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Night-time enhanced atmospheric ion concentrations in the marine boundary layer

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Abstract

Measurements of atmospheric ions in the size range 0.8–42 nm were conducted at the environmental research station of the University of Crete at Finokalia from April 2008 to April 2009 in the frame of the EUCAARI project. Both positive and negative atmospheric ions were found to have a clear annual cycle, with minimum concentrations in summer. Their concentrations were found to strongly vary on the prevailing meteorology and the presence of pollutants in the atmosphere. There were 53 new particle formation events recorded. It was found that under certain meteorological conditions and atmospheric composition, enhanced ion concentrations can be observed during the night. Overall, 39 night-time events were observed, all of them observed for the negatively charged particles while only 21 were observed for the positively charged particles. Night-time enhanced ion concentrations were more frequent during spring and autumn and no such events were recorded from July to September. It was found that the presence of pollutants in the atmosphere leads to a decrease of atmospheric ions, especially at cluster sizes (1.25–1.66 nm). Additionally, the meteorological conditions affect the abundance of atmospheric ions greatly, a strong anti-correlation was found between air ions concentrations on the one hand and temperature and wind velocity on the other. Enhanced ion concentrations at night were found to be more frequent when air masses had traveled over the island of Crete.

1 Introduction

Atmospheric ions (charged clusters and aerosol particles) have been measured at different sites around the world (Kulmala and Tammet, 2007). The main sources of air ions are radon decay and cosmic radiation (Israël, 1970; Bazilevskaya et al., 2008). Although atmospheric ions account only for a small fraction of ambient particle population near the earth's surface, they can produce significant amounts of ion-clusters that could, further on, grow to become atmospheric aerosols. Several studies have shown that ion-induced nucleation does occur in the atmosphere (e.g., Virkkula et al., 2007b; Hirsikko et al., 2007; Laakso et al., 2004; Vana et al., 2008; Gagné et al., 2008; Manninen et al., 2010). It has to be pointed out that ion induced nucleation is not directly related to ion pair production but it is related to ion concentration and therefore the study of atmospheric ions concentration especially for the cluster sizes is important. Hirsikko et al. (2007) found that the ion spectrometer could detect particle formation events that were suppressed, due to low concentrations of condensing vapors or high sink by pre-existing aerosol particles, before the DMPS (detection limit 83 nm) detected any particles. Thus such studies of ion mobility distributions provide valuable insights into mechanisms of particle formation and growth.

So far several observations for air ions in the marine or coastal environment exist (e.g., Eichmeier and von Berckheim, 1979; Wilding and Harrison, 2005; Vana et al., 2008). A review of observations of ions in marine and coastal areas can be found in Hirsikko et al. (2011). For the Mediterranean area very few observations exist (Retalis et al., 1977, 2009) and they refer to the urban environment in Athens. During the EUCAARI project (European Integrated Project on Aerosol Cloud Climate Air Quality Interactions; Kulmala et al., 2009; Kerminen et al., 2010) air ions were monitored continuously for one year at the remote coastal site of Finokalia, Crete (Manninen et al., 2010).

In this work we present atmospheric ion measurements at the marine environment of the Eastern Mediterranean and explore their variability with respect to various atmospheric parameters. It has already been shown that air ion concentrations are strongly dependent on the prevailing meteorological conditions (e.g., Vana et al., 2008; Virkkula et al., 2007b). Special focus is given to nighttime ion behavior as despite the increasingly active research on air ions during the last decade, very few studies on the evolution of small ion concentrations during night time have been published to date.

Junninen et al. (2008) reported increases in both concentration and mean size of small ions observed in a boreal forest environment in Hyytiälä during night-time. Furthermore, Siingh et al. (2005) observed higher night-time than day time concentrations in fair weather conditions during their cruise on the Arabian Sea. Junninen et al. (2008) reported that the observed increases were most frequent on nights following a new particle formation event day, suggesting a possible contribution from the same vapours in both day and night-time growth. Furthermore, Lehtipalo et al. (2011) showed that the night-time events in Hyytiälä are seen equally frequently for neutral particles, and that the night-time concentrations of sub-3 nm particles and ions have a clear connection to oxidized organic molecules. Another aim of this study is to explore the nighttime ion behavior in a completely different environment (coastal Mediterranean area) by checking also for a link with day time nucleation events.

