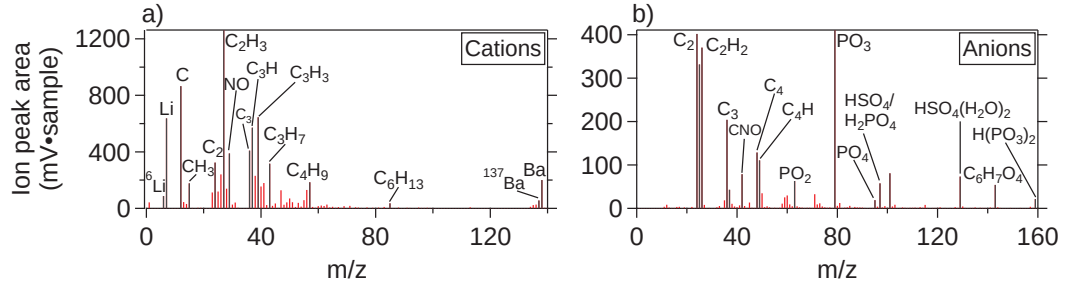


Figure A.15: Mean mass spectrum of cations (a) and anions (b) of the particle type *motor oil* detected during ND-MAX.

The *MetOrgPhoSO* cluster is another type potentially associated with aircraft engine exhaust. The mean cation spectrum in Fig. A.15 is dominated by carbon (m/z +12, +24, +36) and hydrocarbon signals (m/z +15, +27, +37, and +39). Still, the characteristic signals are the carbonaceous compounds detected on m/z +57 and +85 that are attributed to engine oil (Clemen et al., 2024). Additional marker peaks on m/z -143 ($C_6H_8O_2P^-$) and -159 ($C_7H_{12}O_2P^-$) in the anion spectrum were mainly driven by carbon (e.g. m/z -24 and -36) and phosphate (e.g. m/z -79 and -95) compounds. These ion signals are assumed to refer to organophosphates that were previously found in jet engine lubrication oils (Schindler et al., 2014). Other signals are assigned to lithium (m/z +6 and +7) and barium (m/z +136/137/138), though their origin and contribution is still unclear. In consequence, this type is interpreted as *motor oil*.

A high abundance of magnesium (m/z +24/25/26) and iron (m/z +54/56) as well as minor cation peaks of sodium (m/z +23), aluminium (m/z +27), potassium (m/z +39/41), calcium (m/z +40), and oxides of iron (m/z +72, and +73) characterize the mean cation spectrum of *NaMgFe* depicted in Fig. A.16. The combination of these markers is typical for particles of meteoric origin. Besides, the anion spectrum mostly consists of sulphate signals in agreement with findings in Schneider et al. (2021). Even the cation spectrum contains

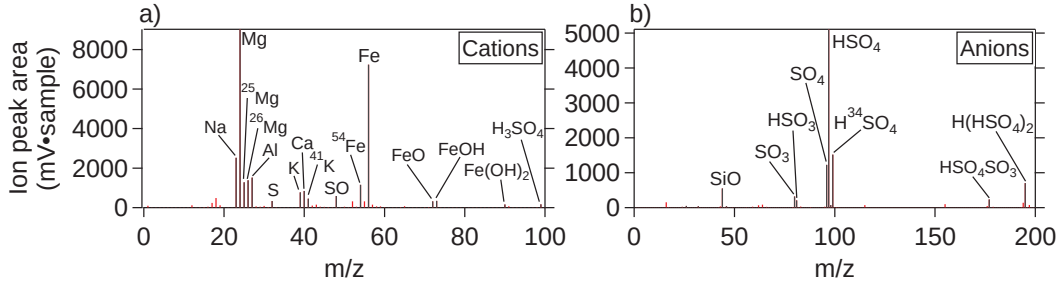


Figure A.16: Mean mass spectrum of cations (a) and anions (b) of the particle type *meteoric material* detected during ND-MAX.

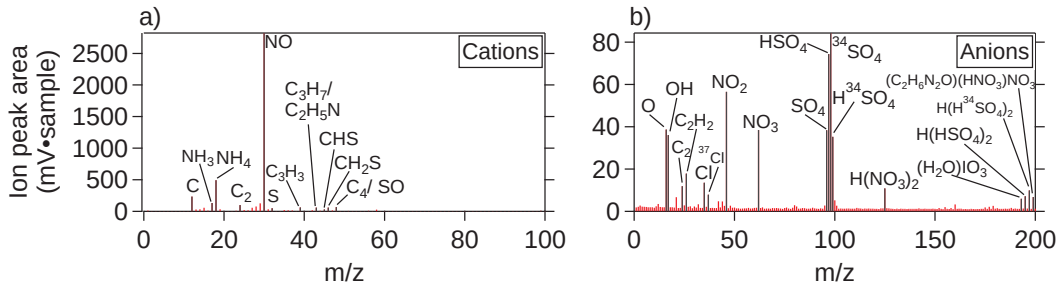


Figure A.17: Mean mass spectrum of cations (a) and anions (b) of the *nitrate-rich particle type* detected during ND-MAX.

signals of sulphate (m/z +32, +48, +99). As these particles of cosmic origin accumulate terrestrial compounds on their way along the UTLS-region, they are referred to as *particles containing meteoric material*. In the framework of this thesis, they are referenced as *meteoric material*.

Figure A.17 exhibits the mass spectra of the *NOSO* type which primarily contains signals nitrate (m/z +30, -46, and -62), sulphate (m/z -96, -97/99), and ammonium (m/z +18). Besides, small signals of carbon (e.g. m/z +12, +24, and +48), hydrocarbons (e.g. m/z +39, and +45), and sulphate (m/z +32, and +48) are detected in the cation spectrum. Major anion peaks of nitrate and sulphate were also found next to signals of O⁻ and OH⁻. Minor peaks are related to chloride (m/z -35, and -37) and iodide (m/z -193). Except for the halogen components, a similar type was detected during the StratoClim campaign 2017 as part of the Asian tropopause aerosol layer (Appel et al., 2022). As this *NOSO* type was detected in January and February over Central Europe, it can be linked neither to the Asian tropopause aerosol layer nor to aged air masses shed from the Asian monsoon anticyclone that mainly occur during northern hemisphere summer. It is a matter of current research where this particle type originates from. Here, it is referred to as *nitrate-rich* particle type because of its extraordinary large nitrate signal in the cation spectra.

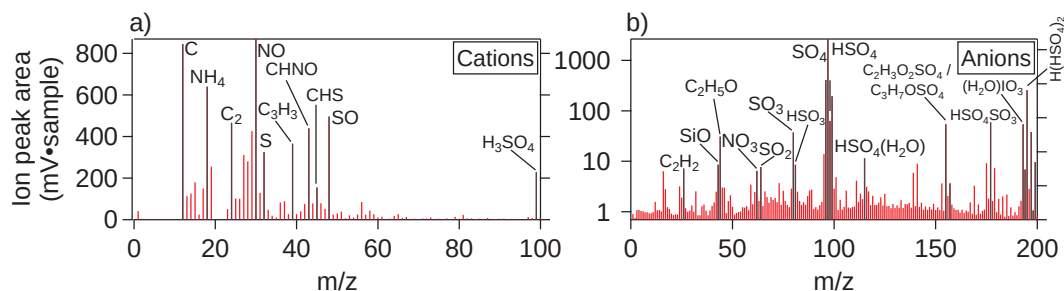


Figure A.18: Mean mass spectrum of cations (a) and anions (b) of the particle type *internally mixed elemental and organic carbon (ECOC) with nitrate and sulphate compounds* detected during ND-MAX.

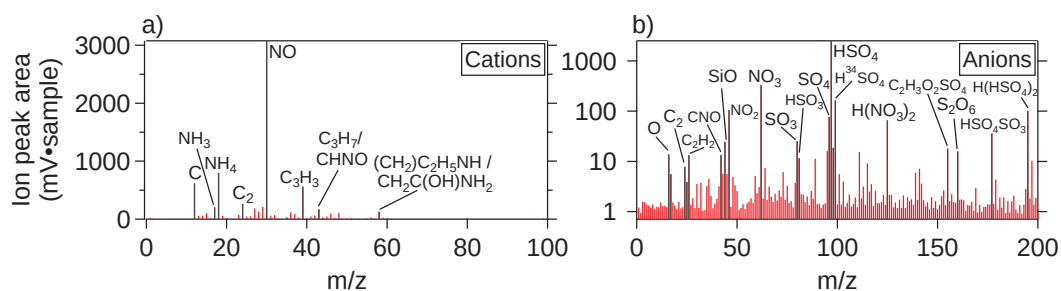


Figure A.19: Mean mass spectrum of cations (a) and anions (b) of the particle type *processed organic carbon (OC)* detected during ND-MAX.

The mean cation spectrum of *OrgNOSO* in Fig. A.18 has signals of nitrate ($m/z +30$), carbon ($m/z +12$, and $+24$), and ammonium ($m/z +18$). With the exception of meteoric material, this cluster is the only one providing cation sulphate signals on $m/z +32$, $+48$, and $+99$. The anion spectrum mainly exhibits sulphate peaks (e.g. $m/z -80$, -81 , -96 , $-97/99$, and -195). Minor signals are detected on $m/z -44$ and -62 denoting SiO and NO₃. Gunsch et al. (2018) detected a similar particle type without cation sulphate signals that was named *ECOC-sulfate*. In accordance with Gunsch et al. (2018), the *OrgNOSO* is also interpreted as an *internal mixture of elemental and organic carbon with nitrate and sulphate*. Nevertheless, this particle type features additional sulphate signals in the cation spectrum.

The second type *OrgNOSO2* (Fig. A.19) contains major cation peaks of nitrate ($m/z +30$), ammonium ($m/z +18$), carbon ($m/z +12$), and hydrocarbon ($m/z +39$), similar to the *nitrate-rich particle type*. Even though nitrate is the strongest peak, the mass spectrum contains larger fragments of organic carbon, and is thus referred to as *processed organic carbon (OC)*. The anion spectrum mainly consists of organic ($m/z -24/25/26$), nitrate ($m/z -46$, -62 ,

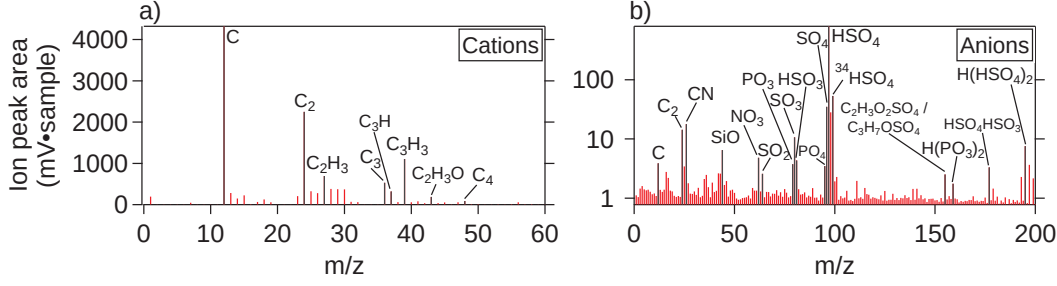


Figure A.20: Mean mass spectrum of cations (a) and anions (b) of the particle type *coated soot* detected during ND-MAX.

and -125), and predominant sulphate signals (e.g. m/z -80, and -97/99). The characteristics of this type are analyzed in more detail in Sect. 4.1.5.

OrgSO (Fig. A.20) is mainly characterized by a small series of carbon cluster ions (m/z +12, +24, +36, and +48) and organic ions (m/z +27, +37, +39, and +43) in the cation spectrum. Carbonaceous compounds are also detected in the anion spectrum beside constituents of phosphate (m/z -79, -95, and -159) and sulphate (e.g. m/z -80, -97, -177, and -195). As this particle type has a similar spectrum to *elemental carbon* but depicts more signals of additional material as introduced in Sect. 4.1.5, it is referred to as *coated soot*, adapted from Moffet and Prather (2009). A detailed analysis is given in Sect. 4.1.5.

A.3 UNCERTAINTY ANALYSIS

Particle fraction and source fraction

The uncertainty of the particle fraction (PF) was calculated using binomial statistics. The ablation process of a single particle can be described as a Bernoulli process (Köllner, 2020). Hence, the uncertainty σ_{PF}^{bin} can be calculated by (Clemen et al., 2020; Köllner, 2020; Eppers, 2023):

$$\sigma_{PF}^{bin} = \frac{\sqrt{C_{hits} \cdot PF \cdot (1 - PF)}}{C_{hits}} \quad (\text{A.1})$$

The source fraction and corresponding error were calculated analogously to PF .

Detection efficiency

The absolute uncertainty of the detection efficiency σ_{DE} was calculated using Poisson statistics and Gaussian propagation of uncertainties:

$$\sigma_{DE} = \frac{N_{coinc}}{N_{ref}} \sqrt{\left(\frac{1}{\sqrt{C_{coinc}}}\right)^2 + \left(\frac{1}{\sqrt{C_{ref}}}\right)^2 + \left(\frac{\sigma_{f_{ERICA}}}{f_{ERICA}}\right)^2} \quad (\text{A.2})$$

with the relative statistical uncertainty of the particle coincidence of both detection stages in ERICA ($\frac{1}{\sqrt{C_{coinc}}}$), the relative statistical uncertainty of the particle counts detected by the reference instrument ($\frac{1}{\sqrt{C_{ref}}}$), and the relative uncertainty of the aerosol particle flow into ERICA ($\frac{\sigma_{f_{ERICA}}}{f_{ERICA}}$). As the uncertainty of the flow was assumed to be proportional of the uncertainty of the aerodynamic lens pressure $\sigma_{p_{ERICA}}$, the latter was adopted. Thus, the relative uncertainty of the particle flow into ERICA was approximated with $\frac{\sigma_{p_{ERICA}}}{p_{ERICA}}$ in Eq. A.2.

Hit rate

The calculation of the absolute uncertainty of the hit rate σ_{HR} was based on binomial statistics (Clemen et al., 2020; Köllner, 2020; Eppers, 2023):

$$\sigma_{HR} = \sqrt{\frac{C_{hits} \cdot (1 - HR)}{C_{shots}}} \quad (\text{A.3})$$

with the number of particles that are hit by the ablation laser and, thus, create a mass spectrum (C_{hits}), the number of successfully triggered laser shots (C_{shots}), and the hit rate (HR).

Collection efficiency

The absolute uncertainty of the collection efficiency (σ_{CE}) was calculated using Gaussian propagation of uncertainties:

$$\sigma_{CE} = \sqrt{(HR \cdot \sigma_{DE})^2 + (DE \cdot \sigma_{HR})^2} \quad (\text{A.4})$$

APPENDIX: SUPPLEMENTARY INFORMATION FOR CHAPTER 3

B.1 ND-MAX RESEARCH FLIGHTS

An overview of all eight RFs is provided in Table B.1 that were considered for the analysis within this framework. In general, the analysis covered the entire number of RFs. However, for the analysis of the flight distance between the NASA DC-8 and the DLR-ATRA all flights except for RF7 were taken into account since several commercial airplanes were followed during RF7. Also, the impact of individual fuel types was only analyzed for the flights mentioned above since no information were available about the fuel types of the public aircraft.

Table B.1: Overview of the ND-MAX flights considered in this study. For the analysis of particle fractions, weather pattern, and propagation of trajectories all flights were taken into account. The analysis of the flight distance and the impact of individual aircraft fuel types on the abundance of individual particles was considered with the exception of RF7.

