

# Ultrafine Particle Emissions in the Mediterranean

Wolfgang Junkermann

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**Abstract** An overview of ultrafine particles (UFP) and their sources in the Mediterranean basin is presented based on historical and new measurements in the framework of ChArMEx (the Chemistry-Aerosol Mediterranean Experiment). UFP and meteorological variables were measured from an ultralight aircraft focusing on particles in the nucleation and Aitken modes, and their potential properties as cloud condensation nuclei (CCN). Observed UFP could be assigned to different source areas and occasionally to certain types of emitters. An assessment of ship emissions contribution to the nucleation and Aitken particle modes budget over the Mediterranean is derived. Shipping along the main route from Suez to Gibraltar is a source of UFP in a similar order of magnitude or even larger than anthropogenic emissions along the shorelines and well above any natural sources. In areas far from major emission sources, the majority of UFP were identified as CCN in concentrations far above natural abundance and significantly enhanced compared to

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Chapter reviewed by **Daniel Rosenfeld** (Institute of Earth Sciences, The Hebrew University of Jerusalem, The Edmond J. Safra Campus, Jerusalem, Israel), as part of the book *Part V Emissions and Sources* also reviewed by **Claire Granier** (Laboratoire d'Aérodologie (LAERO), CNRS – Univ. Toulouse III Paul Sabatier, Observatoire Midi-Pyrénées, Toulouse, France)

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W. Junkermann (✉)  
Institute of Meteorology and Climate Research (IMK-IFU), Karlsruhe Institute of  
Technology, Garmisch-Partenkirchen, Germany

pre-climate change (~1970) conditions. This enhancement in CCN concentrations over the whole basin by anthropogenic UFP is an important input parameter for aerosol-cloud interaction models and could be a timely, well-correlated, and essential factor for the observed changes in rainfall patterns within the last decades.

## 1 Introduction

The preceding chapter reviewed anthropogenic emissions of various reactive gases and fine particulate compounds in the Mediterranean region (Borbon et al., 2022). Here the focus is put on the anthropogenic contribution to the budget of ultrafine particles (UFP) in the Mediterranean atmosphere. Most emission inventories are based on mass emissions, and UFP represents only a minor fraction of the mass. Despite their climate relevance, the number emission is not included in emission databases like those considered in the preceding chapter. To our knowledge, the first number emission scenario was published by Paasonen et al. (2016). The main sources were industrial and residential combustion processes and traffic. However, these numbers are still highly uncertain, and they cover only continental sources, whereas in the Mediterranean, the contribution from intense ship traffic (see the chapter in Vol. 1 by Doussin, 2023) has to be taken into account given documented UFP emissions by large ship engines (e.g., Contini et al., 2015; Villa et al., 2019 and references therein).

UFP constitute the fraction of the airborne particle size spectrum below 100 nm in diameter. This size range covers particles in both the nucleation mode, <1–20 nm, and the Aitken mode, 20–100 nm (Young & Keeler, 2007). In the upper range of the Aitken mode (>40 nm) and further extending into the accumulation mode (>100 nm), ultrafine particles may act as cloud condensation nuclei (CCN) (Charlson et al., 1987; Andreae, 2009). The threshold for CCN activity at sizes >40 nm is not fixed as it depends on aerosol chemistry, the fraction of water-soluble and water-insoluble compounds, and their physical distribution within the particle. Further on, meteorological and cloud dynamical parameters like updraft velocity and supersaturation of water vapor in clouds control the growth of cloud condensation nuclei to real cloud droplets (Rosenfeld et al., 2019). A reduction in droplet size by additional UFP-derived CCN is expected to delay rainfall from shallow clouds (Rosenfeld, 2000; Bigg, 2008), although a direct causality for regional drought is difficult to prove (Heinzeller et al., 2016). On the other hand, more latent heat energy originates from more rapid evaporation of warm shallow cloud droplets and also from in-cloud processes involving condensation on UFP/CCN inside strong convective cells. This latent energy invigorates torrential rains leading locally to even more intense precipitation (Bell et al., 2008; Rosenfeld et al., 2008; Fan et al., 2018; Guerreiro et al., 2018). Increased lightning intensity over major shipping lines was also reported (Thornton et al., 2017).

Due to the impact of ultrafine particles as CCN on clouds and subsequently on the hydrological cycle, knowledge about these particles and their emissions and budgets is crucial for climate modelling (Charlson et al., 1987). The Mediterranean is suffering from changes of the hydrological cycle, rainfall, drought, and surface runoff as well as torrential rains and Mediterranean tropical-like cyclones called medicanes (Gudmundsson et al., 2016). Understanding UFP and the fraction of the UFP active as CCN might be contributing to the understanding of these changes. Enhanced CCN might even be responsible not only for longer droughts but also for an increase in lower troposphere water vapor as a major greenhouse gas and thus directly affect the earth's radiation balance (Riuttanen et al., 2016; Bister & Kulmala, 2011).