2 Experimental

2.1 Site description

The measurements took place at the environmental research station of the University of Crete at Finokalia, Lassithiou, Greece (35° 20′ N, 25°40′ E, 250 m a.s.l) during the period April 2008–April 2009 in the frame of the EUCAARI project. The Finokalia station is a remote coastal site in the northeast part of the island of Crete situated in the middle of the Eastern Mediterranean. The station is situated 70 km northeast of Heraklion which is the major urban area of the island with approximately 170 000 inhabitants. A detailed description of the site and the prevailing meteorology in the area can be found in Mihalopoulos et al. (1997). The site is considered representative for the MBL (Marine Boundary Layer) conditions of the Eastern Mediterranean (Lelieveld et al., 2002).

2.2 Instrumentation

The mobility distribution of air ions was measured using an Air Ion Spectrometer (AIS) as part of the EUCAARI project (Manninen et al., 2010). The mobility diameters recorded were in the range 0.8–42 nm with a time resolution of five minutes. Details on operational principles of the AIS can be found in Mirme et al. (2007). The AIS used at Finokalia had been calibrated and intercompared. The instrument took part in a calibration and inter-comparison workshop before and after the EUCAARI field measurements (see Asmi et al., 2009; Gagné et al., 2011). Asmi et al. (2009) performed mobility, concentration and flow calibrations and concluded that the AISs have a good performance for mobility and concentration measurements. The AISs detected similar concentrations as reference instruments at concentrations corresponding to particle formation events, whereas the mobilities were slightly overestimated. Furthermore, it has been shown that the ion spectrometer compares well with other aerosol instruments also in real environmental conditions in the field (Kulmala et al., 2007; Manninen et al., 2009).

In order to evaluate the atmospheric conditions governing the air ion concentration levels at Finokalia, additional data obtained from the station's routine measurements were used. The particle number size distribution of ambient aerosol (dried at RH $<$ 40%) was measured with a custom-built Scanning Mobility Particle Sizer (SMPS) (Birmili et al., 1999) in the size range 8–900 nm. Ozone concentrations were measured using a Thermo Electron 49C ozone monitor. Calibration and maintenance procedures can be found in Kouvarakis et al. (2000). Black Carbon (BC) concentration in the atmosphere was determined using a Magee Scientific Aethalometer. The data were corrected for filter loading artifacts using the adjustment procedures of Virkkula et al. (2007a). Meteorological parameters were recorded by the automatic weather station installed at Finokalia at 2 m a.g.l. The time resolution for all of the measurements was 5 min. The inlet of the AIS was at $\sim$ 1.5 m above ground level and situated at 15 m southeast of the weather station.

3 Results and discussion

3.1 Air ion features at Finokalia

Atmospheric ions were measured continuously for one year with the aim to detect annual trends and seasonal variations of their number concentration and its dependence on the prevailing atmospheric conditions and composition at Finokalia. The average monthly number concentrations of charged particles were calculated so that the annual variability can be explored. Number concentrations of atmospheric ion with size 0.8–42 nm were found to have a clear annual cycle (Fig. 1). Minimum levels were observed during summer both for negative and positive particles. Although the main trend was common to both polarities, somewhat different features were observed with regard to maximum values. Positive ions presented maximum concentrations during winter. However, negatively charged ions number concentrations were found to be maximum in March and presented two secondary maxima in June and in November. Throughout the measuring period negative ions had slightly higher values than the positive: $521.6 \pm 295.7\,\mathrm{cm}^{-3}$ against $473.2 \pm 284.1\,\mathrm{cm}^{-3}$. The diurnal cycle of atmospheric ion is similar for both polarities (Fig. 2). Minimum concentrations are observed during daytime, while maximum during the night. A first explanation for this would be that after sunrise, thermal mixing in the PBL leads to dilution and therefore to lower concentrations of atmospheric ions while during night the suppression of the PBL results to higher concentrations.