Flight name	Date in 2018	Take-off and landing time (UTC)
RF1	17 January	10:09:13 - 14:56:11
RF2	19 January	10:51:53 - 16:21:05
RF3	23 January	11:07:27 - 16:04:32
RF4	24 January	10:59:03 - 17:02:50
RF5	29 January	09:15:21 - 15:27:03
RF6	30 January	10:09:06 - 16:01:37
RF7 ¹	31 January	09:51:53 - 15:27:38
RF8	1 February	08:34:25 - 13:45:03

¹ no chase of the DLR-ATRA, but of several commercial airplanes

B.2 WEATHER CONDITIONS DURING ND-MAX

Meteorological conditions on RF2

RF2 was conducted during the cold air period. This is shown in Fig. B.1 where the air space area was under the influence of a large trough reaching from Greenland to the Baltic States, leading to a northwesterly circulation and advection of cold and marine air masses to Northern Germany. The temperatures ranged between -8 and -4 °C. The synoptic weather map in Fig. B.2 also reveals the inflow of air masses from the North Atlantic across the British Isles which was triggered by the cyclone over the Norwegian Sea. As for RF1 in the cold period (see Sect. 3.3.1), the flight space area was located in the back of a low pressure system over Eastern Europe. As a consequence, the region was affected by rain showers. Moreover, the tropopause was observed at low levels around 8 km according to Fig. 3.4 which was in agreement with the vertical profiles of relative humidity and trace gases that have been analyzed in detail in Sect. 3.3.1. The cloud mask in Fig. B.3 mostly consisted of stratus clouds but cumulus clouds were observed next to the German North Sea coast that indicated an unstable stratification in the area of interest. According to the Schmidt-Appleman-Temperature (Fig. B.4), the UTLS-region provided favorable conditions to the formation and persistence of contrails during the flight.

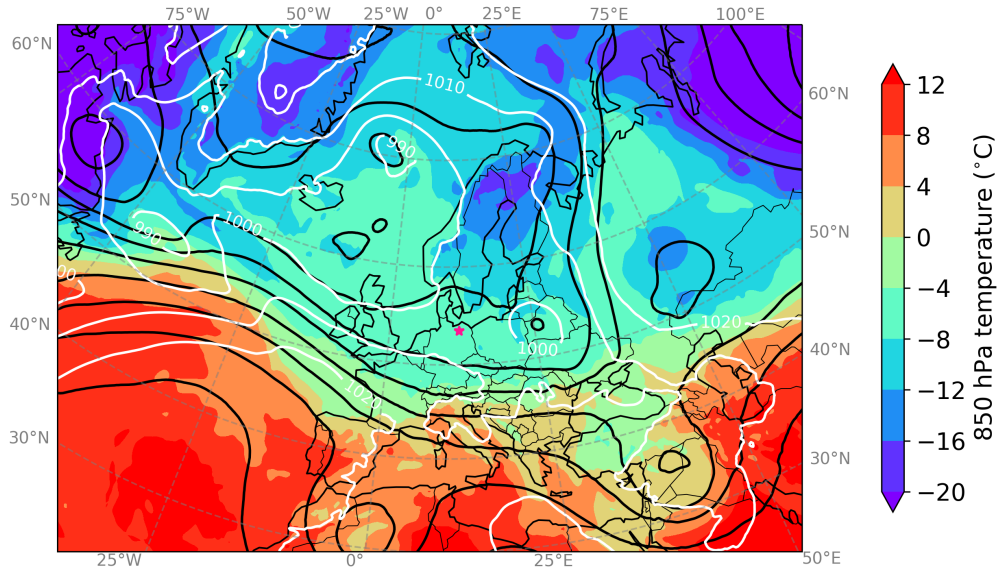


Figure B.1: Weather map of 19th January 2018, 12:00 UTC as in Fig. 3.2. The red star denotes the area used for RF2. Plotted with ERA5-data provided by Hersbach et al. (2018).

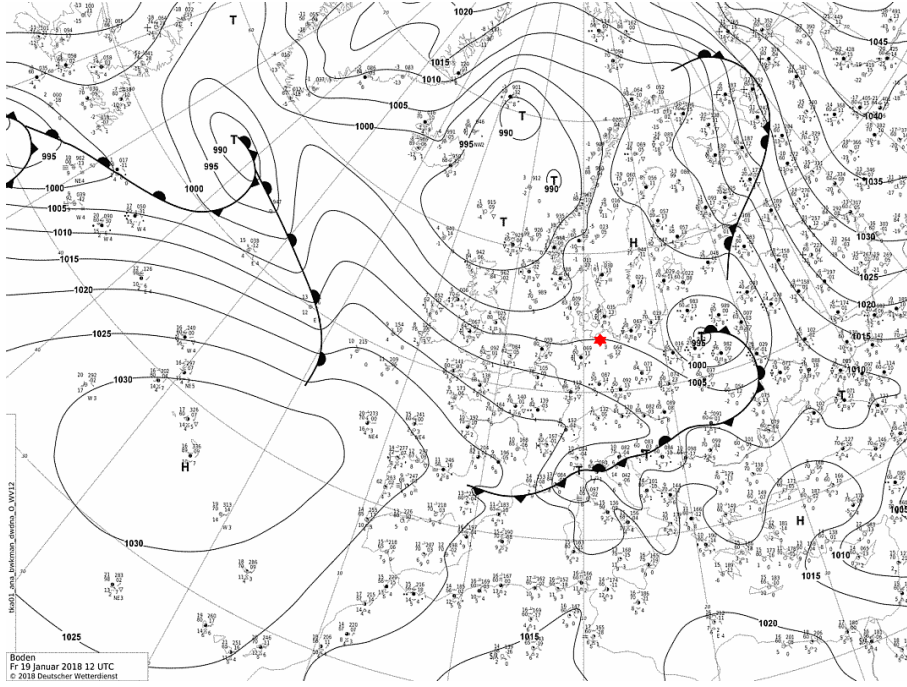


Figure B.2: Synoptic weather map of German Weather Service (Deutscher Wetterdienst; DWD) of 19th January 2018, 12:00 UTC as in Fig. 3.3. The red star denotes the area used for RF2. Adapted from wetter3 (2018).

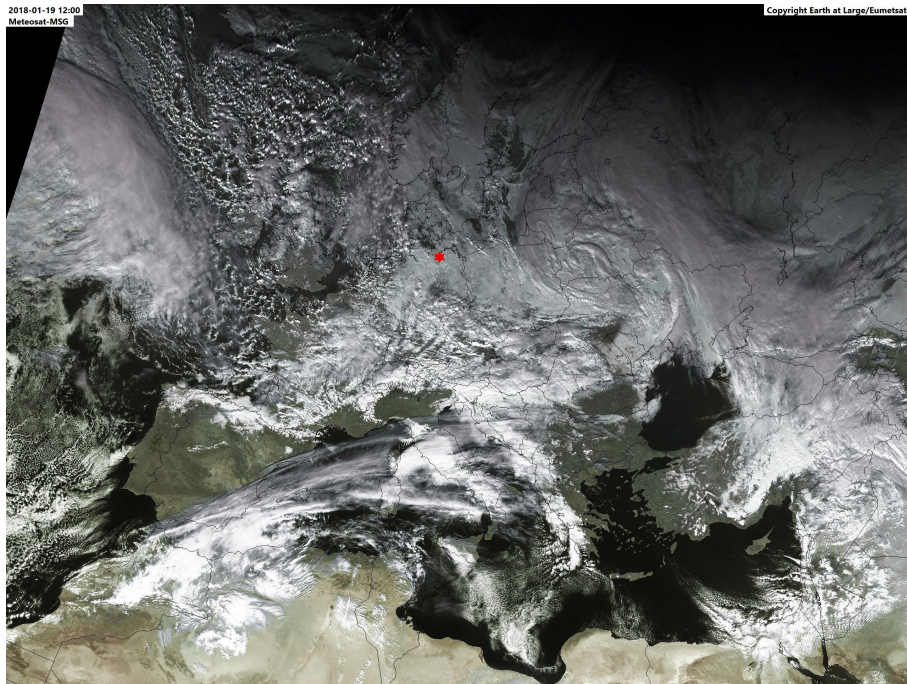


Figure B.3: Satellite image of EUMETSAT of 19th January 2018, 12:00 UTC, Meteosat Second Generation, VIS-Channel $0.6\ \mu\text{m}$. The image shows the cloud coverage over Europe and the unstable stratification (indicated by convection) along the flight region. The red star denotes the area used for RF2. Adapted from Valk (2018) with permission from EUMETSAT.

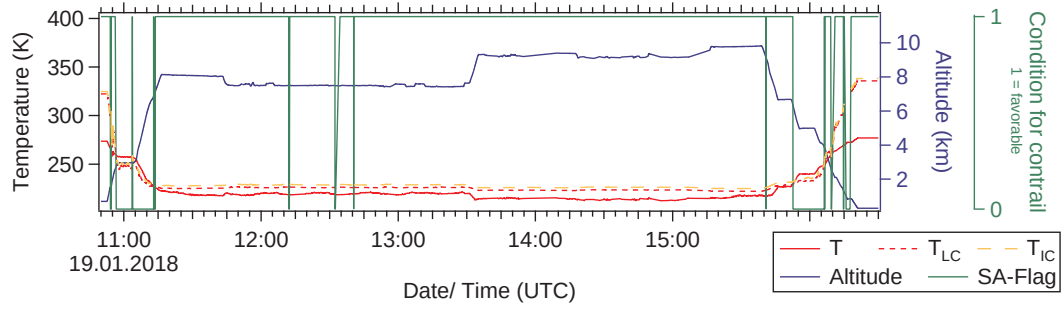


Figure B.4: Ambient temperature (red), flight level (blue), the Schmidt-Appleman-Temperatures for contrail formation (T_{LC} , red, short-dashed) and persistence (T_{IC} , orange, long-dashed). The green line marks the legs on which contrails can form and persist, i.e. where both thresholds are underpassed. Over long stretches of RF2, the aircraft passed regions providing appropriate conditions for the formation and persistence of contrails.

Meteorological conditions on RF4

RF4 was part of the warm period (see Sect. 3.3.3) which was characterized by an intensive trough next to Scotland. Located at the western flank of a high-level ridge (Fig. B.5), the region of interest was exposed to a cyclonic circulation ahead of a high-level depression. This led to a strong advection of warm and moist air masses from the South Atlantic. As a result, the temperatures at the 850 hPa-level ranged between 4 and 8 °C, providing atmospheric boundary conditions appropriate for the formation of contrails. Fig. B.6 shows the warm front and sector of a corresponding storm system over the Norwegian Sea, indicative for cirrus clouds, and thus, favorable conditions to contrail formation. The satellite image in Fig. B.7 reveals a stable stratification as a result of a stratiform cloud mask over the flight space area that belonged to the warm front. However, the cloud mask impeded the detection of cirrus clouds. The cold front reached from the Iberian Peninsula across the British Isles to the Norwegian Sea and was not affecting yet the flight area. As expected, the tropopause was at a higher altitude level above 10 km according to Fig. 3.15 due to the uplift of air masses ahead of the cyclone. The Schmidt-Appleman-Temperature (Fig. B.8) provided a time window up to 14:30 UTC for the potential of contrail formation. Later on, the flight track remained on FL260 in an environment providing too high temperatures because of warm advection.

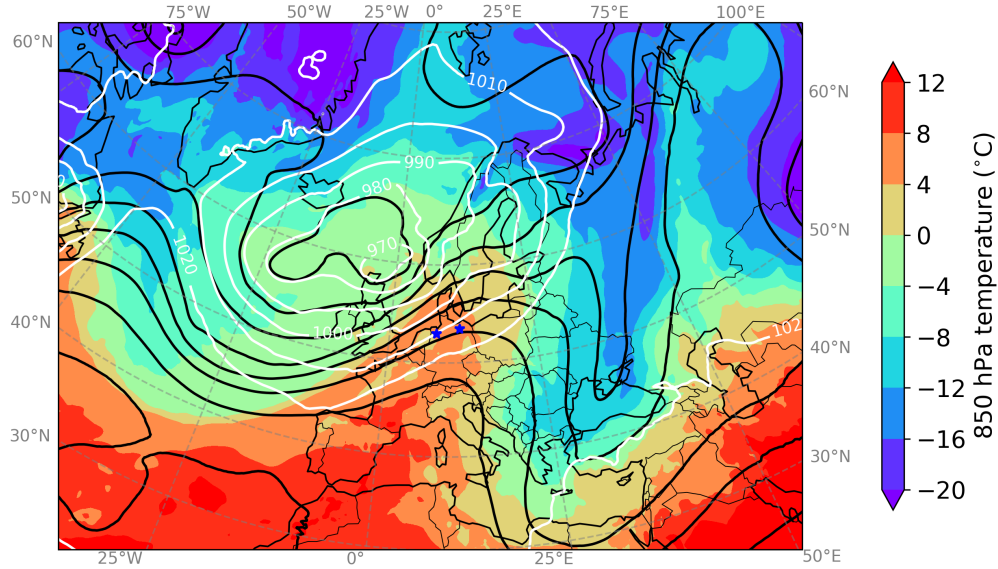


Figure B.5: Weather map of 24th January 2018, 12:00 UTC as in Fig. 3.2. The blue stars denote the areas used for RF4. Plotted with ERA5-data provided by Hersbach et al. (2018).

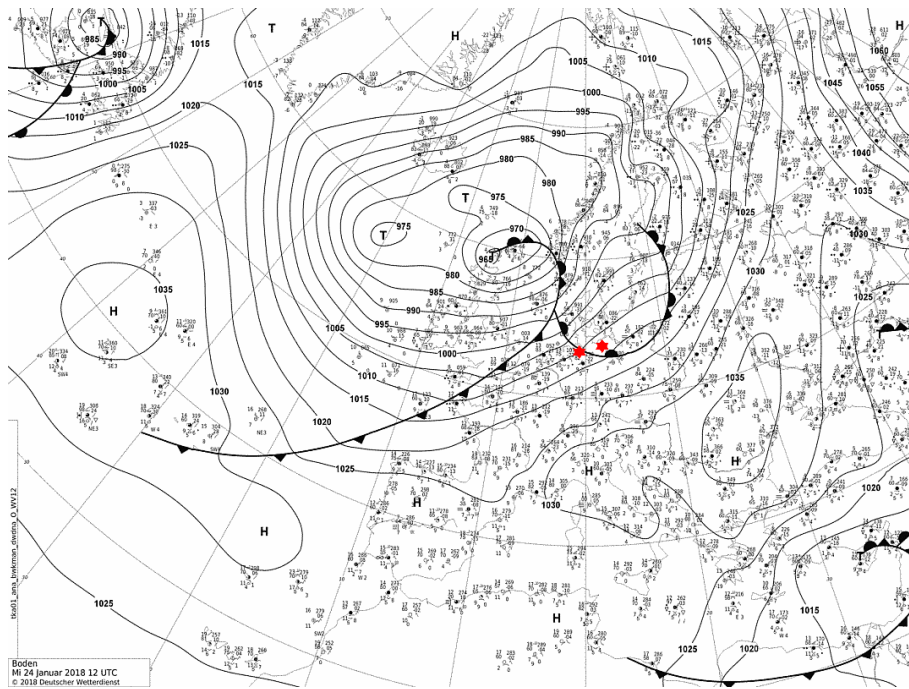


Figure B.6: Synoptic weather map of German Weather Service (Deutscher Wetterdienst; DWD) of 24th January 2018, 12:00 UTC as in Fig. 3.3. The red stars denote the areas used for RF4. Adapted from wetter3 (2018).

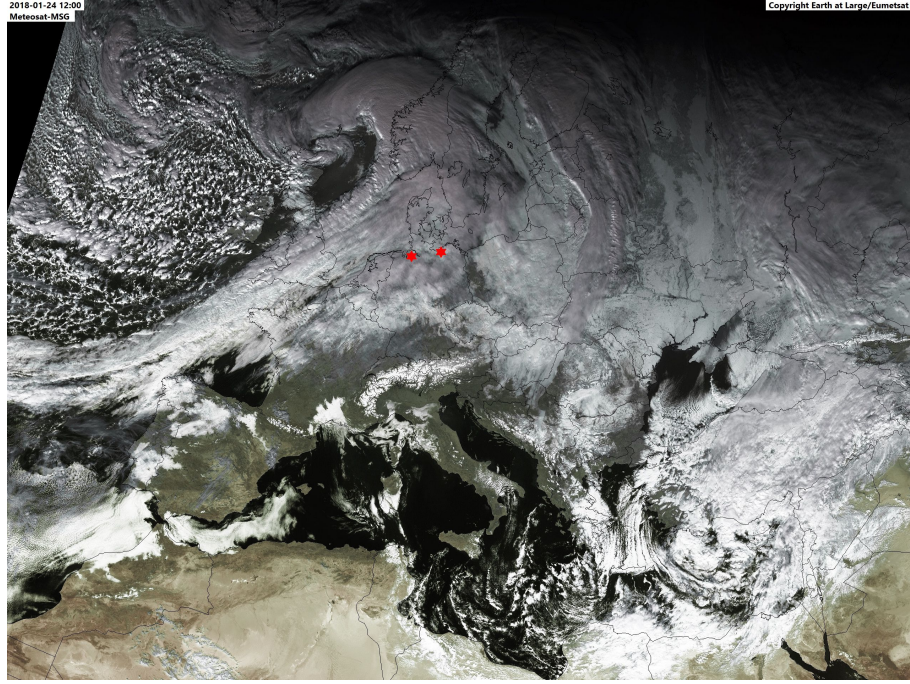


Figure B.7: Satellite image of EUMETSAT of 24th January 2018, 12:00 UTC, Meteosat Second Generation, VIS-Channel $0.6\ \mu\text{m}$. The image shows the cloud coverage over Europe and the unstable stratification (indicated by convection) along the flight region. The red stars denote the areas used for RF4. Adapted from Valk (2018) with permission from EUMETSAT.