Ultrafine particles in the atmosphere, especially in the lowest size ranges, originate from a production from gas phase molecules or gas to particle conversion (GPC). The initial step, the nucleation, is the production of a more or less stable cluster of about 1 nm in diameter that then further grows and stabilizes within a few hours (Kulmala et al., 2013). This nucleation and growth process may happen everywhere in the atmosphere where a suitable mixture of chemical compounds is available. It has already been observed by Aitken at the Scottish northwest coast and also at the coastline of Tasmania at Cape Grim. Such a natural particle production from maritime emissions or related compounds (O'Dowd et al., 2005) has, however, never been observed in the Mediterranean although volcanic emissions could emit additionally the required chemical precursors. Key substances for the initial cluster production are compounds like sulfuric or nitric acid as well as ammonia, and the intensity of new particle formation is, like in all other chemical reactions, depending on the "ambient" "laboratory" conditions. Natural UFP in the maritime environment are either derived from biogenic emissions of organic sulfur compounds oxidizing in the atmosphere to reactive sulfur and subsequently slowly growing GPC particles (Charlson et al., 1987) or derived from sea spray and bursting gas bubbles. Particle concentrations over pristine ocean surfaces are in the order of a few hundred  $\text{cm}^{-3}$ , of which about 100 to 150 are cloud condensation nuclei (Schmale et al., 2018). However, under conditions with marine biogenic material exposed to sunlight at some coastal sites, locally enhanced number concentrations well exceeding 10,000  $\text{cm}^{-3}$  were observed (O'Dowd et al., 2005, 2007). Everywhere in the atmosphere, sulfur dioxide emitted naturally from volcanic activity or from marine emissions like DMS, or emitted by anthropogenic sources, may produce nanoparticles upon interaction with ammonia from agriculture. The natural continental background source strength, however, is not well known. Bigg and Turvey (1978) estimated the natural background for remote Australia to  $\sim 700$  particles  $\text{cm}^{-3}$ . Strong anthropogenic induced gas to particle conversion was observed to produce large numbers of particles in sulfur-rich plumes released from power stations (Kiang et al., 1973) and smelters (Ayers et al., 1979) or also in the industrial applications burning at high temperatures sulfur containing fossil fuel (Bai et al., 1992) as part of the SCR flue gas cleaning systems. For these applications, the addition of ammonia was proposed as a technique to convert harmful gaseous compounds  $\text{SO}_2$  and  $\text{NO}_x$  into filterable particulate matter.

The growth of the initial nucleation clusters in the atmosphere with growth rates of a few nm per hour is finally dependent on the presence of additional condensable substances like extreme low volatility organic compounds (ELVOC) (Kulmala et al., 2013; Ehn et al., 2014). Such VOCs would be readily available from the Mediterranean vegetation. After several hours, particles grown into the size range of cloud condensation nuclei are then composed of a mixture of an inorganic core, i.e., ammonium sulfate or nitrate, and organic compounds with a more or less hydrophilic composition which controls the later droplet activation process in the cloud and the probability of the UFP to become a CCN (Wang et al., 2019).

Frequent biomass burning over and around the Mediterranean is an alternate source for particles in the CCN range, but it is producing large amounts of mainly accumulation mode particles. The main emission mode is larger, and the number size distribution main mode of fresh biomass burning aerosol is normally above 80 nm with a tail well into the visible size range >300 nm (Alonso-Blanco et al., 2014). Besides the number concentration thus, to disentangle different sources and production processes, the size distribution is a powerful key to investigate the origin, or age, of ultrafine particulate matter. For example, in case that the nucleation mode is suppressed and only particles >10 nm are observed, this is normally an indication of a medium- to long-range transport due to the fast growth of freshly produced particles from the nucleation into the Aitken mode (Boy & Kulmala, 2002; Dal Maso et al., 2005). Also, the shape of the observed modes can be used as an indicator of underlying production and aging processes. Unfortunately, ultrafine particles are invisible and thus not detectable by remote sensing techniques which would allow a better spatial coverage and monitoring. They have to be measured in situ, and spatial investigation requires aircraft.

An extended overview about the historical and technological development of instrumentation for the measurement of UFP is given by Mohnen and Hidy (2010). Although instrumentation for the detection of particles >15 nm has been available since the late nineteenth century (Coulier, 1875; Aitken, 1888), the knowledge of ultrafine particles and their sources and budget is still limited. One reason for the limited database is the fact that, despite the early knowledge of particle numbers as a proxy for pollution levels (Aitken, 1890; Landsberg, 1938), regulations concerning particles normally consider the mass fraction, particulate matter with size ranges <10  $\mu\text{m}$  or 2.5  $\mu\text{m}$  (PM<sub>10</sub> or PM<sub>2.5</sub>). This was one of the initial parameters reproducible measurable and claimed to be health relevant (Pope et al., 2002). Environmental monitoring sites were thus normally equipped with instrumentation neither for long-term monitoring of particle number concentration nor for the particle size distribution. That ultrafine particles may be even more health relevant than particulate mass came up about a decade ago (Franck et al., 2011) and is now generally accepted. The health effect is described to be due to the smaller size and subsequent deeper penetration of UFP into the lung. However, only a few monitoring networks have been established since (Birmili et al., 2016). In the Mediterranean, only two sites were installed since 2000 following the detection of more or less regular diurnal patterns of ultrafine particles within the nucleation mode in a boreal forest