In order to investigate the factors controlling the annual variability, the dependence of ion concentrations on various atmospheric parameters was examined. The analysis performed revealed that the concentrations of atmospheric ions at Finokalia depend greatly on the meteorological conditions. It was found that ion concentrations are clearly anti-correlated with wind velocity (Fig. 3b,d) regardless the wind direction; for both polarities it is clear that for wind velocities greater than $10\,\mathrm{m\,s}^{-1}$ no enhanced concentrations were found and as the wind speed increases ion number concentrations are limited below $1000\,\mathrm{cm}^{-3}$ with an average concentration of ca. $500\,\mathrm{cm}^{-3}$. Since radon is thought to be the major source of atmospheric ions (e.g., Hatakka, 1998), high wind speeds suggest more intense vertical mixing and thus dilution of radon at ground level. Furthermore, at temperatures greater than 30 °C, typically observed on Crete during summer when the lower concentrations are observed, ion concentrations were limited and hardly any episodes of enhanced values were observed (Fig. 3a,c). When it concerned ambient relative humidity (RH), no clear dependence was found, however RH values below 40%, not commonly met at coastal conditions, did not favor high concentrations (not shown). These observations suggest that high concentrations of atmospheric ions are favored when stagnant meteorological conditions prevail in the area. This dependence of air ion concentrations on the meteorological conditions has been reported in earlier work as well (Vana et al., 2008; Virkkula et al., 2007b).

To explore the dependence of air ions in the size range 0.8–42 nm on atmospheric composition we investigated their variability with respect to BC and ozone concentrations in the atmosphere as tracers of anthropogenic air pollutants. Ion concentrations were found to be highly anti-correlated with BC for both negatively and positively charged particles (Fig. 4b,d). A possible explanation would be that higher BC values suggest the abundance of accumulation mode particles that result in high coagulation sinks. Maximum BC concentrations in the area are found during summer (Sciare et al., 2008), partly explaining the minimum values observed for air ions concentrations. A weaker dependence on ozone levels was found (Fig. 4a,c). Enhanced values of atmospheric ion concentrations were observed in a window of ozone concentrations between 30 and 60 ppbv. Values higher than 60 ppbv, suggest either intense photochemistry or long range transport of polluted air masses in the area. Either way, these conditions can restrict air ion concentrations. Intense photochemistry results in the abundance of condensable species. It has already been shown for Finokalia that, during summer, the condensation of sulfuric acid vapors on small aerosols can result effectively to their complete depletion (Kalivitis et al., 2008). On the other hand values for ozone levels lower than 30 ppbv can be attributed to advection and dry deposition mechanisms reducing air ions concentrations as well. The above observations are in line with the previous conclusion that stagnant meteorological conditions enhance ions concentrations. Indeed these levels of ozone and especially the very low values of BC are typical of the pristine environment of Finokalia when it is not under the influence of long range transport processes (Kouvarakis et al., 2000; Gerasopoulos et al., 2007).

3.2 New particle formation at Finokalia

During the measurement period, several new particle formation events were recorded. Details about the frequency of occurrence, formation rates, growth rates and condensational sinks of these events can be found in Manninen et al. (2010). There were 53 nucleation events recorded during day-time. Common observation for all the events was that the initial nucleation evident in AIS data was then followed by condensational growth of the new particles to larger diameters and the subsequent recording of the event by the SMPS system. In the morning of 29 January 2009 a typical nucleation event was recorded both by the AIS and SMPS (Fig. 5). It is worth noticing that nucleation is more pronounced for negatively charged ions than for positive ions. This was typical throughout the measurement period at Finokalia, nucleation of negatively charged particles is favored, a result which is in line with previous observations (Hirsikko et al., 2011). New particle formation was found to be more frequent in winter than in summer at Finokalia (Manninen et al., 2010) following closely the annual biogenic activity in the area.