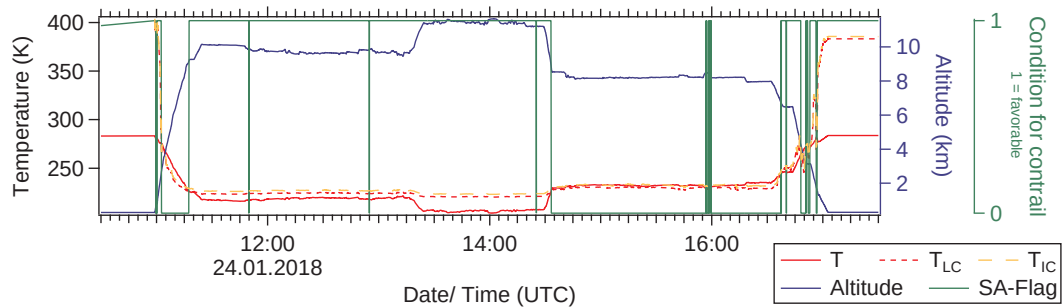


Figure B.8: Ambient temperature (red), flight level (blue), the Schmidt-Appleman-Temperatures for contrail formation (T_{LC} , red, short-dashed) and persistence (T_{IC} , orange, long-dashed). The green line marks the legs on which contrails can form and persist, i.e. where both thresholds are underpassed. On FL320 and 380 of RF4, the atmosphere provided appropriate conditions for the formation and persistence of contrails. On FL260, the ambient temperatures did not underpass the Schmidt-Appleman-Temperature.

Meteorological conditions on RF5

RF5 was attributed to the warm period (see Sect. 3.3.3). The high-level map (Fig. B.9) displays the frontal zone over Northern Germany. The isohypses implied a zonal flux and the advection of cooler air masses from the west. Nevertheless, the temperatures at the 850 hPa-level still ranged between 0 and 4°C. According to the synoptic weather map in Fig. B.10, the region of interest was located in the warm sector of a small cyclone over Denmark following another low-pressure system over the Baltic States. Consequently, the tropopause remained at a high level above 10 km (Fig. 3.15). The flight area was covered by stratiform clouds as part of the frontal zone. Since cumulus clouds were not observed in and nearby the region of interest, the stratification in Fig. B.11 was assumed to be stable. Furthermore, cirrus clouds were not detected within the airspace area. Referring to the Schmidt-Appleman-Temperature (Fig. B.12), only the legs on FL320 and 380 provided atmospheric conditions for the formation and persistence of contrails. Obviously, the advection of warm air masses still resulted in warm thermal conditions at FL260 which suppressed the creation of contrails.

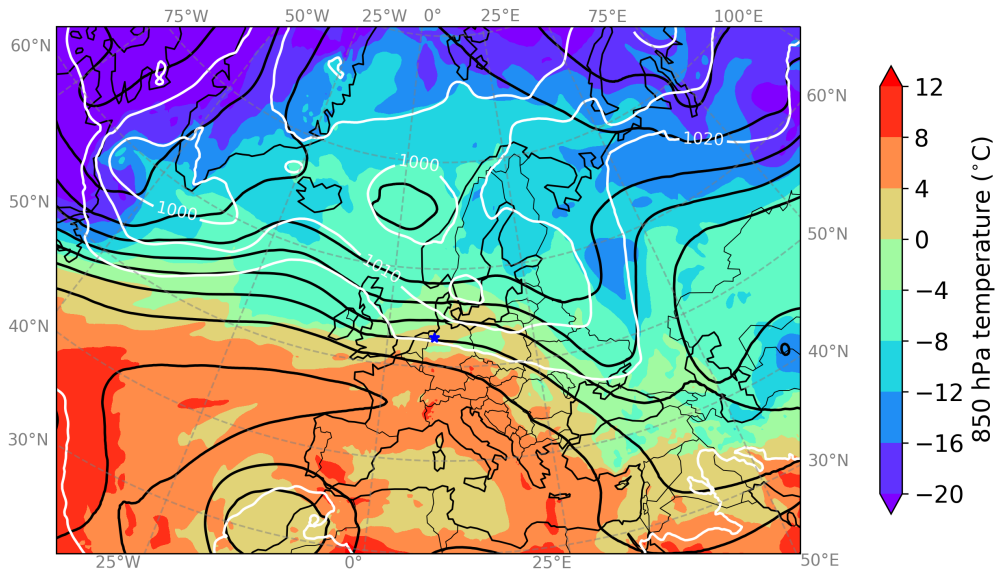


Figure B.9: Weather map of 29th January 2018, 12:00 UTC as in Fig. 3.2. The blue star denotes the area used for RF5. Plotted with ERA5-data provided by Hersbach et al. (2018).

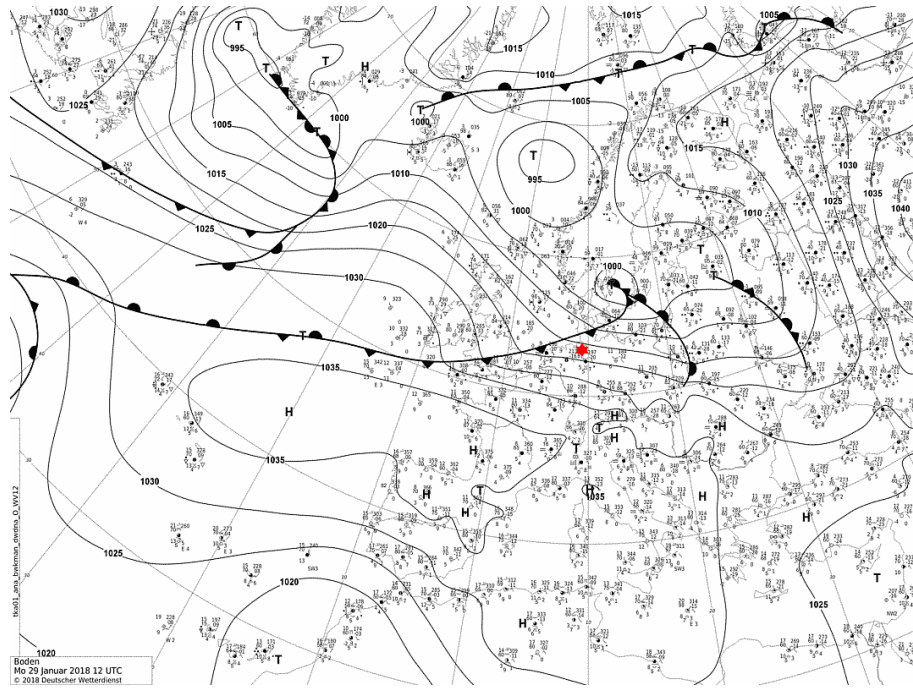


Figure B.10: Synoptic weather map of German Weather Service (Deutscher Wetterdienst; DWD) of 29th January 2018, 12:00 UTC as in Fig. 3.3. The red star denotes the area used for RF5. Adapted from wetter3 (2018).

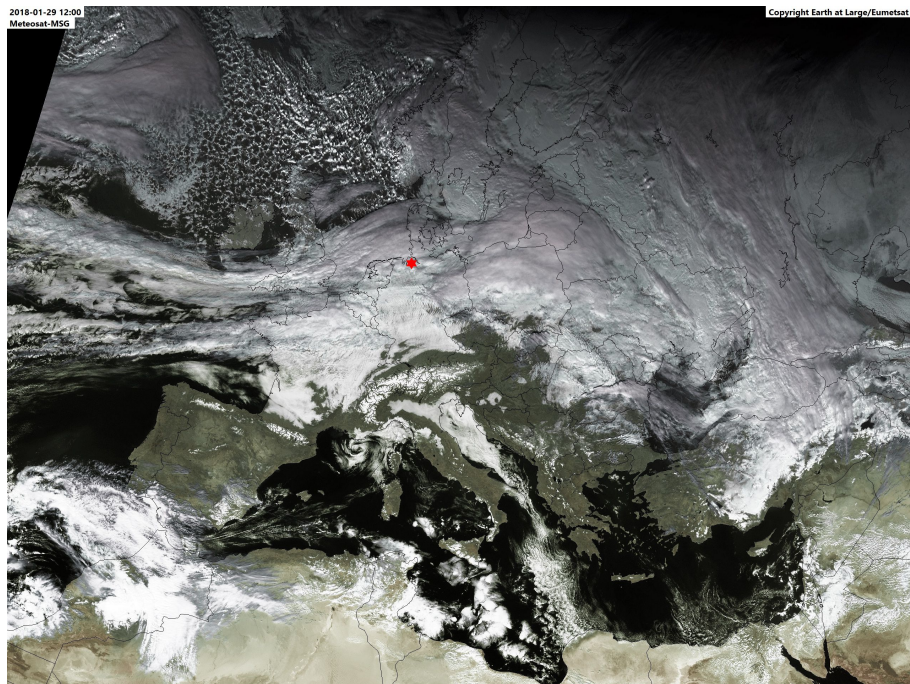


Figure B.11: Satellite image of EUMETSAT of 29th January 2018, 12:00 UTC, Meteosat Second Generation, VIS-Channel $0.6\ \mu\text{m}$. The image shows the cloud coverage over Europe and the unstable stratification (indicated by convection) along the flight region. The red star denotes the area used for RF5. Adapted from Valk (2018) with permission from EUMETSAT.

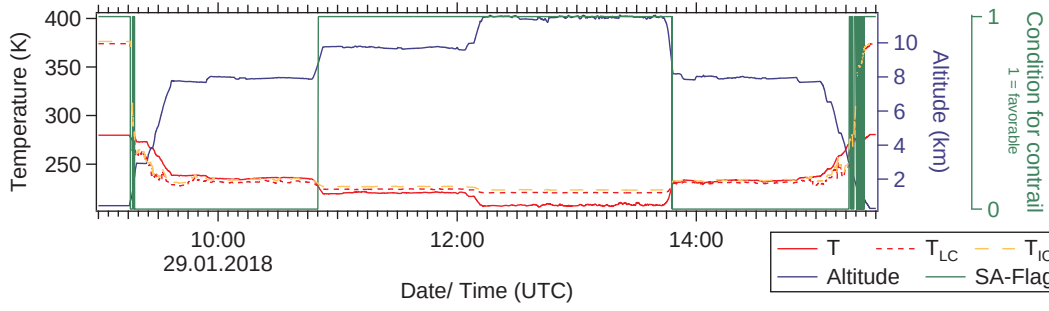


Figure B.12: Ambient temperature (red), flight level (blue), the Schmidt-Appleman-Temperatures for contrail formation (T_{LC} , red, short-dashed) and persistence (T_{IC} , orange, long-dashed). The green line marks the legs on which contrails can form and persist, i.e. where both thresholds are underpassed. On FL320 and 380 of RF5, the atmosphere provided appropriate conditions for the formation and persistence of contrails. On FL260, the ambient temperatures did not underpass the Schmidt-Appleman-Temperature.

Meteorological conditions on RF7

RF7 was the last flight taking place during the warm period (see Sect. 3.3.3). The flight space area was located at the southern flank of a high-level trough over the Norwegian Sea in a cyclonic flow. Even though warm and moist air masses still dominated parts of Northern Germany, low-temperature air masses were advected from the Atlantic Ocean and led to a decreasing temperature-level ranging from -4 to 0°C in 850 hPa (Fig. B.13). According to Fig. B.14, the two cold fronts over Northern Germany and the North Sea already approached the air space area. However, the vertical profiles of temperature and relative humidity (Fig. 3.15) depicted a high-level location of the tropopause at approximately 10 km. The satellite image in Fig. B.15 displayed an inhomogeneous cloud belt reaching from the Biscaya to the Baltic Sea which contained stratus and cumulus clouds. This indicated a partly instable stratification as it is expected in the vicinity of the cold-front. Cirrus clouds were not detected within the region of interest. Furthermore, the Schmidt-Appleman-Temperature was only underpassed on the legs of FL320 and 380 (Fig. B.16), implying a warm surrounding air mass at FL260 that did not support contrail formation.

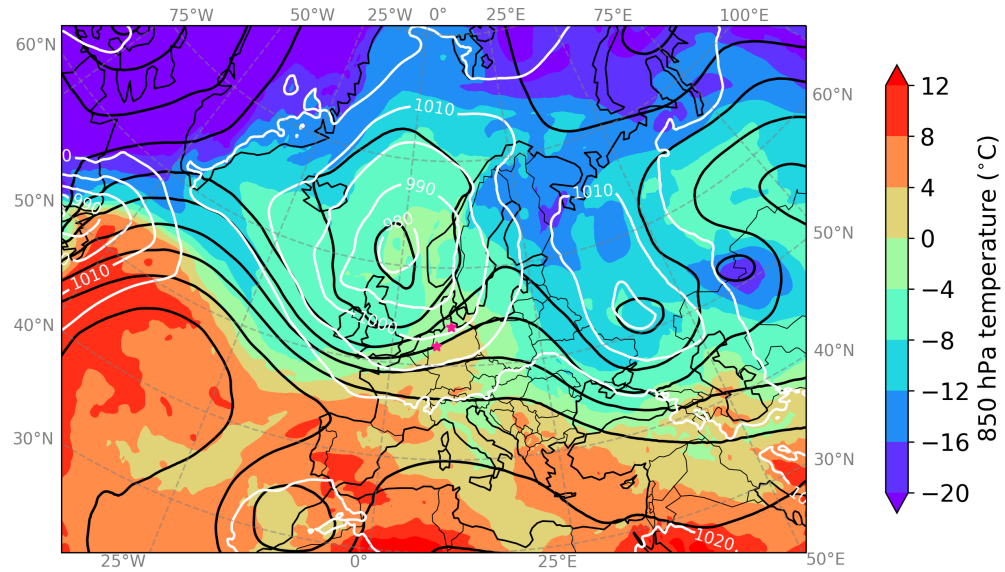


Figure B.13: Weather map of 31st January 2018, 12:00 UTC as in Fig. 3.2. The red stars denote the areas used for RF7. Plotted with ERA5-data provided by Hersbach et al. (2018).

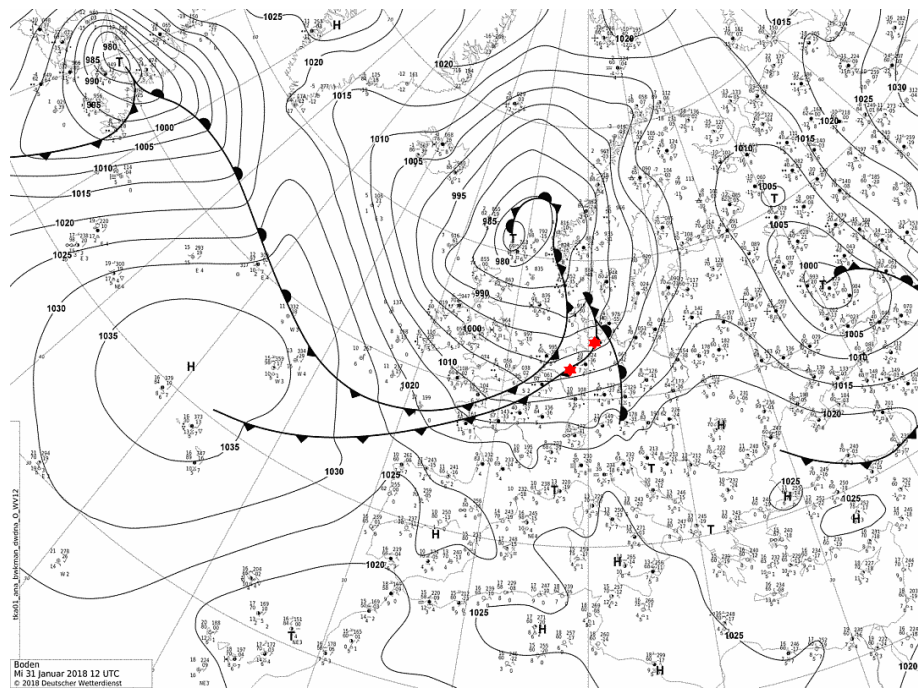


Figure B.14: Synoptic weather map of German Weather Service (Deutscher Wetterdienst; DWD) of 31st January 2018, 12:00 UTC as in Fig. 3.3. The red stars denote the areas used for RF7. Adapted from wetter3 (2018).