environment (Kulmala et al., 2004). The instrumentation is relatively complex so that data are mostly available from short-term campaign activities. In Italy, the first site in the eastern Po Valley was established at San Pietro Capofiume about 30 km from the Adriatic coast in a predominant agricultural area surrounded by several large pollution sources (Laaksonen et al., 2005). Data are covering several years, for example, from the QUEST-EU (Quantification of Aerosol Nucleation) campaign, and long-term measurements were analyzed and published by Hamed et al. (2007). In the eastern Mediterranean, a station has been established in Crete (Finokalia), and analyses covering several years are now reported (Kalivitis et al., 2019). A station on the island of Gozo was installed in 2012, but to our knowledge, no data have been published yet.

To cover the gaps in observations, a few more stations were installed to extend the existing infrastructure temporarily in relatively clean locations on the islands of Mallorca and Corsica, and aircraft were used for additional three-dimensional investigations within the framework of the Chemistry-Aerosol Mediterranean Experiment (ChArMEx; [https://www.atmos-chem-phys.net/special\\_issue334.html](https://www.atmos-chem-phys.net/special_issue334.html)). Field operations were mainly over the western basin (Rose et al., 2015) and over the island of Corsica in summer 2012 (project VESSAER: Vertical Structure, Sources, and Evolution of Aerosols in the Mediterranean Region; Roberts et al., 2013) and extended further south east over Malta and Gozo islands in summer 2013. On a short time scale and on a campaign basis, further ultrafine particle data are available from campaign activities in ChArMEx from field sites in Mallorca Isl. and at Ersa (north of Cap Corse on Corsica Isl.) in the western Mediterranean and at Finokalia (Crete Isl.) in the eastern Mediterranean (Berland et al., 2017; Kalivitis et al., 2019). Data from a later campaign in Madrid in 2017 (Carnerero et al., 2018) fit well into the overall picture.

One advantage of the available database for the characterization of the anthropogenic contribution to the particle budget is the fact that besides measurements with the latest available instrumentation, at least a few historical data on particle number concentrations are published. John Aitken spent at the end of the nineteenth century already several weeks on the French coastline east of Toulon with his mobile counter. Later, in the early 1970s, a ship cruise for the investigation of ultrafine particle number concentrations was performed in the Sardinia and Sicily Channels which were considered at that time as remote maritime areas (Colacino & Dalu, 1972), followed by a cruise in 1975 throughout the whole western and eastern Mediterranean (Elliott, 1976). These measurements now can be compared to number concentrations measured during ChArMEx in 2012 and 2013 considering that the early Aitken and Pollak (Metnieks & Pollak, 1959) counters are comparable in the lower detectable size limit but were not able to measure nucleation mode particles below ~15 nm. Nevertheless, the currently available size distributions down to ~3 nm allow a comparison.

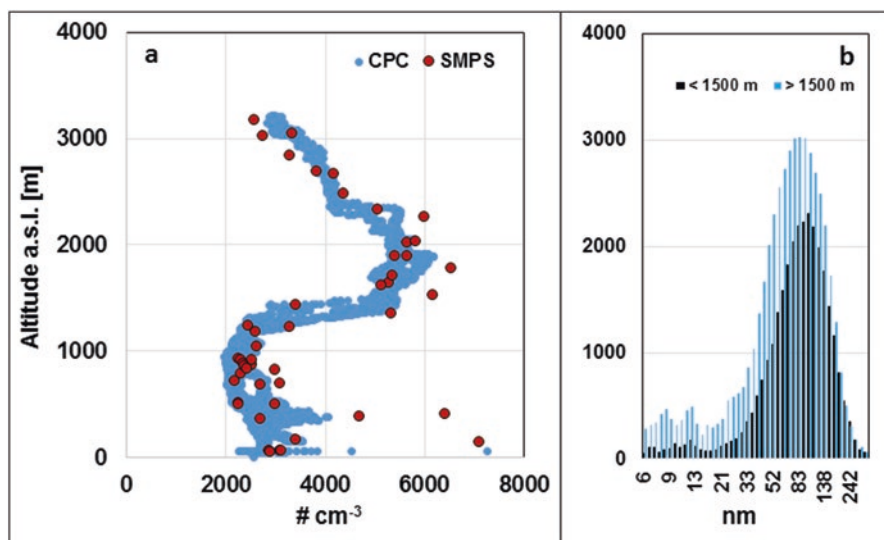
## 2 Airborne Experiments in the Mediterranean