Prior to or after the initiation of some daytime nucleation events it was evident that a process of enhanced ion concentrations was taking place at night. When looking at the size range 1.25–1.66 nm, the size class representing the upper limit of the pre-existing cluster ion pool, an apparent growth is evident accompanied by simultaneous increase of the ion concentration. During some cases, enough growth was observed so that the event was captured by the SMPS as well (Fig. 6). The observation of a night-time increase in ion concentrations prior to a day-time nucleation event could theoretically be the first step of the two-step nucleation process proposed by Kulmala et al. (2000), at first the ion-induced formation of a cluster occurs followed by the subsequent growth when enough available vapors due to photochemical processes exist. Due to the scarcity of such observations especially for the MBL, no references exist so far, we will next focus on the characteristics governing such phenomena.

3.3 Enhanced ion concentrations during the night at Finokalia

Henceforth we will describe an enhanced ion concentration event as an event which initiates after sunset when solar irradiance is practically zero. In order to identify such an event, the variation of the ion number concentration in the 1.25–1.66 nm size bin was used, provided that a phenomenal growth of the clusters is observed. During the measurement period 39 events were recorded. Only for three of the cases there was enough growth so that there was evidence of these events in simultaneous measurements in the 8–900 nm size range performed with the SMPS (Fig. 6). Similar observations have been made by Junninen et al. (2008). All of the events observed presented a clear lift above the cluster mode in the contour plot and an increase in 1.25–1.66 nm cluster number concentration.

For the night-time events observed, 28% of them were followed by a day-time nucleation event and 18% of the cases were observed after a day time nucleation event so that for almost half of the cases, these two features of air ions are connected. As mentioned already, these night-time events were evident for the negatively charged ions but not all of the events had correspondence in the positive ions, only 21 of them did. However, all the events for the positive polarity were observed for the negative polarity too.

The available measurement days were classified in event and non-event days. The average event to non-event day ratio was found to be 0.16 for negative and 0.07 for positive ions. Looking at the annual variation of the ratio some interesting features were revealed (Fig. 7). High concentration events for negative atmospheric ions at night were more frequent in April and November while from June to September no events were observed. For positive ions the trend was the same; however the maximum observed for November was much weaker. Taking into account that radon concentration at Finokalia is maximum during the summer months (Gerasopoulos et al., 2005) and that radon decay is considered to be a major source of atmospheric ions, the observations concerning the frequency of night-time increased concentration values are somewhat contradictory. However, as shown in Sect. 3.1 atmospheric ion concentrations are highly anti-correlated to wind velocity, BC concentrations and ambient temperature. All of these parameters have peak values during summer at Finokalia.

We then refined our analysis of the effect of various environmental conditions on night-time concentrations of 1.25–1.66 nm clusters. As can be seen in Fig. 8a,d, for temperatures higher than 20 °C no cases of elevated concentration of ion clusters were found. As reported in earlier work for other environments (Curtius et al., 2006; Yu, 2010), low temperatures favor enhanced ion concentrations at Finokalia as well. During summer at Finokalia, temperatures remain well above this threshold. Once again clear anti-correlation was observed with the wind velocity (Fig. 8c,f). Apparently, high wind speeds lead to the dilution of atmospheric ions and enhance advection leading to restriction of higher ion concentration values. Looking at the meteorological data, it was found that ambient RH can be significant as well (Fig. 8b,e). High ion concentrations are observed for RH greater than 60% and it is worth mentioning that high concentrations are found for RH ~ 100% probably implying rain associated air ions (Hirsikko et al., 2007; Tammet et al., 2009).