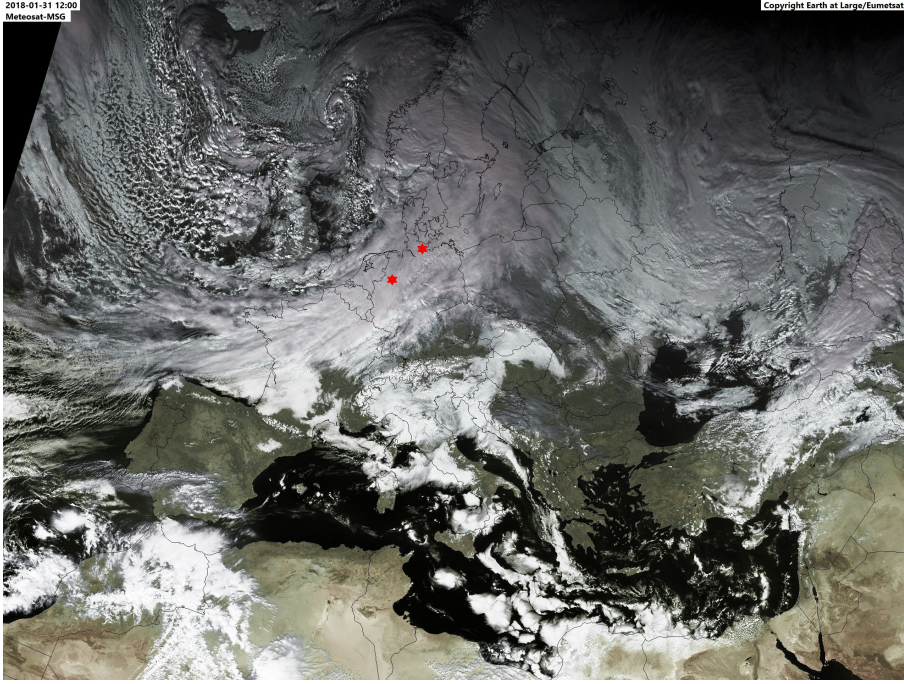


Figure B.15: Satellite image of EUMETSAT of 31st January 2018, 12:00 UTC, Meteosat Second Generation, VIS-Channel 0.6 μm . The image shows the cloud coverage over Europe and the unstable stratification (indicated by convection) along the flight region. The red stars denote the areas used for RF7. Adapted from Valk (2018) with permission from EUMETSAT.

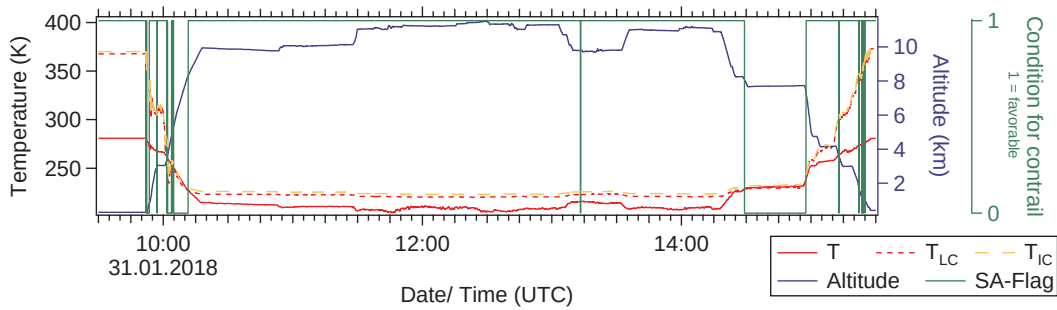


Figure B.16: Ambient temperature (red), flight level (blue), the Schmidt-Appleman-Temperatures for contrail formation (T_{LC} , red, short-dashed) and persistence (T_{IC} , orange, long-dashed). The green line marks the legs on which contrails can form and persist, i.e. where both thresholds are underpassed. On FL320 and 380 of RF7, the atmosphere provided appropriate conditions for the formation and persistence of contrails. On FL260, the ambient temperatures did not underpass the Schmidt-Appleman-Temperature.

Meteorological conditions on RF8

RF8 was the last flight that was attributed to the cold period (see Sect. 3.3.1). The flight space area was placed at the southern flank of a high-level trough centered over West and Central Europe. The isohypses indicated the advection of cold and moist air masses in a cyclonic west to northwesterly circulation, leading to a temperature range of -8 to -4 °C (Fig. B.17). The synoptic weather map unveils that the region of interest was located in the cold air sector of a cyclone over the North Sea in the back of the frontal zone. Consequently, this region was characterized by subsidence and a low-level tropopause at approximately 8 km (Fig. 3.4). The cloud mask implied an unstable stratification in Fig. B.19. Besides the belt of stratiform clouds, many cumulus clouds were observed over Northern Germany and the North Sea indicating a potential for convection. Thus, the observation of cirrus as a "tracer" for contrail formation was nearly impossible. However, the Schmidt-Appleman-Temperature (Fig. B.20) revealed that even at FL260 the atmosphere provided appropriate conditions for the formation and persistence of contrails. Thus, for the majority of the flight time the aircraft passed air masses supporting the creation of contrails. Yet, a small window between 12:00 and 12:15 was characterized by low-level temperatures providing no conditions for contrail formation probably due to very dry conditions of ambient air and indicating a dive into the stratosphere.

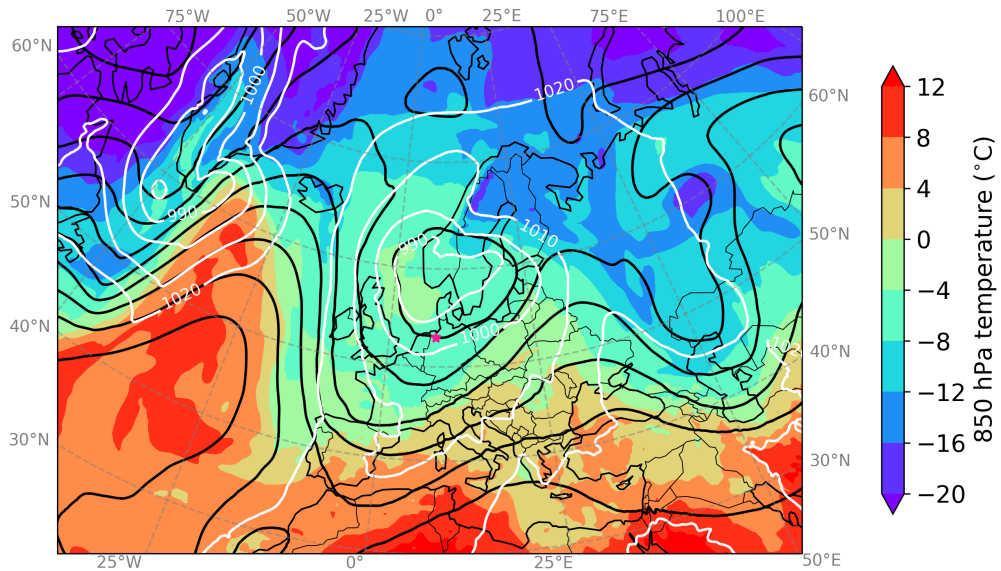


Figure B.17: Weather map of 1st February 2018, 12:00 UTC as in Fig. 3.2. The red star denotes the area used for RF8. Plotted with ERA5-data provided by Hersbach et al. (2018).

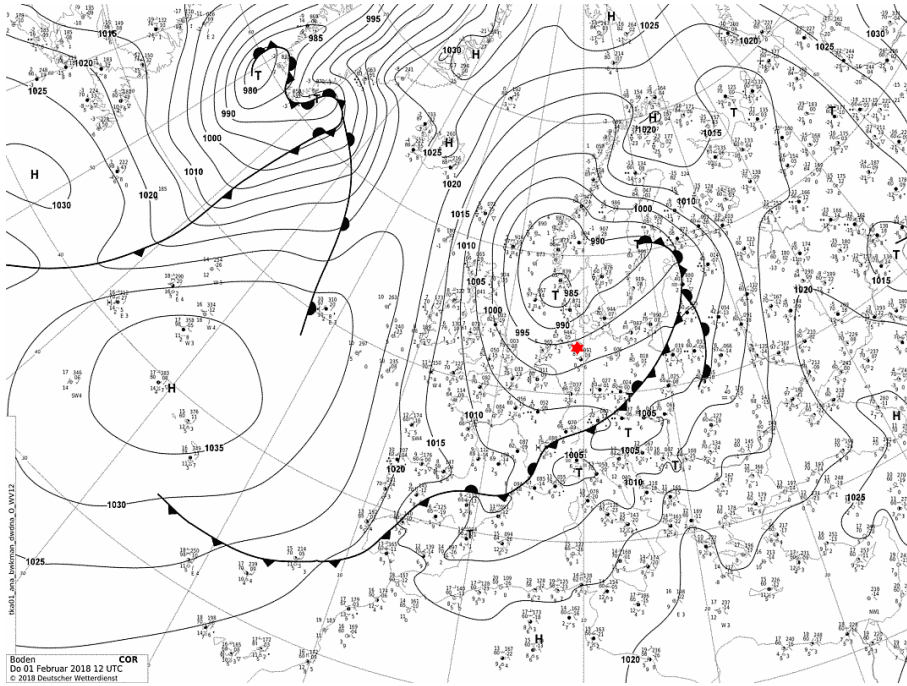


Figure B.18: Synoptic weather map of German Weather Service (Deutscher Wetterdienst; DWD) of 1st February 2018, 12:00 UTC as in Fig. 3.3. The red star denotes the area used for RF8. Adapted from wetter3 (2018).

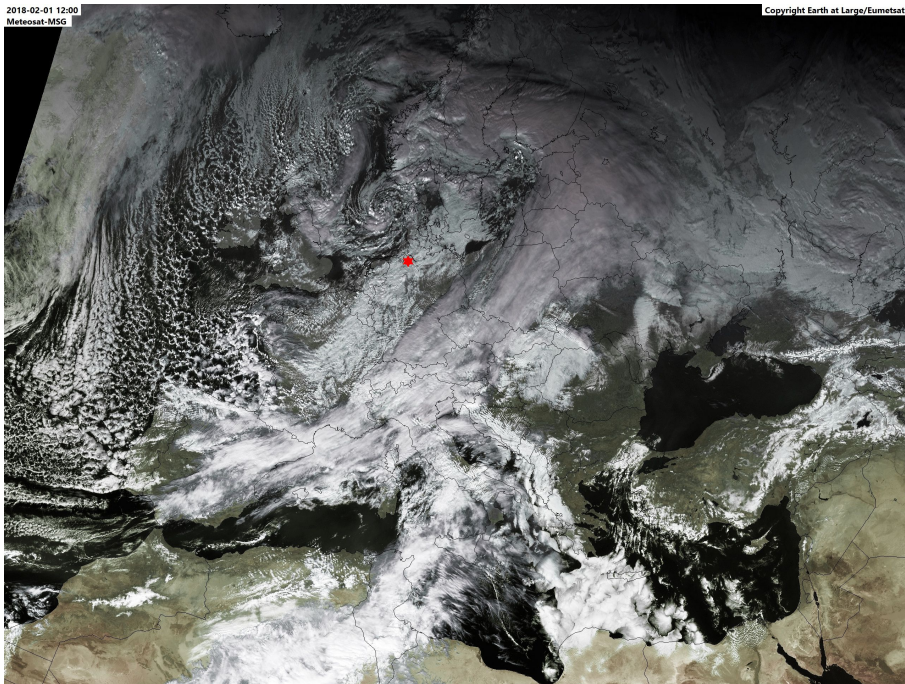


Figure B.19: Satellite image of EUMETSAT of 1st February 2018, 12:00 UTC, Meteosat Second Generation, VIS-Channel $0.6\ \mu\text{m}$. The image shows the cloud coverage over Europe and the unstable stratification (indicated by convection) along the flight region. The red star denotes the area used for RF8. Adapted from Valk (2018) with permission from EUMETSAT.

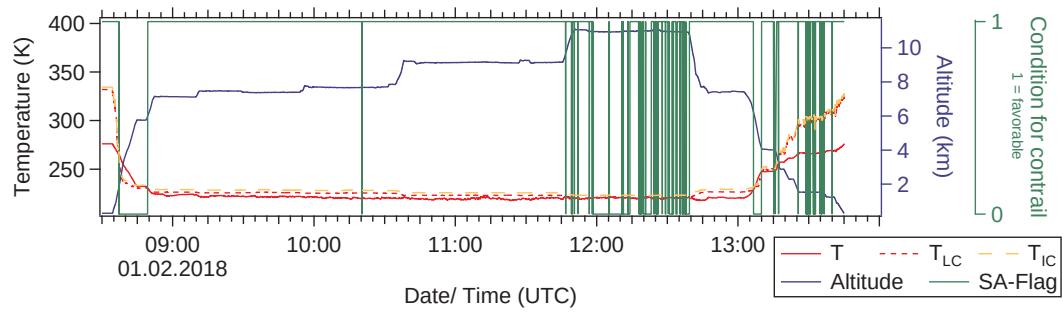


Figure B.20: Ambient temperature (red), flight level (blue), the Schmidt-Appleman-Temperatures for contrail formation (T_{LC} , red, short-dashed) and persistence (T_{IC} , orange, long-dashed). The green line marks the legs on which contrails can form and persist, i.e. where both thresholds are underpassed. Over long distances of RF8, the aircraft passed regions providing appropriate conditions for the formation and persistence of contrails.

APPENDIX: SUPPLEMENTARY INFORMATION FOR CHAPTER 4

Examples of airmass-induced variability of BB particles

Fig. C.1 demonstrates the relative abundance of the three BB particle types in terms of PF for three individual sample events. The exhaust and background periods were chosen within a short time frame next to each other in order to provide constant atmospheric conditions. Moreover, the air mass trajectories were proven for each period to originate from the same source region (not shown). The relative abundance of BB particles did not vary intensively between the exhaust period and the corresponding background (reference) period. However, the relative abundances significantly changed within the three samples, implying that the PF of BB particles was driven by the atmospheric conditions and the prevailing air mass.