Several aircraft were involved in aerosol investigations in the western Mediterranean: the French Safire ATR-42 flew in 2012 during a campaign of the Hydrological Cycle Mediterranean Experiment (HyMeX; Rose et al., 2015) and in cooperation with the Safire Falcon F-20 in 2013 during a ChArMEx campaign (Mallet et al., 2016). A small aircraft operated by Karlsruhe Institute of Technology (KIT) in Germany was used already earlier between 1999 and 2008 in the western Mediterranean for investigations of the regional three-dimensional distribution of aerosols and radiation. These first campaigns included ultrafine particles from a  $> 10$  nm particle counter (CPC) to characterize photochemistry in southern France between Avignon and Marseille (Junkermann, 2005) and the vertical structure of the planetary boundary layer (PBL) over the island of Lampedusa for Saharan dust studies (Meloni et al., 2015). To gather first information on nucleation mode particles, extensive flights over the eastern Po Valley within the QUEST project (Laaksonen et al., 2005) used a twin counter setup with 3 and 10 nm cutoffs.

With a similar two-counter setup plus an additional SMPS (20–480 nm), Rose et al. (2015) indeed found nanoparticles between 5 and 10 nm in elevated layers especially over the Gulf of Lyon and assigned these particles to new particle formation. The data presented do not allow us to identify or to quantify the emission source or the contribution to the CCN budget. A contribution of marine emissions to new particle formation in the elevated layers would require at least convective vertical and synoptic horizontal transport most likely with some anthropogenic contamination. The corresponding three-dimensional distribution and temporal, day and night occurrence, could be as well in agreement with continental emission, meteorology, and long-range transport (Junkermann & Hacker, 2018).

Within the framework of ChArMEx, two airborne campaigns specially focusing on ultrafine particles and CCN followed over islands of Corsica and Malta during summer of 2012 and 2013, respectively. Aerosol particle size distributions and their potential to serve as cloud condensation nuclei were investigated during the VESSAER 2012 campaign on the eastern side of Corsica up to an altitude of about 3500 m a.s.l., probing both the planetary boundary layer and the lower free troposphere. The objective was to characterize ultrafine particle number, size distributions, and cloud condensation nuclei spectra in local (PBL) and long-range transported air masses (lower free troposphere) (Roberts et al., 2013). The aircraft, an instrumented weight shift microlight, carried a set of aerosol sensors, CPC ( $>10$  nm), nano-SMPS (4.5–350 nm with 15 size bins between 4.5 and 20 nm, 120–sec time resolution), optical particle spectrometer (0.3–20  $\mu\text{m}$ ), as well as comprehensive meteorological instrumentation, i.e., temperature, dew point, radiation, wind speed, and turbulence (Junkermann et al., 2016). An additional miniaturized cloud condensation nuclei spectrometer was provided for the Corsica campaign by G. Roberts, Météo-France, Toulouse. During summer 2013, the KIT ultralight flew with a more sensitive CPC ( $>4.5$  nm) from the island of Malta with vertical profiles over Malta and the neighboring island of Gozo to characterize ship emissions close to the Sicilian Channel, nowadays one of the world's major shipping routes (see chapter on anthropogenic pressures; Doussin, 2023).

The results for both island locations were quite different. Corsica is located relatively close to the coastline of Italy with 200 km of Genova and  $\sim 120$  km of Civitavecchia, and  $\sim 900$  km of the Spanish coast, but further away from major shipping routes than Malta. The island is large enough to be subject to thermal convection, mixing planetary boundary layer air up to the mountain summits at 2700 m. During VESSAER, we experienced mainly westerly winds with 24 h back trajectories originating on the Iberian Peninsula and fast transport over  $\sim 900$  km. Number concentrations of ultrafine particles were always moderate, in the range of  $2000\text{--}4000\text{ cm}^{-3}$  up to an altitude of  $\sim 2500\text{--}3000$  m, but occasionally even higher up to  $6000\text{ cm}^{-3}$  in an elevated layer above 1800 m. For westerly winds encountered, the mountain range on Corsica is a barrier with open channels at about 1600 m. Thus, below 1600 m, likely more local conditions prevail. The island is covered with dense Mediterranean vegetation, the source of VOC required for rapid aerosol growth (Ehn et al., 2014). However, during 2 weeks of campaign, no significant signature of fresh nucleation in any of these air masses was ever observed. Geometric mean particle size was normally between 70 and 100 nm and more than 50%, up to 100% of these particles were cloud condensation nuclei at 0.3% supersaturation. In one case, we found a direct transport of smaller particles at mid-elevation (1600–2300 m) passing over Ajaccio and possibly affected by emissions from the local fossil fuel power station (Roberts et al., 2013). The data compare well with the size distributions at the surface site of Ersa at 535 m a.s.l. in altitude north of Corsica and with the traces of nucleation mode aerosol in elevated layers reported by Rose et al. (2015) (Fig. 1). From continuous measurements at Ersa (Cap Corse; Berland et al., 2017; see also the chapter on nucleation by Sellegri & Rose, 2022),