Negatively charged atmospheric ions in this size range were found to be more sensitive to the presence of ozone and BC than positively charged ions at Finokalia. As indicated in Fig. 9c,d high values of negative ions are found below ozone levels of 45 ppbv while it is clear that the less BC in the atmosphere the higher the values the negative ions can reach. Although the same trends are observed for positive ions (Fig. 9a,b), the ozone threshold in this case is around 60 ppbv and high concentrations are not excluded when BC is abundant. These data suggest that the concentration of atmospheric ions is extremely sensitive to the presence of anthropogenic pollutants. High BC and ozone concentrations as tracers of pollution imply quite effective scavenging of small clusters by the accumulation mode particles that govern polluted air masses at Finokalia (Kalivitis et al., 2008) and this is supported by coagulation sinks calculations (not shown). An extreme case of BC and negative ions anti-correlation is presented in Fig. 10 where it can be noticed that the rapid drop in BC concentrations is directly accompanied by an increase of 1.25–1.66 nm negative clusters concentration.

We also studied the dependence of night-time increased ion concentrations on the origin of air masses, since from the previous analysis it was obvious that the concentration of small air ions is strongly dependent on atmospheric composition, which in turn significantly depends on air mass history at Finokalia. For this reason we used trajectory analysis using the HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model, Draxler and Hess, 1998) at the altitude of 1000 m which is considered to be representative of the boundary layer at Finokalia (Kalivitis et al., 2007). Five days back-trajectory analysis revealed that almost 75% of the events observed took place when air masses originated from the wide W sector (Fig. 11). The results showed intrusion of air masses from higher altitudes for the majority of the events and thus influence of cleaner air masses. The fact that the majority of the events were observed when air masses originated from the West sector (W) and thus spent time over the island of Crete was indicative that the contact of air masses with the soil was the major source of atmospheric ions for Finokalia.

To examine this hypothesis, we examined the relationship between the concentration of 1.25–1.66 nm negative clusters and the wind direction. The results are presented in Fig. 12 as a polar diagram centered on the Finokalia station. Indeed, the greatest variability and the highest concentrations of negative ion clusters are observed when air masses come from the inland of Crete and thus have been in contact with solid ground, except of two cases observed at 355° and 55° for which no clear explanation can be given. Therefore we can conclude that the radon contained in soil could be the dominating source of atmospheric ions at Finokalia. Additionally, as reported by Tunved et al. (2006) the sources of nucleating and condensing species are stronger over land than over the marine environment. In order for an observable growth to take place, certain meteorological conditions must prevail: stagnant conditions and recirculation above the area. Under these conditions, it has already been shown that isoprene (a biogenic compound) concentrations increase (Liakakou et al., 2007). It is possible that the concentration of other biogenic compounds such as terpenes is more important under these conditions as well. Therefore, the limited growth observed for the atmospheric ions can be attributed to the condensation of the oxidation products of biogenic volatile organic compounds (VOC's).

4 Conclusions

In the frame of the EUCAARI project, atmospheric ions measurements took place at the research station of Finokalia during the period April 2008–April 2009. On the course of a year, the concentration of both positively and negatively charged ions were observed to be at their lowest level during summer. The maximum values for the positive air ions were observed in winter and in March for the negative ones with secondary maxima in June and November. Negative ions had slightly higher concentrations than positive ions on average. It was found that the clusters and small air ions are extremely sensitive to the presence of pollutants in the atmosphere. A strong anti-correlation was found between their concentrations and black carbon levels while it was observed that high ozone values restrict the abundance of ion clusters. A strong anti-correlation was also observed with temperature and wind velocity.

During the measuring period 53 daytime nucleation events were observed during the measurement period. Additionally, 39 events of enhanced ion concentration were recorded during night-time. A very interesting observation was that almost half of the night-time enhanced concentration events were observed prior or after daytime nucleation events. Night-time enhanced concentration events were found to be more frequent during spring and autumn, peaking in April and November while no events were observed from July to September. It was found that the 1.25–1.66 nm cluster ions are even more sensitive to the prevailing meteorology and the presence of polluted air masses. Through analyzing air mass history, we concluded that this increase takes place when the air masses had spent some time over the land. While examining air ion concentrations with regard to wind direction, it became obvious that the greatest variability was observed when air was blowing from inland and thus after an air mass had been recently in contact with the ground. In general, low ion sink is a necessary condition to observe high concentrations, however we believe that radon is probably the main source of ion variability at Finokalia. Even though radon concentration is maximum in summer, the low ion concentrations observed can be attributed to the very effective removal processes.