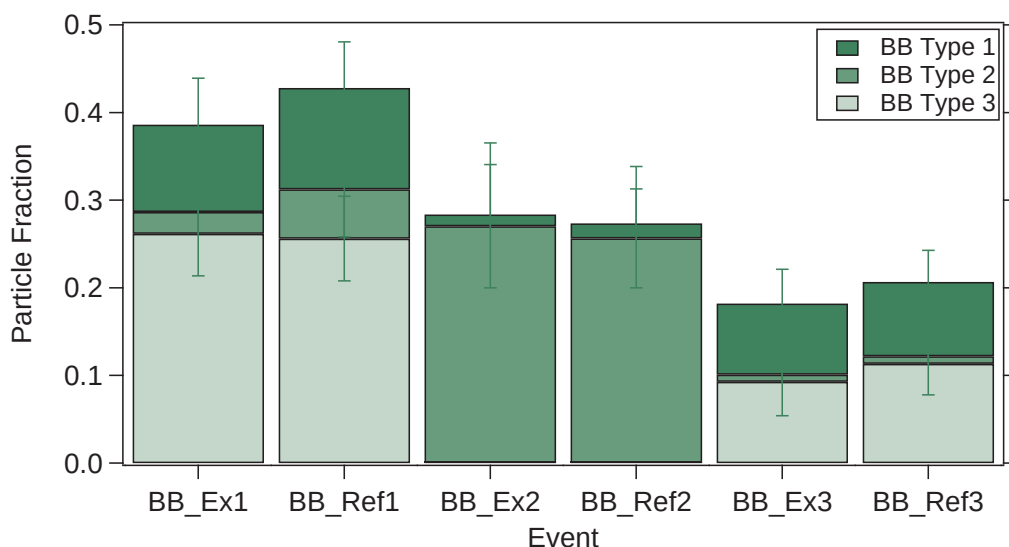


Figure C.1: Relative abundance of BB particles for three samples of exhaust (Ex1, Ex2, Ex3) and corresponding background reference (Ref1, Ref2, Ref3) periods: BB_{Ex1} - RF1, 13:12:57-13:17:46, BB_{Ref1} - RF1, 13:05:00-13:09:49, BB_{Ex2} - RF5, 13:33:29-13:37:39, BB_{Ref2} - RF5, 13:25:00-13:29:10, BB_{Ex3} - RF8, 10:44:50-10:49:51, and BB_{Ref3} - RF8, 10:38:00-10:43:01.

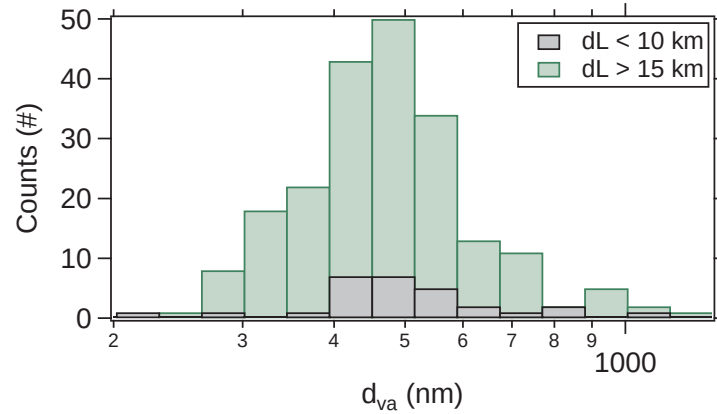
Exhaust-affiliated particle types

Figure C.2: Size distribution of exhaust-affiliated processed OC particles (absolute number, *Counts*) measured by ERICA-LAMS in exhaust plumes ($dL < 10$ km) and ambient air ($dL > 15$ km) between the exhaust plume generating DLR-ATRA and the *Flying Laboratory* NASA DC-8 during ND-MAX.

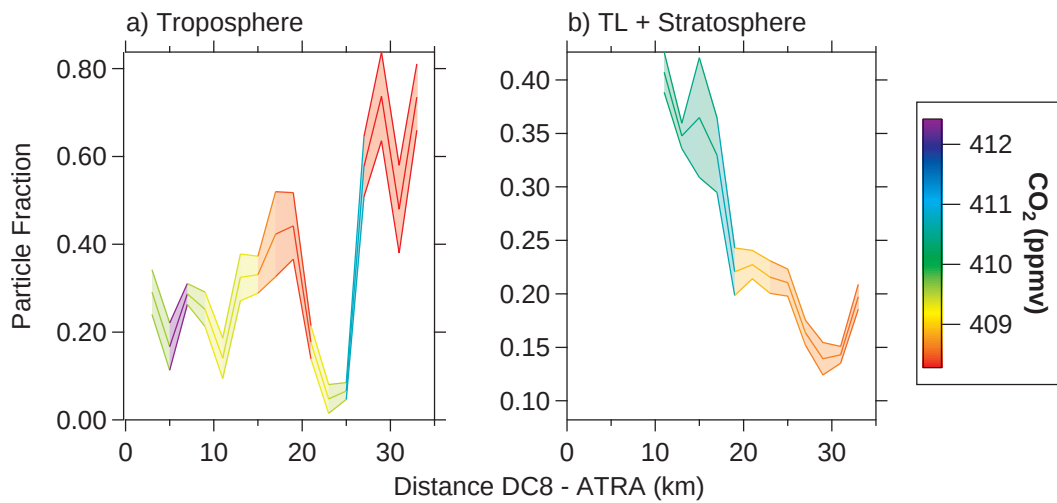


Figure C.3: Distribution of the relative abundance of exhaust-affiliated processed ECOC particles measured within a) the troposphere, b) the (extratropical) TL and stratosphere by ERICA-LAMS per distance between the exhaust plume generating DLR-ATRA and the *Flying Laboratory* NASA DC-8 during ND-MAX, color-coded with measured volume mixing ratio of CO_2 . The shaded area illustrates the uncertainty of the particle fraction as a result of the nonlinearities in the particle ablation process (see App. A.3).

Fig.C.2 depicts the size distribution of OC particles detected in the aircraft exhaust plume within a distance of 10km behind the DLR-ATRA and in background air at a distance of more than 15km. Except for the lower number of OC particles that were attributed to the exhaust plume, the size distribution for both distance scenarios was similar. In consequence, the OC particles did not grow to larger sizes.

Fig. C.3 provides additional information about the relative abundance of processed ECOC particles depending on the distance between the chasing NASA DC-8 and the forward flying DLR-ATRA. Part a) only considers datapoints recorded within the troposphere, part b) is focused on the TL/ ExTL and the stratosphere. For datapoints measured within the troposphere, the particle fraction of processed ECOC increased with distance, indicating this particle type to be entrained by mixing of the exhaust plume with ambient air. For datapoints detected in the layers above, PF dropped, implying an exhaust-related particle type.

Potential origin of mineral dust

Fig. C.4 reveals the fraction of mineral dust in terms of particles detected at the scoop inlet and of cloud residuals collected with the CVI for the individual RFs. The fraction of particles was enhanced on RF3, RF5, RF6, and RF7. The fraction of mineral dust residuals was additionally increased on RF1 and RF4. However, the variations in PF were small compared to the uncertainties of PF .

Backward air mass trajectories

Fig. C.5 to C.11 illustrate the vertical cross section of backward air mass trajectories calculated by HYSPLIT. The trajectories of RF5 and RF7 demonstrated a strong upward motion for a large number of trajectories about one day ahead of the flight, which were attributed to warm conveyor belts of low pressure systems approaching the flight area from the west. Except for RF8, the air mass trajectories of the cold period depicted an irregular ascent driven by other factors such as local convection or orographically induced lifting. As indicated by Fig. C.18, the narrow steep propagation of trajectories for RF8 was probably related to the chain of cyclones along the Greenland coast (Fig. B.18) and a result of the strong eastward circulation across the Atlantic towards the area of interest.

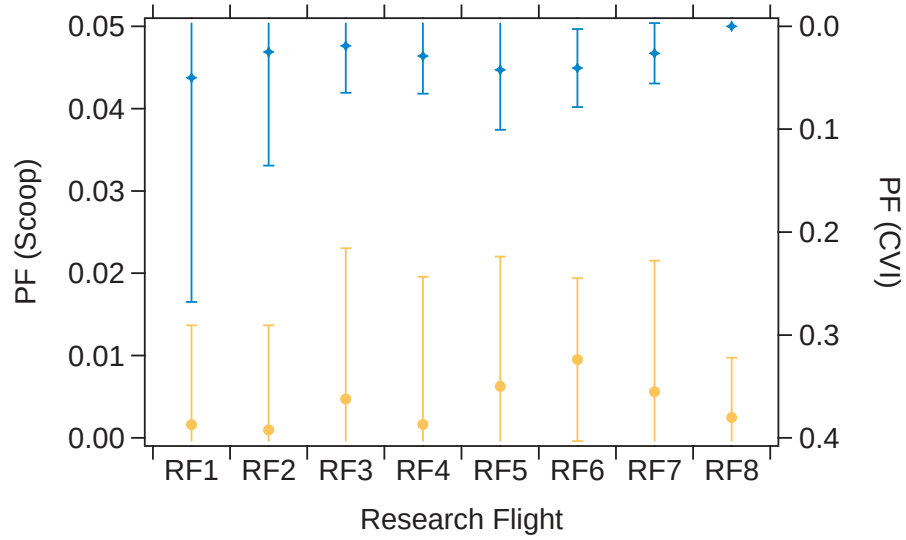


Figure C.4: Abundance of mineral dust particles (orange) and cloud residuals (blue) for the individual RFs during ND-MAX. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see App. A.3).

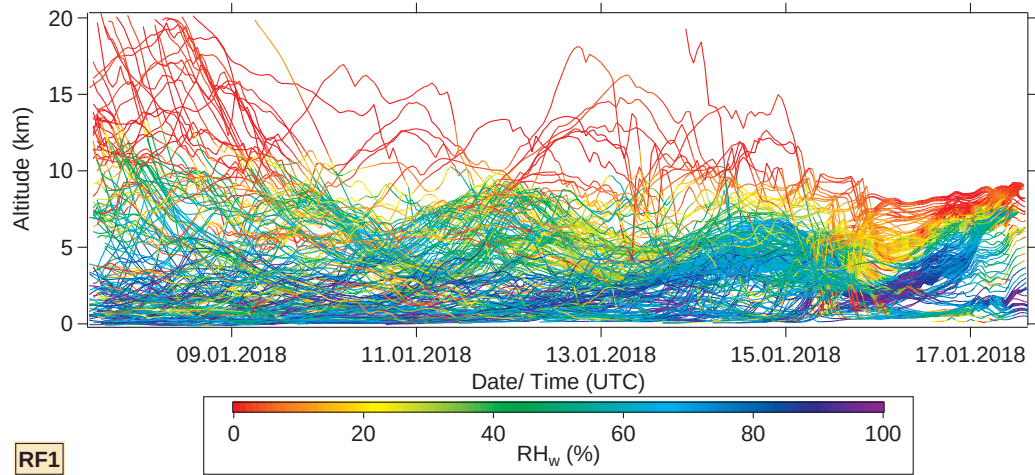


Figure C.5: Vertical cross section of backward trajectories simulated with HYSPLIT for RF1, color-coded with relative humidity (RH_w).

Fig. C.12 to Fig. C.18 show the origins of the air masses detected along flight tracks of ND-MAX. Moreover, the backward air mass trajectories depict the circulation pattern during the campaign. For example, the trajectories calculated for RF3 and RF4 followed a zonal circulation in a wavy structure which was partly driven by the northern polar jetstream. In contrast, RF5 was characterized by a meridional circulation. RF1, RF2, RF6, RF7, and RF8 exhibited elements of both, a zonal and a meridional circulation.

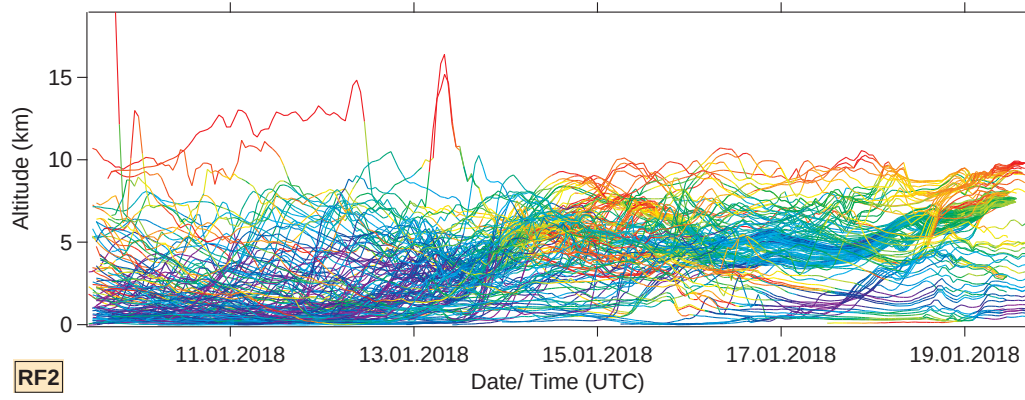


Figure C.6: Vertical cross section of backward trajectories simulated with HYSPLIT for RF2, color-coded with relative humidity (RH_w).

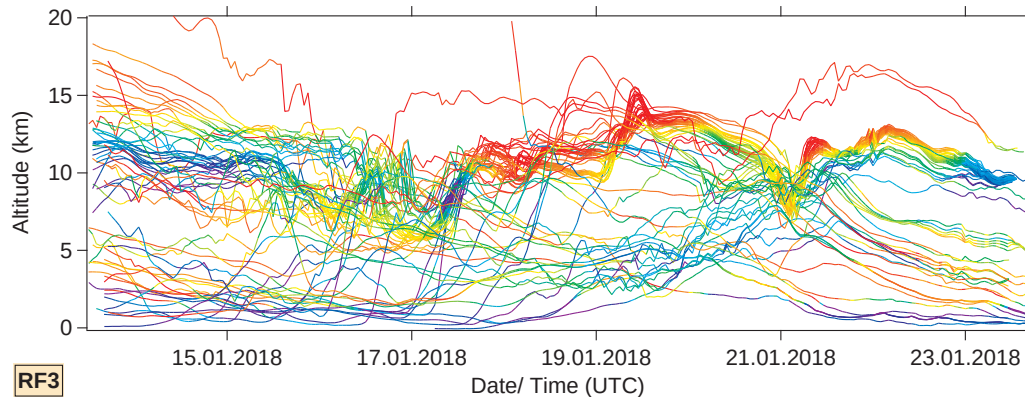


Figure C.7: Vertical cross section of backward trajectories simulated with HYSPLIT for RF3, color-coded with relative humidity (RH_w).

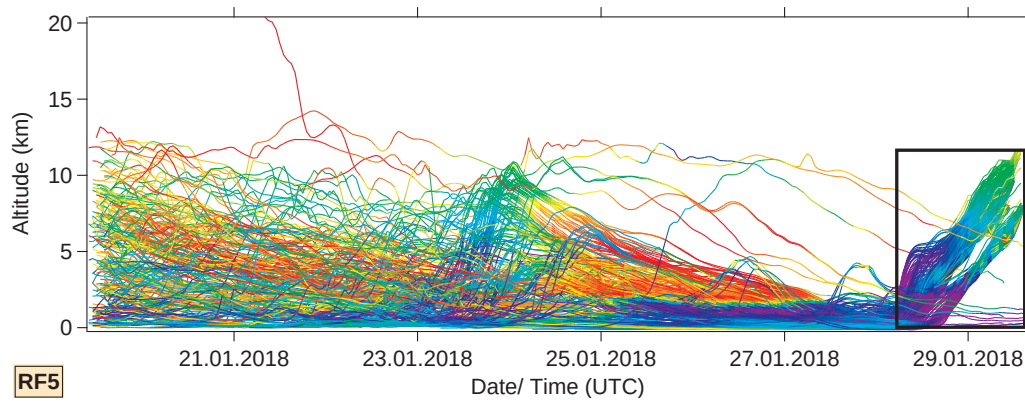


Figure C.8: Vertical cross section of backward trajectories simulated with HYSPLIT for RF5, color-coded with relative humidity (RH_w). The black box marks the ascent period.

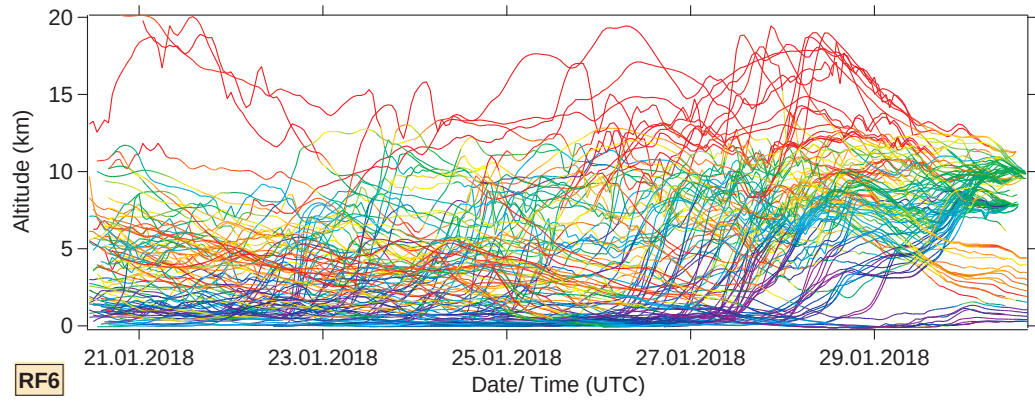


Figure C.9: Vertical cross section of backward trajectories simulated with HYSPLIT for RF6, color-coded with relative humidity (RH_w).