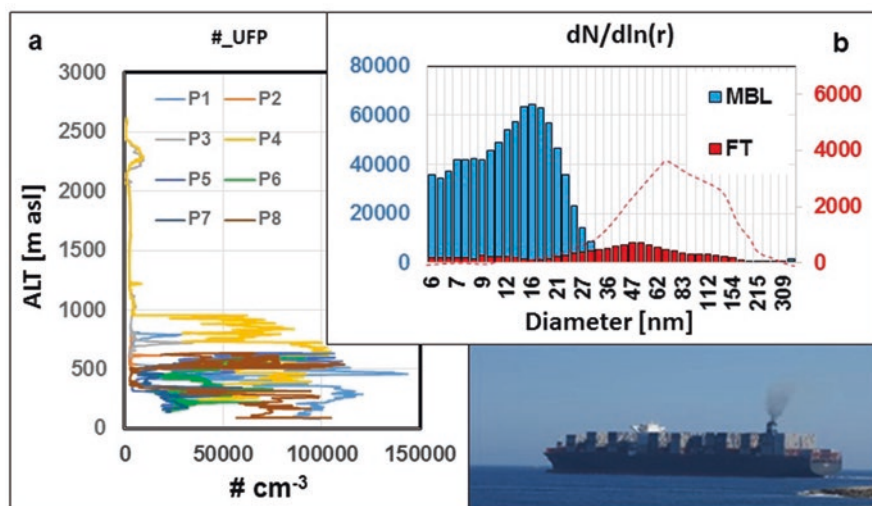


**Fig. 1** (a) Vertical profiles of ultrafine particles  $>10$  nm (CPC, light blue) and total number concentration (SMPS, dark red) over Ghisonaccia (Corsica) July 9, 2012. (b) Average size distribution: (diameter) in the PBL below 1500 m (black) and between 1500 and 2300 m (light blue)



<10 nm nucleation mode particles were visible only occasionally, and the “typical” diurnal “banana curve” patterns, which are often observed at surface sites on the continent, began at or above 15 nm, an indication that favors rather long-range transport advected particles compared to local particle production (Boy & Kulmala, 2002; Dal Maso et al., 2005). During the time of the flights and also at Ersu, the size of the main UFP mode was already generally >50 nm.

The Malta flights revealed a completely different picture. The nucleation mode dominated the atmospheric marine boundary layer (MBL) with concentrations about an order of magnitude larger than observed over Corsica and previously in the campaigns at Lampedusa, where normally several distinct layers of UFP were observed, the first one just marking the top of the MBL (Di Iorio et al, 2003). These stable aerosol layers are a result of the normally stable stratification of the marine planetary boundary MBL compared to the continent, and Lampedusa is too small to significantly produce such a thermal convection as observed over Corsica (Junkermann, 2001; Meloni et al., 2015). Over Malta and Gozo, the UFP in the MBL were not perfectly mixed, an indication of a nearby source, but the average concentrations over both islands were the same each day. Contrary to the moderate number concentrations over Corsica with up to  $\sim 6000 \text{ cm}^{-3}$  over Malta up to  $150,000 \text{ cm}^{-3}$ , typically  $40,000\text{--}80,000 \text{ cm}^{-3}$  were found. Figure 2a shows the vertical structure of ultrafine particles during a morning flight (08:00 to 10:00 UTC) over Malta and Gozo with slight northerly winds on June 14, 2013.