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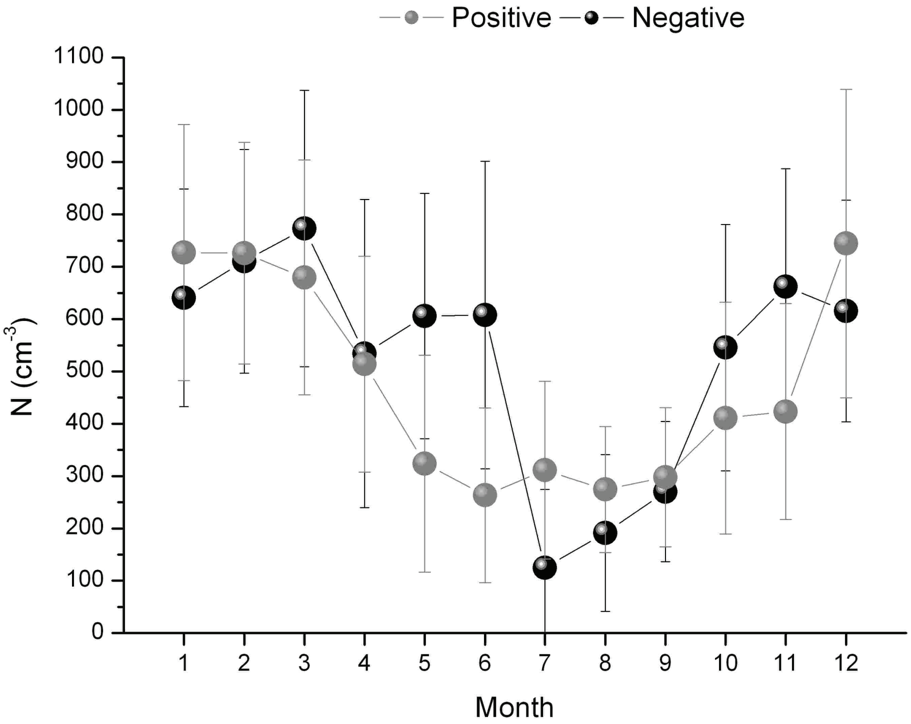

Fig. 1. Annual variability of atmospheric ion concentations in the size range 0.8–42 nm (monthly averages) at Finokalia, Crete.

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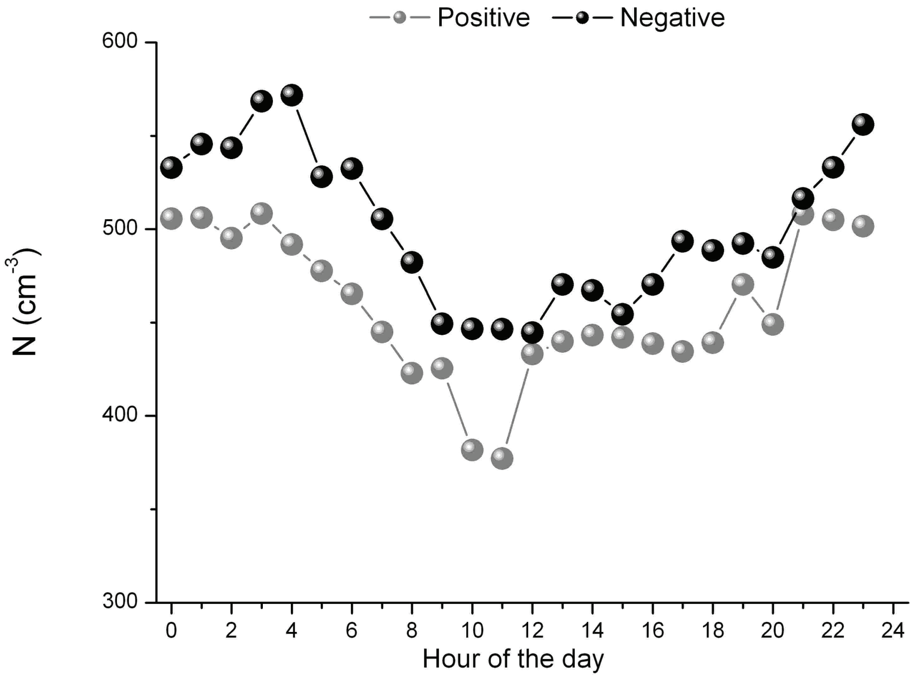