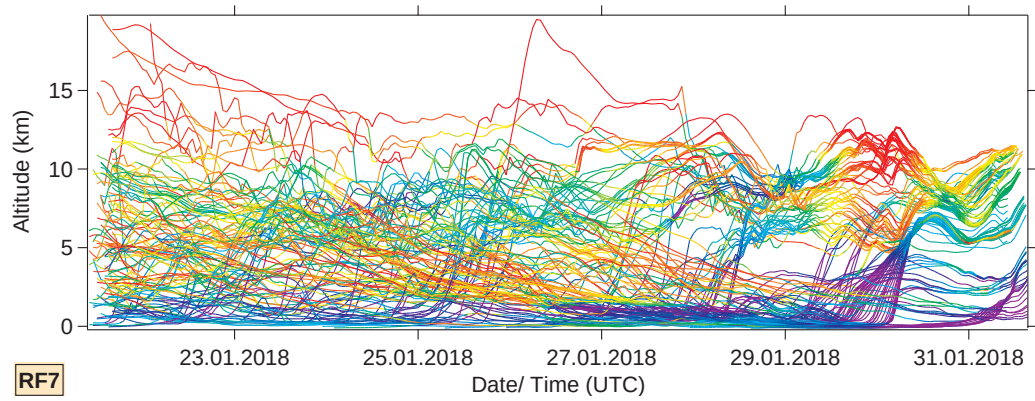


Figure C.10: Vertical cross section of backward trajectories simulated with HYSPLIT for RF7, color-coded with relative humidity (RH_w).

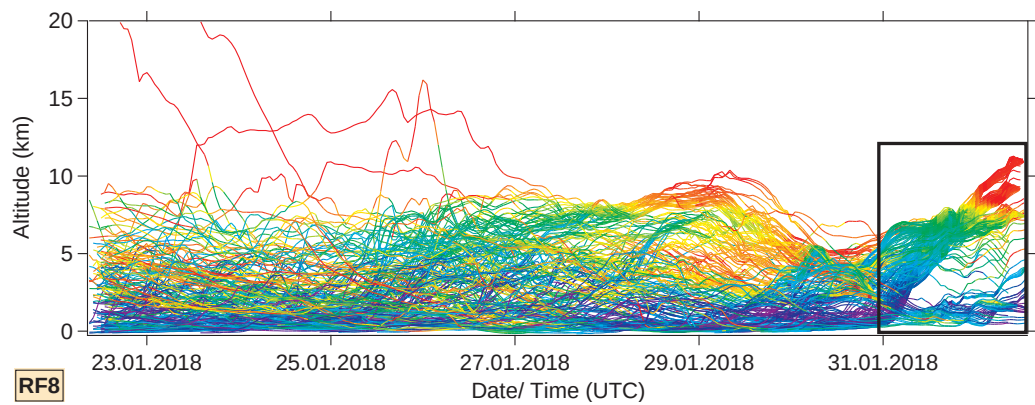


Figure C.11: Vertical cross section of backward trajectories simulated with HYSPLIT for RF8, color-coded with relative humidity (RH_w). The black box marks the ascent period.

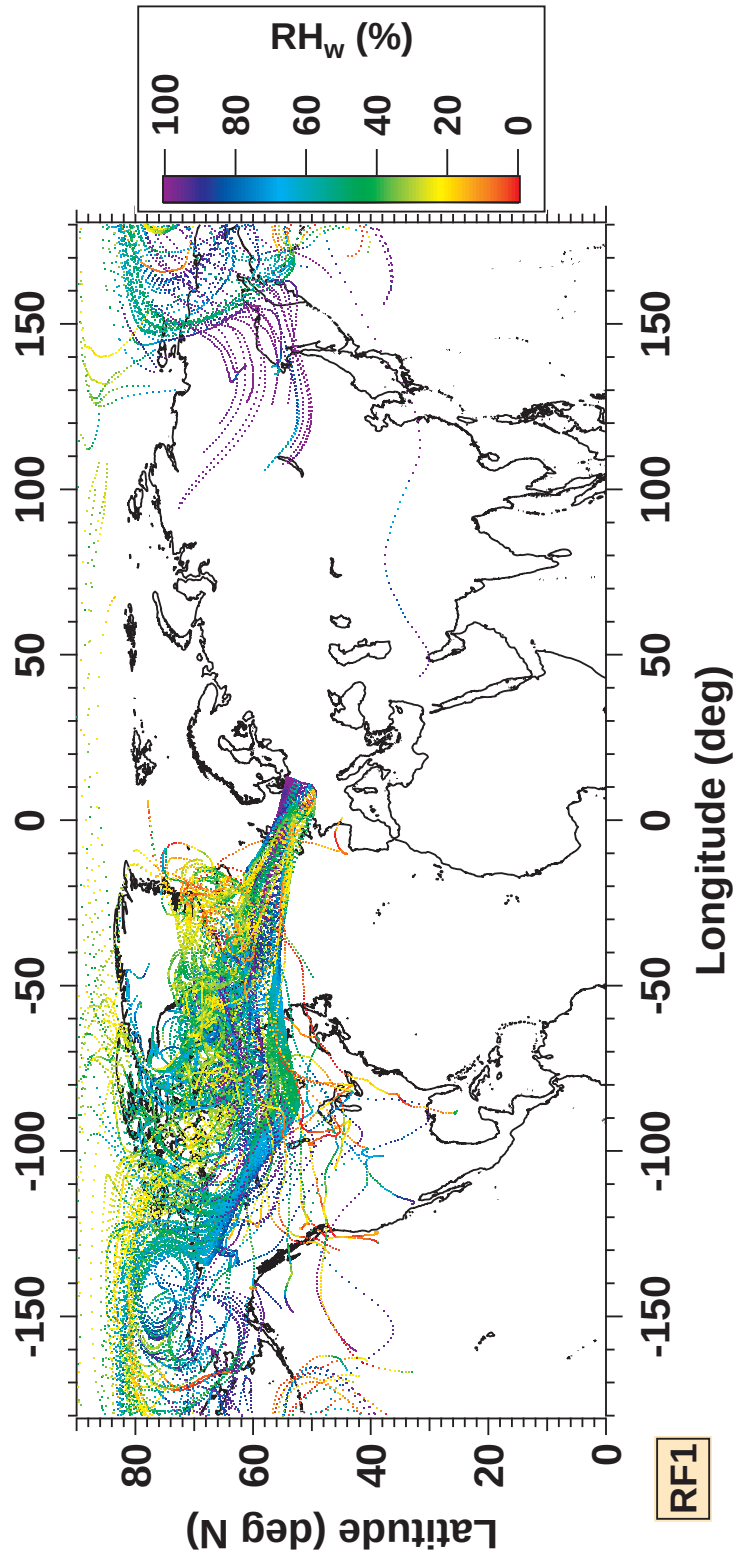


Figure C.12: Overview of the backward trajectories simulated for RF1, color-coded with the relative humidity (RH_w) as an indicator for the altitude level.

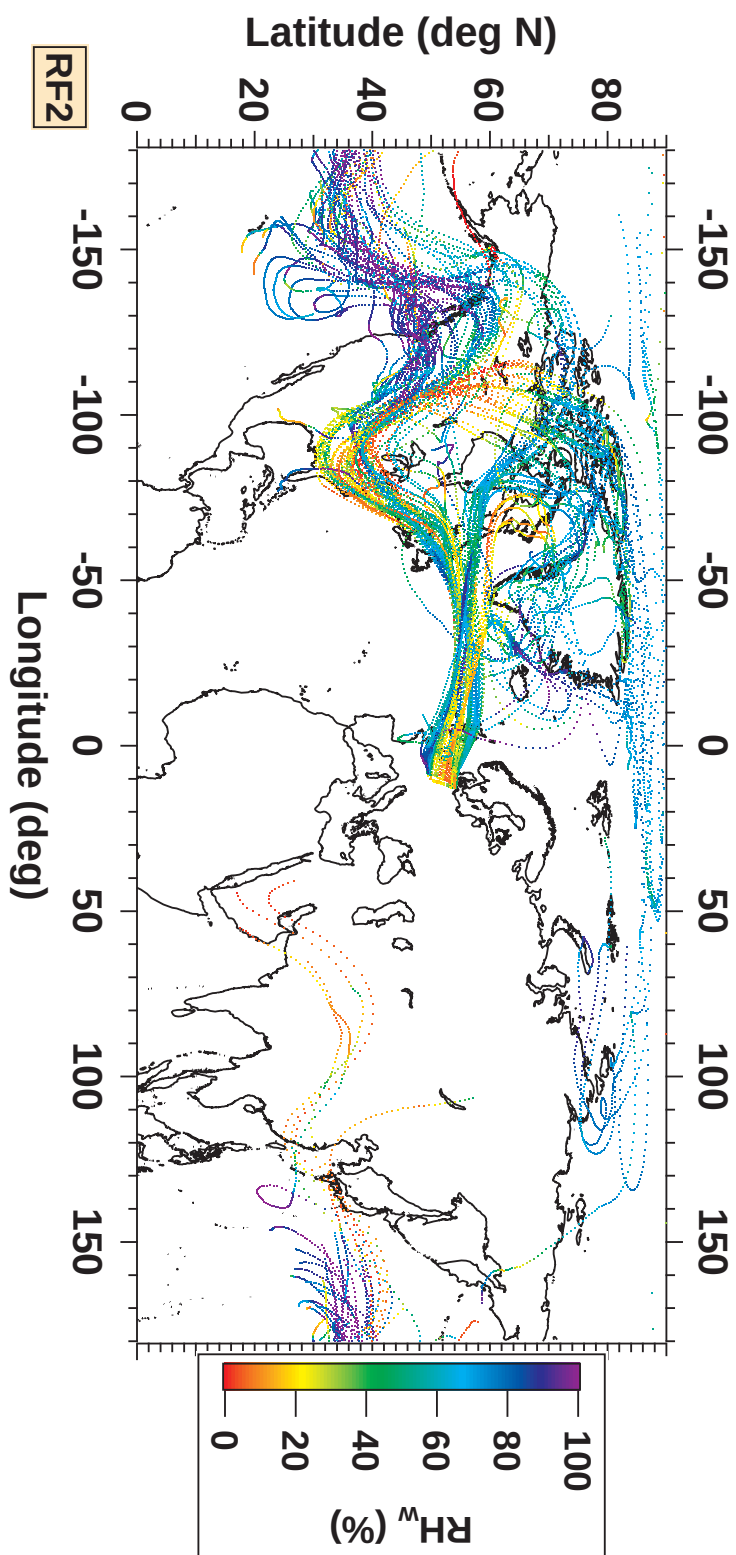


Figure C.13: Overview of the backward trajectories simulated for RF2, colorcoded with the relative humidity (RH_w) as an indicator for the altitude level.

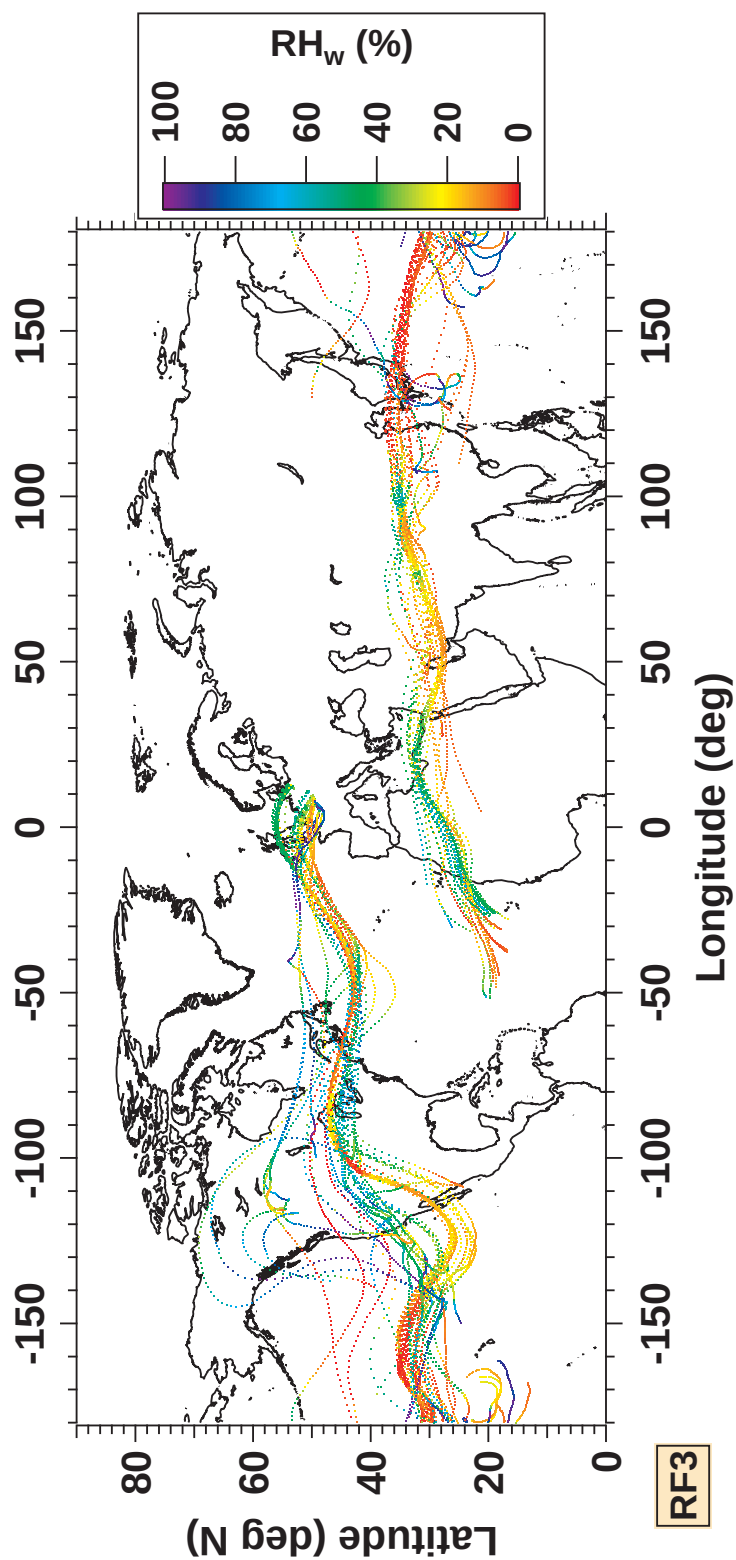


Figure C.14: Overview of the backward trajectories simulated for RF3, color-coded with the relative humidity (RH_w) as an indicator for the altitude level.