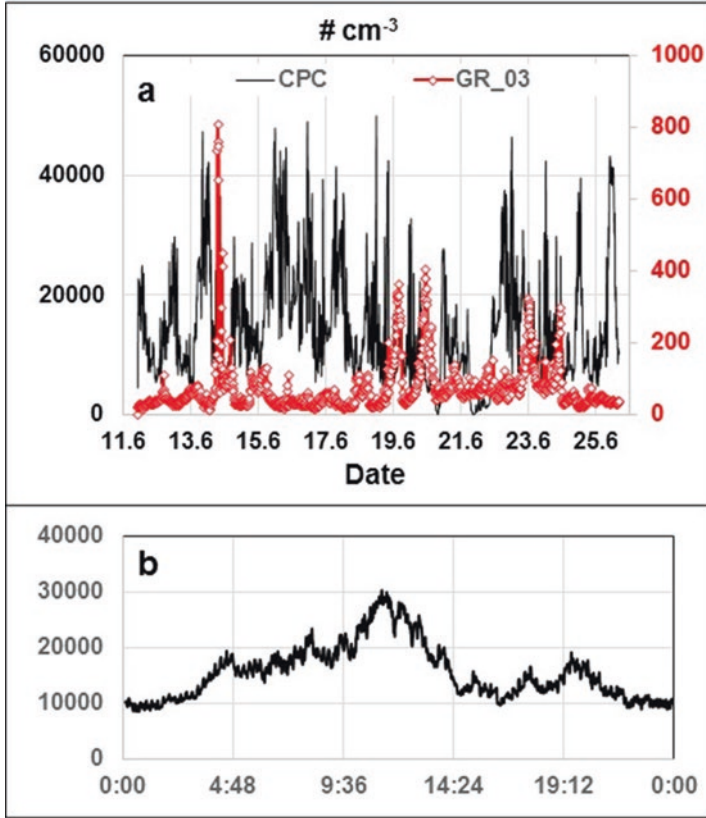


**Fig. 2** UFP over the island of Malta and Gozo: (a) Eight vertical soundings from  $\sim 50 \text{ m a.g.l.}$  to  $\sim 2500 \text{ m a.g.l.}$  for particle number concentrations  $>4.5 \text{ nm}$ . (b) Corresponding averaged size distributions above the MBL and within the MBL. The flight was performed under conditions with about  $2.5 \text{ ms}^{-1}$  northerly winds downwind of the main shipping route between Malta and Sicily. For comparison, a typical MBL size distribution from Corsica is included (dotted line). The photo taken during the campaign shows a cargo ship off Malta with its smoke plume



Due to airspace restrictions with Malta airport, all vertical profiles >600 m were flown over the island of Gozo. Here on June 14, a thin layer with  $\sim 10,000$  particles  $\text{cm}^{-3}$  (already more than in Corsica) was found at 2300 m. The origin of this layer with low concentration for Malta but high compared to Corsica is not known; however, the back trajectory passed quite close to the summit of Mt. Etna. This layer can thus be both natural and anthropogenic. The corresponding size distributions in the MBL (see Fig. 2b) had a major and slightly asymmetric mode at 18–20 nm diameter, while the size distribution above the MBL peaked at  $\sim 60$  nm more similar to the observations of aged particles over Corsica. A size distribution with a main mode at that small diameter is probably a mixture of primary emission and fast secondary production in agreement with the ships emitting high amounts of sulfur dioxide and  $\text{NO}_x$ . A pure secondary production during the morning time window would, however, require a significantly faster growth than known from recent literature. It is interesting to note that the UFP main mode is clearly smaller than the one reported for a container ship burning heavy marine oil outside the SECA (Sulfur Emission Control Area) area of the British channel ( $\sim 80$  nm; Petzold et al., 2008) and much closer to the sizes emitted from modern continental power stations (Junkermann et al., 2016; Junkermann & Hacker, 2018). Such stations apply flue gas cleaning techniques like SCR or SNCR (selective (non)-catalytic reduction) where large amounts of added ammonia suppress the  $\text{NO}_2$  emission but favor the production of new particles. Nucleation then already occurs within the power station, respectively, within the flue gas cleaning section (Bai et al., 1992; Srivastava et al., 2004) or directly after emission in the cooling and spreading flue gas plume. A later comparison with a hybrid ferry in the Baltic Sea operating at low sulfur fuel (<0.1%) and including a pollution scrubber system revealed even higher number emissions under totally overcast conditions. The ferry emitted a clear single particle mode at 30 nm without any indication of fresh nucleation. For the Mediterranean under bright sunshine downwind of the main shipping channel, a slightly smaller main size mode (18 nm) which was found extending into the lowest nucleation mode size bins, a signature of gas to particle conversion.

During the airborne campaign over Malta, an additional ground-based particle counter (TSI 3010) and an optical particle spectrometer (model GRIMM 1.108) were installed on a rooftop (fifth floor) at the harbor of Marsaxlokk on the east side of Malta island as a ground-based reference. On the average over the campaign the instruments measured  $\sim 15,000$  particles  $\text{cm}^{-3}$  with particle numbers reaching  $>50,000$   $\text{cm}^{-3}$  (Fig. 3a). An obvious diurnal pattern with maxima around noon (Fig. 3b) indicates that Malta, although smaller than Corsica, is also likely subject to diurnal convection regularly advecting sulfur- and particle-rich air from ships either passing by or on berth to the island. The pattern is not in agreement with the local car traffic in the area. However, here the size of the UFP and the mixture of primary and secondary particles remains unknown due to the missing size distribution.



**Fig. 3** Ground-based UFP measurements during the June 11–26, 2013, campaign on the island of Malta, at a rooftop fifth floor at the harbor front of Marsaxlokk: (a) concentration levels of particles >10 nm (CPC-TSI 3010; left axis) and the particle number concentration of fine particles >300 nm (GR0\_03, right axis); high values of fine particles indicate Saharan dust events; (b) diurnal cycle of the UFP concentration as a running average for the campaign

### 3 History of Ultrafine Particle Concentration Levels in the Mediterranean

It is interesting to note how particle number concentrations and potential cloud condensation nuclei concentrations changed in the Mediterranean within the last decades. Already back in 1890 John Aitken (1890) identified anthropogenic activities at the harbor town of Toulon as one of the major sources of Aitken particles and other pollution, but, he was not able to identify any chemical process involved. During his measurements, about 30 km from Toulon he found, from the clean maritime sector, ~600 particles cm<sup>-3</sup>. Polluted air reached up to 45,000 particles cm<sup>-3</sup> downwind the city and port of Toulon.