Fig. 2. Median diurnal cycle of atmospheric ion concentrations in the size range 0.8–42 nm (hourly averages) at Finokalia.

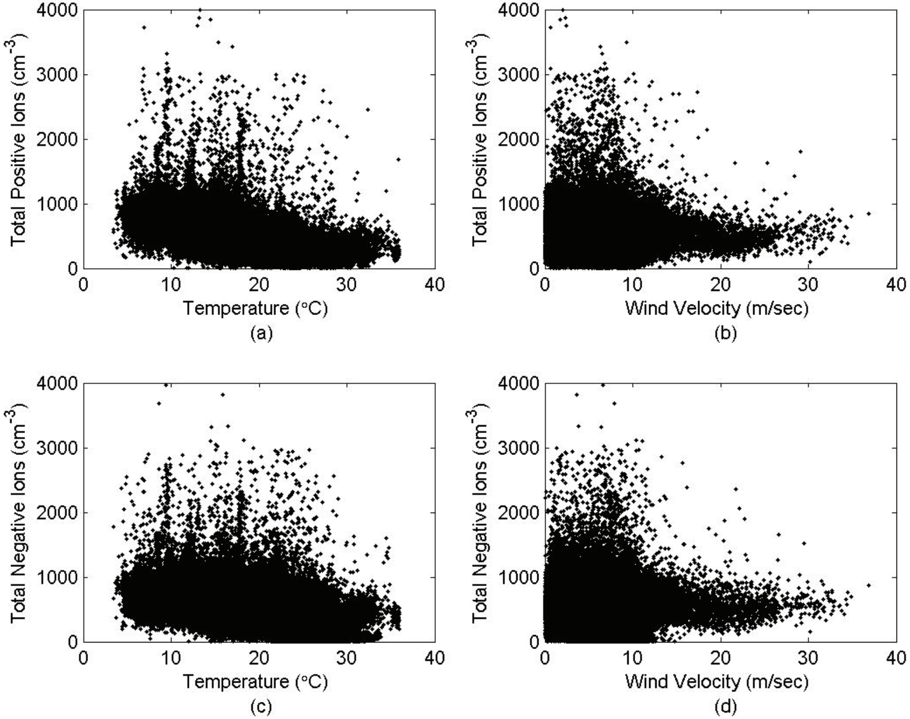

Fig. 3. Variability of atmospheric ion concentrations in the size range 0.8–42 nm depending on temperature and wind velocity for positively **(a, b)** and negatively **(c, d)** charged particles, respectively.