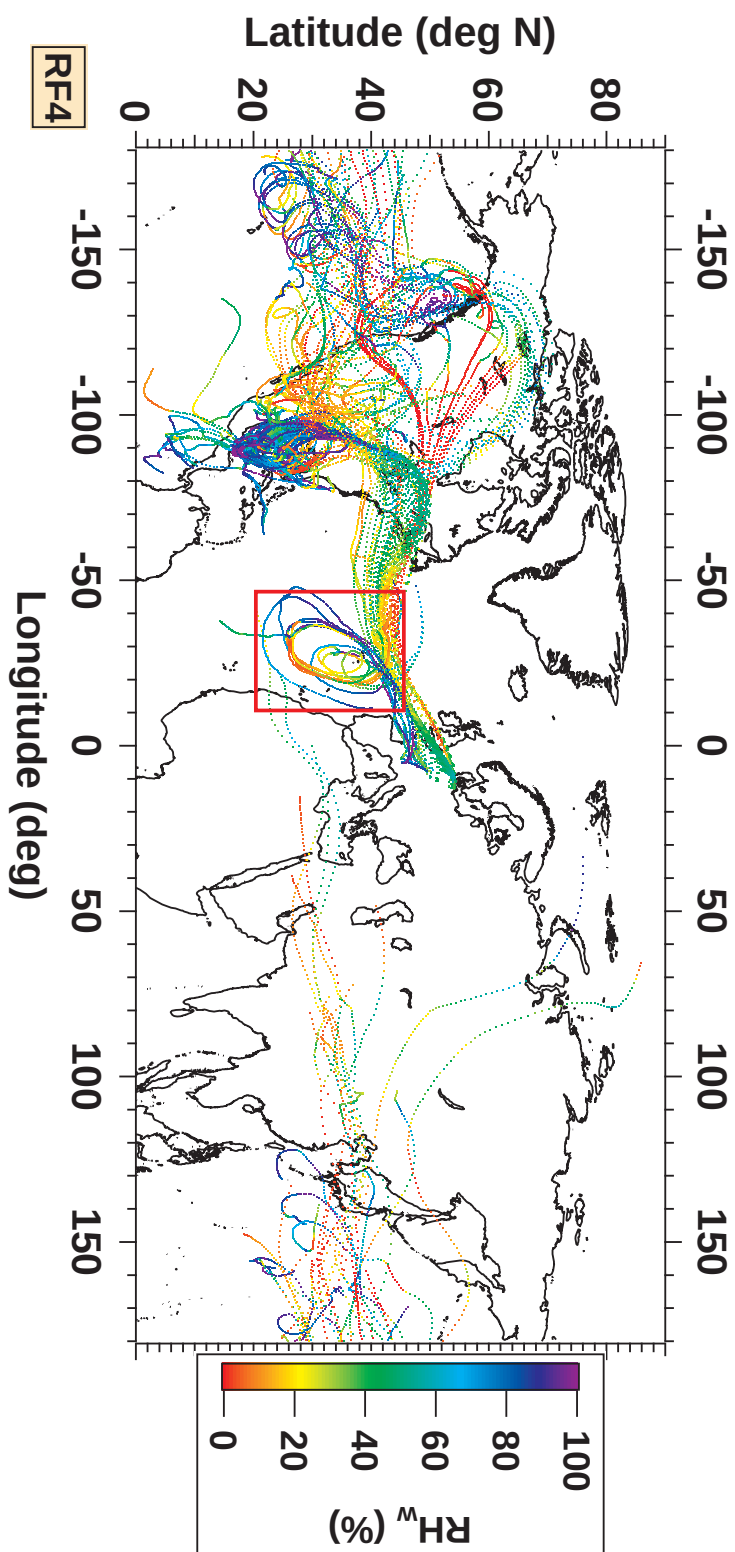


Figure C.15: Overview of the backward trajectories simulated for RF4, colorcoded with the relative humidity (RH_w) as an indicator for the altitude level. The red rectangular depicts the Azore's high, which is present for RF4 to RF7 and impacts the presence of mineral dust and processed mineral dust particles along the flight track.

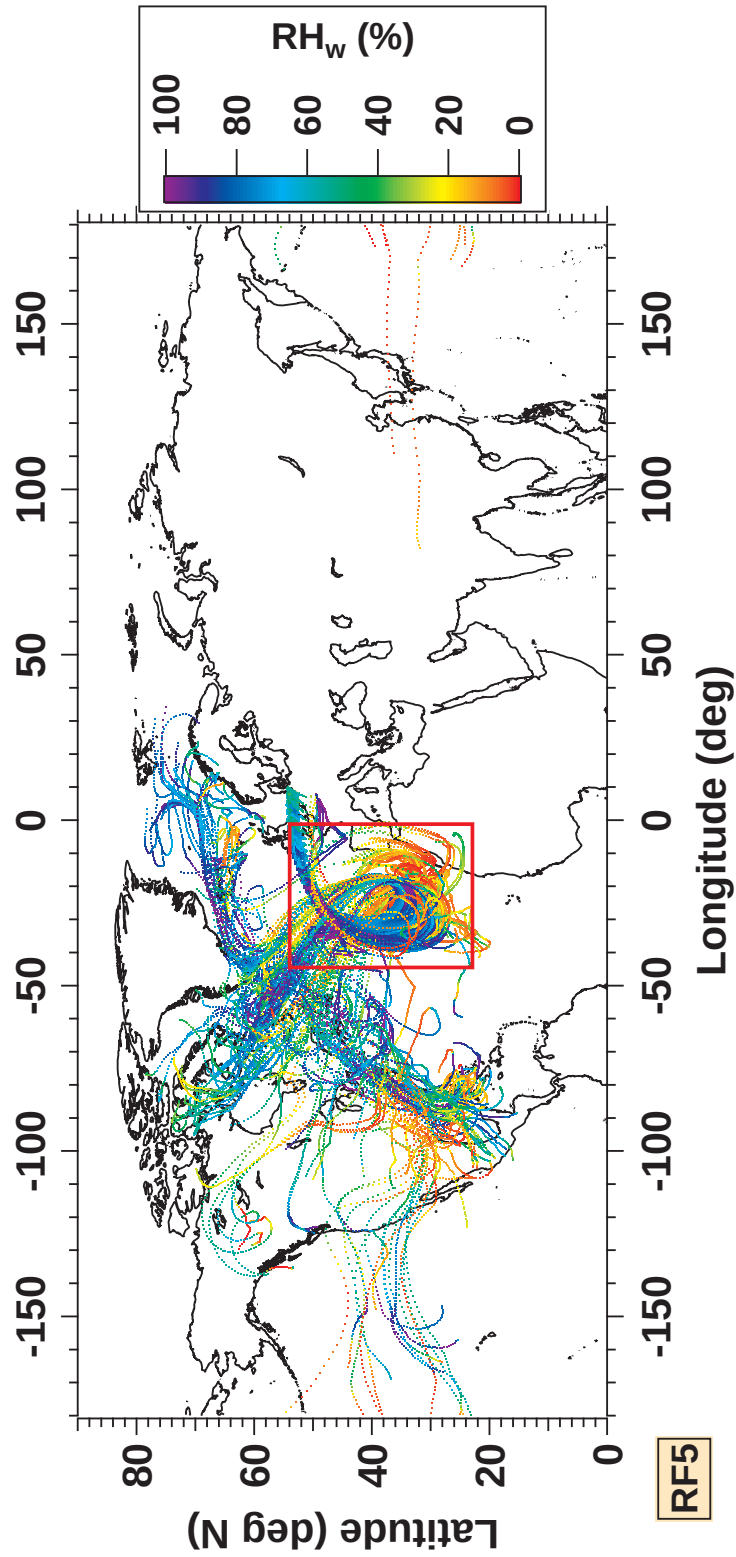


Figure C.16: Overview of the backward trajectories simulated for RF5, color-coded with the relative humidity (RH_w) as an indicator for the altitude level. The red rectangular depicts the Azore's high, which is present for RF4 to RF7 and impacts the presence of mineral dust and processed mineral dust particles along the flight track.

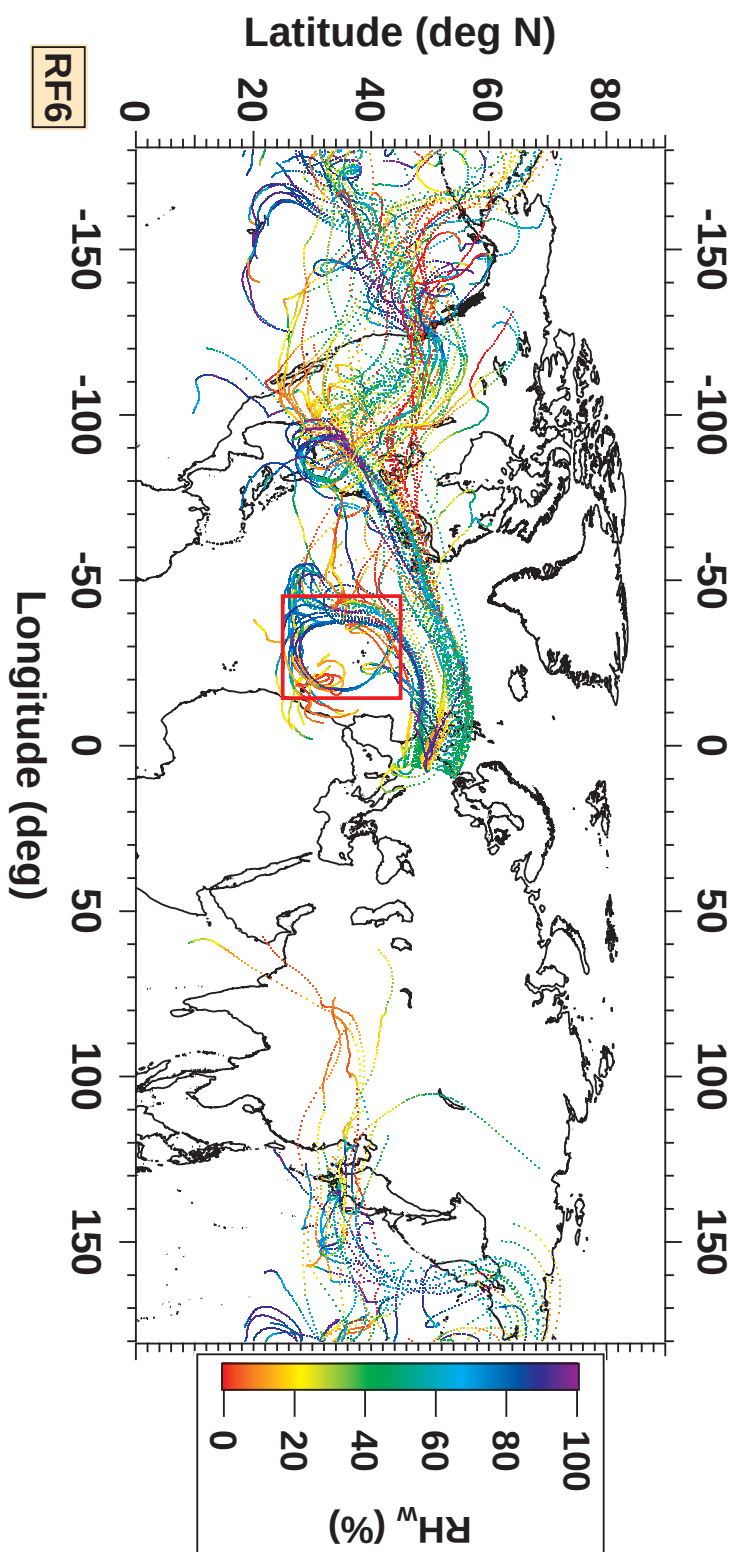


Figure C.17: Overview of the backward trajectories simulated for RF6, colorcoded with the relative humidity (RH_w) as an indicator for the altitude level. The red rectangular depicts the Azore's high, which is present for RF4 to RF7 and impacts the presence of mineral dust and processed mineral dust particles along the flight track.

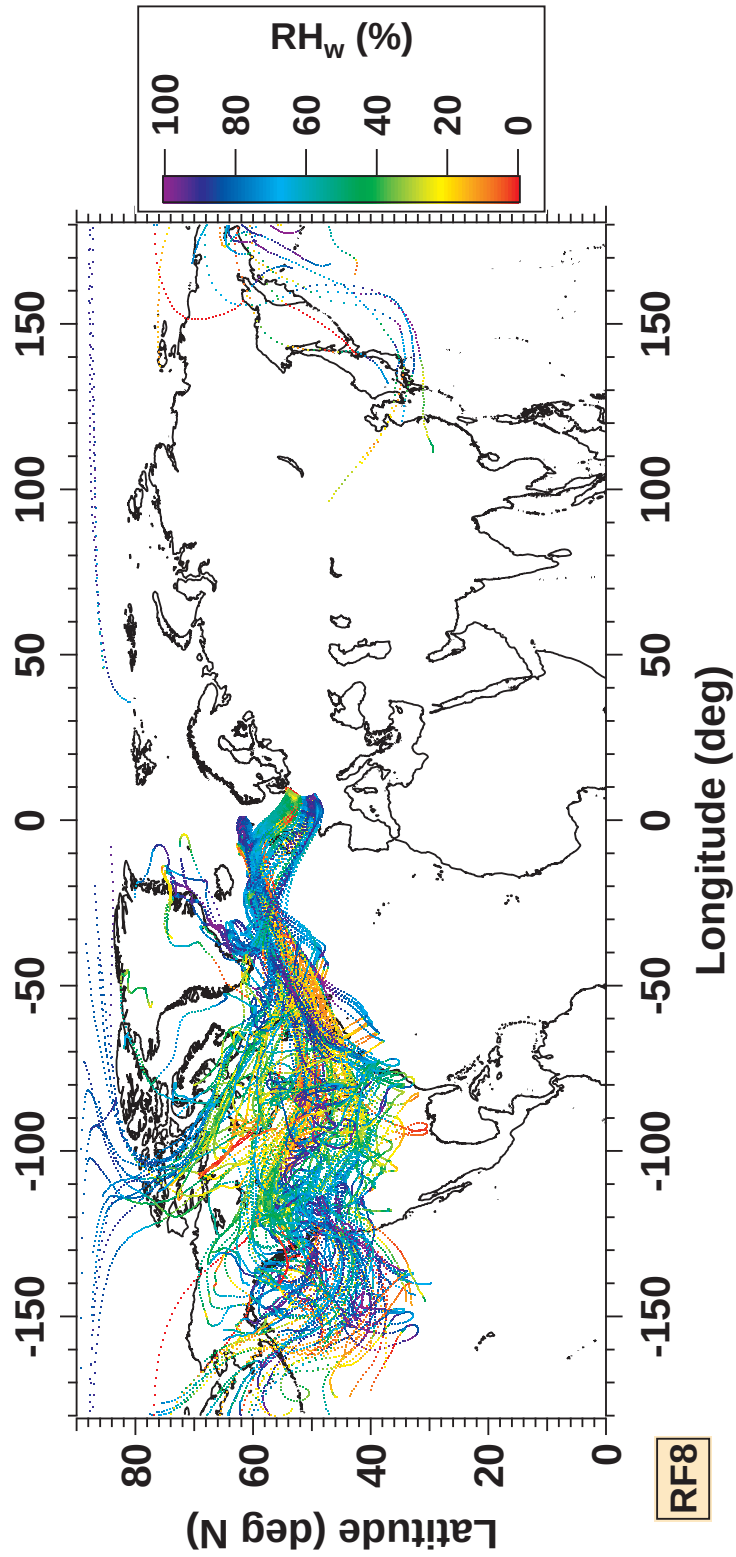


Figure C.18: Overview of the backward trajectories simulated for RF8, color-coded with the relative humidity (RH_w) as an indicator for the altitude level.

Fig. C.19 reveals the relative abundance of the individual particle and cloud residual types during the RFs of ND-MAX. The PF of each type was variable from flight to flight and could not be attributed to the impact of potential source regions.