Colacino and Dalu (1972) found 80 years later about 800 to 1000 particles  $\text{cm}^{-3}$  over the open water of the Sicily and Sardinia Channels, also most probably upwind of the industry in Sicily, and on the mainland. At that time, clean oceanic conditions over the Atlantic and Pacific were expected to have about 300 to 400 particles  $\text{cm}^{-3}$ , and the Mediterranean, as expected, was no longer completely clean. Compared to Aitken's measurements 80 years earlier, there was no obvious change in cleaner parts of the Mediterranean Sea. Elliott (1976) found a few years later on a cruise extending into the eastern basin and into the northern Aegean Sea between 1000 and 2000  $\text{cm}^{-3}$  and occasionally up to 15,000  $\text{cm}^{-3}$ , which were assigned to anthropogenic sources at the coast. The increase in background number concentrations could be already related to growing shipping traffic emissions that finally in the twenty-first century led to  $\sim 15,000\text{--}20,000$  particles  $\text{cm}^{-3}$  in 2013 in the same area.

Especially within the central part of the Mediterranean, the emissions changed significantly in the last decades. Power stations and refineries were in operation in the 1970s in Sicily and at the southern tip of the Italian mainland, where one of the largest industrial sites is located, in Taranto, since the late 1960s. However, these particle sources were not equipped with flue gas cleaning systems until the end of the twentieth century and emitted a major fraction as fine particles. Fine particles serve as a condensation sink and suppress the number of ultrafine ones. Thus, although the total emitted mass (PM) was higher, number concentrations was probably lower than today as a drawback of modern "clean" technology.

Despite the introduction of air pollution control measures the levels in urban environments in the twenty-first century did not change much compared to 1890 with the exception of black carbon and fine dust, which is significantly reduced. This is due to the more intense traffic now. The coastline with expanding urban settlements and increasing traffic is thus becoming a continuous line source these days, compared to the patchy patterns at the turn of the nineteenth century. Traffic emissions in urban environments and also from in between these agglomerations are now one of the larger sources of primary nanoparticles (Olin et al., 2020; Rönkkö et al., 2017). From the available data we have, it is impossible to estimate whether and how far UFP emissions changed. However, a number of new, important and dominating sources have been introduced. Growing emissions from fossil fuel power stations and refineries have shifted from fine particles to ultrafine ones since  $\sim 1980$ . Different to urban and car emissions, these UFP emitters release into elevated altitudes of about 200–300 m. These emissions occur during the day into the boundary layer, during night above the nocturnal inversion, favoring mid-elevation transport up to a few hundred km (Junkermann & Hacker, 2018). This agrees with the elevated layers observed over the less convective MBL (Junkermann, 2001; Meloni et al., 2015; Rose et al., 2015) and with the diurnal pattern of size distributions at the ground-based field sites (Berland et al., 2017; Junkermann & Hacker, 2018). Within the Mediterranean, large industrial UFP sources are found in increasing numbers and increasing size. Currently, about 35 units burning coal (<https://www.endcoal.org>) are located along and  $\sim 200$  km inland of the coastline from Gibraltar, along the Spanish coast over southern France towards Italy and further east to Greece and

Turkey. Additionally, several large refineries and heavy oil-fired units are also now operational (Malta, etc.). The source for ultrafine mode aerosol identified by Kalkavouras et al. (2017) for particles observed at the Finokalia site is such a region with several coal fired power stations. Intense UFP events at the Cyprus coast can be traced back to stations at the Turkish south coast (Brilke et al., 2020). The Italian field site at San Pietro Capofiume (Laaksonen et al., 2005) is similarly affected by fossil fuel emissions from nearby Mestre, Porto Tolle, and Rimini. Correspondingly, the local fossil fuel-fired power stations located in Mallorca, Corsica, Malta, Crete, and Cyprus have to be considered. The possible nucleation source areas identified by Berland et al. (2017) are close to such UFP emission hotspots. In addition, maritime fossil fuel extraction sites like gas and oil rigs have not been investigated yet. The fuel there is not burnt in significant amounts, but they could contribute, especially in the eastern Mediterranean where their number could increase rapidly following recent hydrocarbon fields' discoveries (Ellinas et al., 2016).

## 4 Major Contributions to the Mediterranean UFP Budget

Local traffic, urban environments, fossil fuel processing (refineries), power generation, and ship traffic all contribute to the ultrafine particle budget over the Mediterranean (Junkermann & Hacker, 2015, 2018) with, depending on the source, different emission heights. Ships are emitting always into the MBL, and power stations at night above the nocturnal MBL, leading to different transport patterns day and night. Above the MBL, long-range transport might cover the whole basin (Elliott, 1976), and diurnal convection is rapidly mixing these layered emissions both down to the ground and up to the cloud base. Ships in the Sicilian Channel were identified to be a major source of ultrafine particles initially too small for CCN activity but growing within a few hours into the respective size range. Ships burning sulfur-rich fuel were estimated to emit slightly less per MW, but at larger sizes (Petzold et al., 2008), their emission is also dependent on speed, size, engine, and fuel. However, cleaner fuel as required after 2020 also for the Mediterranean does not mean that the UFP emission is decreasing. Experiments in the Baltic Sea indicated that with a reduction of fine particles, the primary emission of ultrafine or nanoparticles might be even increasing to similar values as were obtained from the modern continental power stations in the order of  $3 \cdot 10^{15}$  particles per MW. This would agree with the results of Hamed et al. (2010) who observed that the number of cloud condensation nuclei at a field site surrounded by several lignite power stations increased during transition from “dirty” to “clean” operation, despite sulfur dioxide reduction. A doubling of nucleation mode particles was observed a few hours downwind of a modern power station, and even after transport for 48 h and about 800 km downwind of a major UFP source, the signature of enhanced nucleation appeared under “clean Mediterranean” conditions over Australia (Junkermann & Hacker, 2015; see also Rosenfeld 2000). That indicates that even in a diluted plume still sufficient precursor material is available.