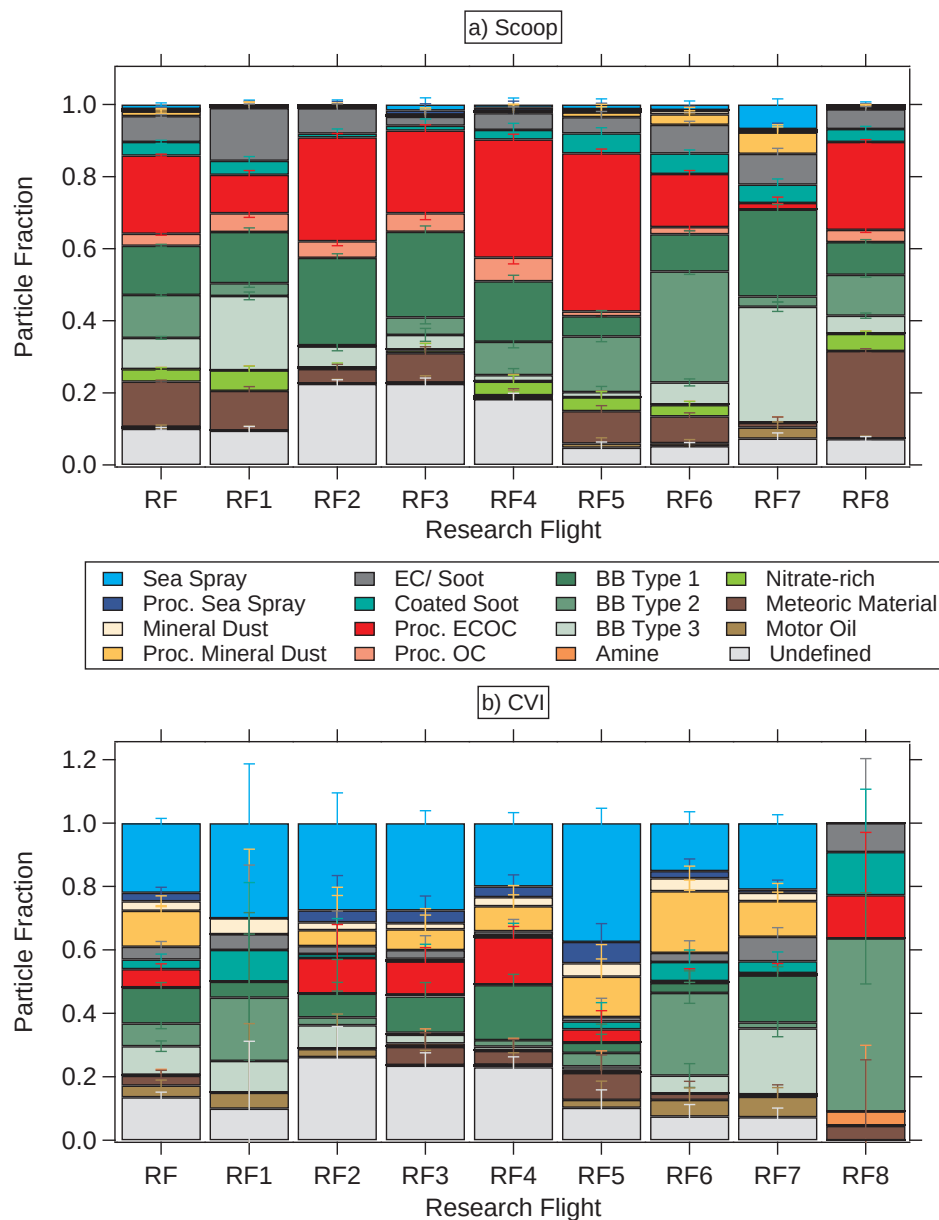


Figure C.19: Overview of the relative abundance of particle (sampled with the Scoop inlet, a) and cloud residual (sampled with the CVI, b) types for the individual RFs of ND-MAX. The error bars illustrate the uncertainty of the particle fraction as a result of the binomial counting statistics (see App. A.3).

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ACRONYMS

ACCLIP	Asian Summer Monsoon Chemical and CLimate Impact Project
ACI	aerosol-cloud interaction
ADL	aerodynamic lens
ALABAMA	Aircraft-based Laser ABlation Aerosol MAss spectrometer
AMA	Asian monsoon anticyclone
AMS	(bulk) Aerosol mass spectrometer developed by Aerodyne Research Inc.
AS	ammonium sulphate
ATAL	Asian tropopause aerosol layer
DLR-ATRA	Advanced Technology Research Aircraft
BB	biomass burning
BC	black carbon
BL	boundary layer
B-ToF-MS	Bipolar Time-of-Flight Mass Spectrometer
CAPS	Cloud, Aerosol, and Precipitation Spectrometer
CCN	cloud condensation nuclei
CFC	chlorofluorocarbon
CIP	Cloud Imaging Probe
CLaMS	Chemical Lagrangian Model of the Stratosphere
CN	cloud nuclei
contrail	condensation trail
CPC	Condensation Particle Counter
CPI	constant pressure inlet
CPR	cloud particle residual

CRDS	Cavity Ring Down Spectroscopy
CRISP	Concise Retrieval of Information from Single Particles
CVI	counterflow virtual impactor
C-ToF-MS	Compact Time-of-Flight Mass Spectrometer
NASA DC-8	NASA McDonnell Douglas DC-8 jetliner
DDS	DC-8 Data Distribution System
DL	detection laser
DLH	Diode Laser Hygrometer
DLR	Deutsches Zentrum für Luft- und Raumfahrt
DMA	differential mobility analyzer
DU	detection unit
DWD	Deutscher Wetterdienst (German Weather Service)
EC	elemental carbon
ECOC	elemental and organic carbon
ECLIF	Emission and Climate Impact of Alternative Fuels
ECMWF	European Centre for Medium-Range Weather Forecast
EP	extraction plate
ERc	European Research Council
ERICA	ERc Instrument for Chemical composition of Aerosol particles
ERICA-AMS	ERICA-Aerosol Mass Spectrometer
ERICA-LAMS	ERICA-Laser Ablation Mass Spectrometer
ERF	effective radiative forcing
EUMETSAT	European Organisation for the Exploitation of Meteorological Satellites
ExTL	Extratropical transition layer/ Extratropical tropopause layer
FFSSP	Fast Forward Scattering Spectrometer Probe
FL	flight level
FT	free troposphere
GDAS	Global Data Assimilation System

GPS	Global Positioning System
HALO	High Altitude and Long Range Research Aircraft
HEFA-SPK	Hydroprocessed Esters and Fatty Acids Synthetic Paraffinic Kerosene
HIAPER	High-performance Instrumented Airborne Platform for Environmental Research
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory Model
INP	ice nucleating particle
IPA	Institute for Atmospheric Physics, JGU Mainz
ISSR	ice super-saturated region
IWC	ice water content
JGU	Johannes Gutenberg University Mainz
Lagranto	the Lagrangian Analysis Tool
LAS	Laser Aerosol Spectrometer
LDI	laser desorption and ionization
LMS	lowermost stratosphere
MCP	multi-channel plate
MPIC	Max Planck Institute for Chemistry
MS	mass spectra
ND-MAX	NASA and DLR Multidisciplinary Airborne eXperiments
NASA	US National Aeronautics and Space Administration
NCAR	US National Center for Atmospheric Research
NCEP	US National Centers for Environmental Prediction
NIST	US National Institute of Standards and Technology
NOAA	US National Oceanic and Atmospheric Administration
NPF	new particle formation
NSRC	NASA National Suborbital Research Center
OC	organic carbon

OPC	optical particle counter
PHILEAS	Probing High Latitude Export of air from the Asian Summer Monsoon
PMT	photomultiplier tube
PSI	potential source inventory
PSL	polystyrene latex
PS	pumping stage
PT	particle type
PV	potential vorticity
Ref	reference fuel, standard kerosene Jet A-1
RF	research flight
SAF	sustainable alternative jet fuel
scoop	scoop-style aerosol sampling inlet
SMPS	scanning mobility particle sizer
SOA	secondary organic aerosol
SPMS	single particle mass spectrometer
StratoClim	Stratospheric and upper tropospheric processes for better climate predictions
SU	shutter unit
TL	transition layer
TMP	turbo molecular pump
TPN	test point
UT	upper troposphere
UTLS	upper troposphere and lower stratosphere
UV	ultraviolet
VOC	volatile organic compound
WBF	Wegener-Bergeron-Findeisen

LIST OF SYMBOLS

Symbol	Unit/Value	Description
a	s	m/z calibration coefficient (including shot-to-shot variability)
b	s Da ^{$\frac{1}{2}$}	m/z calibration coefficient (including ion flight properties)
C_{All}	-	absolute counts of all clustered particles
$C_{BL,Traj.Points}$	-	absolute counts of trajectory points detected within the BL
$C_{CirrusResiduals}$	-	absolute counts of detected cirrus residuals by ERICA-LAMS
C_{Counts}	-	absolute counts of detected particles
C_{MS}	-	absolute counts of detected mass spectra with ERICA-LAMS
c_p	J kg ⁻¹ K ⁻¹	specific heat capacity at constant pressure
C_{shots}	-	counts of successfully triggered laser shots
C_{hits}	-	counts of successfully ablated/ionized particles by the ablation laser of the ERICA
CE	-	collection efficiency
C_{Type}	-	counts of a certain particle type
d_{ij}	-	difference between mass spectrum i and reference spectrum j
d_{mob}	nm	mobility diameter
d_{opt}	nm	optical diameter
d_p	nm	particle diameter
d_{va}	nm	vacuum-aerodynamic diameter
d_{DU}	mm	flight distance between both DUs
dir_v	°	wind direction
DE	-	detection efficiency
e	hPa	partial pressure of water vapor
e_c	C	elementary charge

E	-	expectation of the lognormal distribution
EI_{H_2O}	kg kg ⁻¹	emission index of water
f	-	fuzzifier
f_{ERICA}	cm ³ s ⁻¹	volumetric flow through the ERICA instrument
G	-	slope of isobaric mixing line of the exhaust plume and ambient air
HR	-	hit rate
IWC	g m ⁻³	ice water concent detected by CIP
k	nm	size calibration factor
K_0	nm	coefficient of the polynomial size calibration function
K_1	nm μs ⁻¹	coefficient of the polynomial size calibration function
K_2	nm μs ⁻²	coefficient of the polynomial size calibration function
Lat_{DC-8}	°N	latitude position of the NASA DC-8
Lat_{ATRA}	°N	latitude position of the DLR-ATRA
Lon_{DC-8}	°E	longitude position of the NASA DC-8
Lon_{ATRA}	°E	longitude position of the DLR-ATRA
m_{ik}	-	membership coefficient of a spectrum i towards a reference spectrum k
m/z	Da	ion mass to charge ratio
$N_{10,STP}$	cm ⁻³	particle number concentration in a size range above 10 nm, obtained with a CPC, normalized to standard temperature and pressure
N_{coinc}	cm ⁻³	number concentration of particles detected by both detection laser stages of ERICA
N_{CPC}	cm ⁻³	number concentration of particles detected with GRIMM CPC
N_{ice}	cm ⁻³	number concentration of ice particles obtained with FFSSP
N_{LAMS}	cm ⁻³	particle number concentration detected with ERICA-LAMS

$N_{LAS,STP}$	cm^{-3}	particle number concentration detected with LAS, normalized to standard temperature and pressure
N_{ref}	cm^{-3}	number concentration of particles obtained by a reference instrument
p	hPa	air pressure
p_{ERICA}	Pa	aerodynamic lens pressure of the ERICA instrument
$\vec{P}$	-	position vector of an air parcel
PF	-	particle fraction
PF_{Type}	-	fraction of a specific particle type
Q	J kg^{-1}	fuel combustion heat
RH_w	%	relative humidity with respect to water (liquid phase)
r_{ij}	-	pearson correlation coefficient of mass spectrum i and reference spectrum j
$sample$	-	sampling interval of the oscilloscope, set to 1.6 ns
SD	-	standard deviation of the lognormal distribution
S_p	-	Jayne shape factor of the particle
s_{ToF}	m	ion flight path
T	$^{\circ}\text{C}$	temperature
T_{LC}	K	Schmidt-Appleman-Temperature
T_{LM}	K	temperature on isobaric mixing line at which liquid saturation is reached
$t_{p,tof}$	s	travel time of a single particle between both DUs
t_{ToF}	s	ion flight time
TE	-	transmission efficiency
$U(s_{ToF})$	V	voltage along the ion flight path
$upcount$	-	time counter value between the two detection events
v	m s^{-1}	mean wind speed
$\vec{v}$	m s^{-1}	vector of the average velocity of an air parcel
v_0	m s^{-1}	gas expansion velocity

v_g	m s^{-1}	gas velocity after the expansion into the evacuated part of ERICA
VMR_{CO_2}	ppmv	volume mixing ratio of carbon dioxide
VMR_{H_2O}	ppmv	volume mixing ratio of water vapor
VMR_{O_3}	ppbv	volume mixing ratio of ozone
v_p	m s^{-1}	particle velocity
$x_{t,an}$	mV·sample	threshold of background noise of the anion signal in ERICA-LAMS
$x_{t,cat}$	mV·sample	threshold of background noise of the cation signal in ERICA-LAMS
z_{DC-8}	m a.s.l.	GPS altitude of the NASA DC-8
z_{ATRA}	m a.s.l.	GPS altitude of the DLR-ATRA
Δt	s	time step between the initial and final position of the air parcel
η	-	propulsion efficiency of the DLR-ATRA
Θ	K	potential temperature
μ	-	expectation of the normal distribution
ρ_0	g cm^{-3}	standard particle density (1 g cm^{-3})
ρ_p	g cm^{-3}	density of specific particle type
σ	-	standard deviation of the normal distribution
σ_{ref}	-	standard deviation of the reference period histogram
$\sigma_{f_{ERICA}}$	$\text{cm}^3 \text{ s}^{-1}$	standard deviation of the volumetric flow through the ERICA instrument
$\sigma_{p_{ERICA}}$	Pa	standard deviation of the aerodynamic lens pressure of the ERICA instrument

LIST OF PUBLICATIONS

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In Chapter 2, I used CLaMS data for verification of the location of the TL and the dissection of measurement data into troposphere, TL, and stratosphere. These trace gas data were calculated with CLaMS and interpolated along the flight track by Hans-Christoph Lachnitt¹. Further, complementary data of the CPC and FFSSP as well as trace gas records of CO₂ and O₃ were provided by Christiane Voigt² and Hans Schlager², respectively. These data were used for the definition of events of interest such as exhaust plumes and background periods as well as cirrus and contrail events.

In Chapter 3 and 4, the raw measurement data of ERICA during the ND-MAX campaign were recorded and provided by Sergej Molleker³, Antonis Dragoneas³, Oliver Appel^{1,3} and Andreas Hünig³. The weather maps at 500-hPa-level were plotted with a python code provided by Oliver Eppers³. Flight parameter and meteorological data were downloaded in a merged dataset provided by Ryan Bennett⁴ and Melissa Yang-Martin⁵ (for data availability, see Bennett and Yang-Martin (2021)). Further, LAS data were provided by Bruce Anderson⁵. Oliver Eppers³ provided the HYSPLIT output upon which I analyzed the potential source regions of probed air masses. The laboratory measurements were performed by myself and Oliver Appel^{1,3}. All data were analyzed with guidance and critical feedback from Oliver Appel^{1,3}, Stephan Borrmann^{1,3}, Tiziana Bräuer², Hans-Christian Clemen³, Oliver Eppers³, Thorsten Hoffmann⁶, Peter Hoor¹, Andreas Hünig³, Franziska Köllner^{1,3}, and Johannes Schneider³.

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CONTRIBUTIONS TO OTHER STUDIES

In addition to the data analysis and laboratory work presented in this study, I participated in the airborne research campaigns ACCLIP and PHILEAS. The *Asian Summer Monsoon Chemical and Climate Impact Project* (ACCLIP) was located at the Osan Air Base, Pyeongtaek, South Korea of the United States Air Force and the Republic of Korea Air Force from July 30 to September 1, 2022. This campaign was actually planned as the focus of my PhD-project but was rejected due to the COVID lockdown and an unexpected rescheduling. After the end of the lockdown, I prepared and arranged together with colleagues the transport of ERICA and additional equipment to the United States and to the Republic of Korea. For the entire duration of the campaign, I took care of ERICA and conducted airborne measurements during several research flights aboard the *High-performance Instrumented Airborne Platform for Environmental Research* (HIAPER) which is a modified Gulfstream V aircraft. In advance to the ACCLIP campaign, I joined the pre-campaign in Boulder, Colorado, USA in January and February 2020 in order to test the performance of ERICA that flew in a novelly designed rack for the first time onboard the HIAPER. Among the stay in Boulder, I participated in the international ACCLIP Science Team Meeting at the US National Center for Atmospheric Research (NCAR).

Moreover, I attended the PHILEAS (Probing High Latitude Export of Air from the Asian Summer Monsoon) mission in summer 2023 that was based in Oberpfaffenhofen, Germany at the DLR and in Anchorage, Alaska, USA. Within the phase located in Germany, I conducted airborne measurements during several research flights aboard the HALO (High Altitude and Long Range Research Aircraft) and supported the colleagues in Oberpfaffenhofen concerning transport, installation, characterization, and data retrieval with ERICA.

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CURRICULUM VITAE

The curriculum vitae is not included in the electronic version.

DECLARATION

I hereby declare that I wrote the dissertation submitted without any unauthorized external assistance and used only sources acknowledged in the work. All textual passages which are appropriated verbatim or paraphrased from published and unpublished texts as well as all information obtained from oral sources are duly indicated and listed in accordance with bibliographical rules. In carrying out this research, I complied with the rules of standard scientific practice as formulated in the statutes of Johannes Gutenberg-University Mainz to insure standard scientific practice.

Mainz, 9. Juli 2024



Philipp Brauner