Using the Malta vertical profiles for shipping emissions, an emission rate estimate can be calculated although it cannot be disentangled how primary emission and fast secondary gas to particle production are contributing. Measurements a few km downwind from large point sources always summarize the primary and immediate secondary production. It is thus a measure of the direct contribution of a single source to the total budget, and this is the number emission finally needed for a model grid cell. Using the information from the flight of Fig. 2, an average particle number concentration along the shipping line over  $\sim 40$  km (Malta-Gozo) of  $30,000 \text{ cm}^{-3}$ , a height of the MBL of 800 m, and an average perpendicular wind vector of  $2.6 \text{ ms}^{-1}$ , the effective particle production from the shipping line is on the order of  $\sim 6 \cdot 10^{16} \text{ s}^{-1} \text{ km}^{-1}$ . Extrapolated to the full distance from Suez to Gibraltar, that would be equivalent to more than 70 medium-size fossil fuel-fired power stations (Junkermann et al., 2011, 2016). Maritime UFP emissions in the Mediterranean are thus in a similar order of magnitude as continental emissions along the coast. Data about shipping intensity are available from the AIS data archive (<https://www.marinetraffic.com/>). These data contain at least the type, size, and speed of all individual ships, especially all cargo ships, and allow a calculation how much cargo (gross register tonnage) is transported along the shipping route. Ship emission reported by Petzold et al. (2008) and calculation of particle emission for the amount of cargo shipped through the Mediterranean are in good agreement with the above shipping emission estimate for the summer time conditions from the Malta campaign.

## 5 Conclusion and Recommendations

Ultrafine particles over the Mediterranean are dominated by anthropogenic activities along the surrounding coastline, by emissions from urban agglomerations, from industrial installations, and from shipping. These emissions are spread over the basin by regional-scale horizontal advection, often in distinct layers, and are finally vertically mixed by thermal convection during daytime. This thermal convection is stronger over land, and larger islands than over the open water. Considering the lifetime of small ultrafine particles, transport distances of about 500 km have to be considered, occasionally even more, similar to Saharan dust transport. Single events can be analyzed for source apportionment, for example, using HYSPLIT or FLEXPART back trajectory models. In many cases, the most likely source can be identified (e.g., Junkermann & Hacker, 2015). Aging and loss processes involved during transport modify size distributions, mainly to larger sizes, toward CCN sizes and to the accumulation mode. A reduction in fine particles due to emission control measures, the condensation sink of UFP, might even increase the lifetime for smaller particles in the ultrafine mode. Important for the climate impact of ultrafine aerosols, among changes in size distributions and chemistry of UFP with aging, the fraction of cloud condensation nuclei is increasing (close to 100% CCN in aged particles over Corsica). Compared to 1970 with a maximum of  $600\text{--}800 \text{ CCN cm}^{-3}$ ,

in the unlikely case that all particles at that time were active CCN, nowadays  $>2000$  and more  $\text{CCN cm}^{-3}$  are normal over the Mediterranean. This is due to the aging UFP from continental sources along the coastline and to the emissions from shipping.

Due to missing data, no trend or even a quantitative estimate can be made for coastal and urban emissions throughout the basin. However, the source from increasing global ship transport is obvious. Shipping is nowadays a major source of ultrafine particulate matter, especially in the marine environment of the central Mediterranean, which was originally remote or only moderately polluted (at least up to the 1970s). ChArMEx results allow a better estimate of the shipping contribution and provide new insights into size distributions related to particulate shipping emissions. Given the large impact of ultrafine particle-derived CCN on the hydrologic cycle through aerosol-cloud interactions, it is suspected that these additional emissions contributed to the observed modification of rainfall patterns with the last decades and the subsequent changes in horizontal and vertical water vapor distributions. There is also experimental evidence that in other areas with reported exceptional rainfall deficiencies, the number concentrations of UFP were enhanced in a similar way to the Mediterranean and that rainfall decline timely correlates with an increase in ultrafine particles, respectively, CCN (Bigg, 2008; Junkermann et al., 2009, 2011; Junkermann & Hacker, 2015; Heinzeller et al., 2016). These climate-relevant processes need more observations and further sophisticated climate modeling with updated primary emission scenarios and detailed aerosol and cloud physics.

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