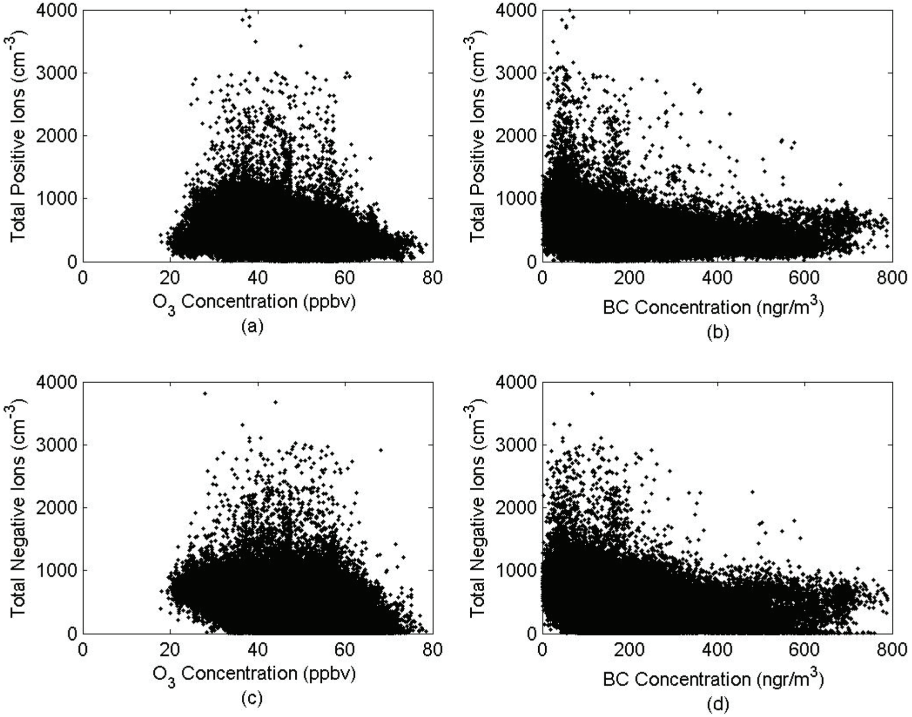

Fig. 4. Variability of atmospheric ions concentrations in the size range 0.8–42 nm depending on ozone and BC concentration for positive **(a, b)** and negative charges **(c, d)**, respectively.

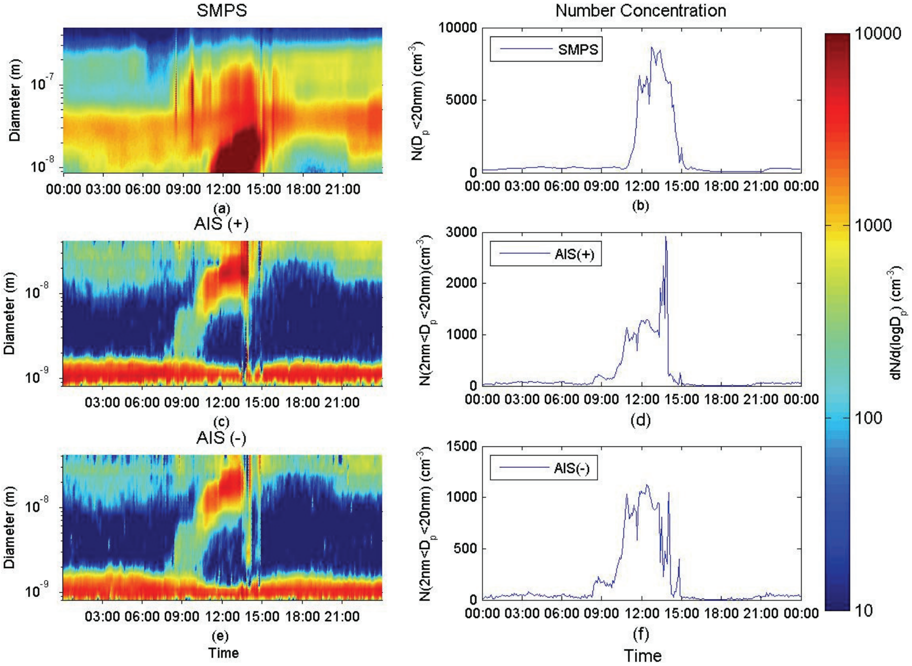

Fig. 5. New particle formation event recorded at Finokalia on 29 January 2009. Time evolution of aerosol particles size distribution in the size range 8–900 nm **(a)** and number concentration for diameters smaller than 20 nm as recorded by the SMPS **(b)**, atmospheric ions size distribution in the size range 0.8–42 nm and number concentration for diameters between 2 nm and 20 nm for positive **(c, d)** and negative **(e, f)** ions measured with the AIS.

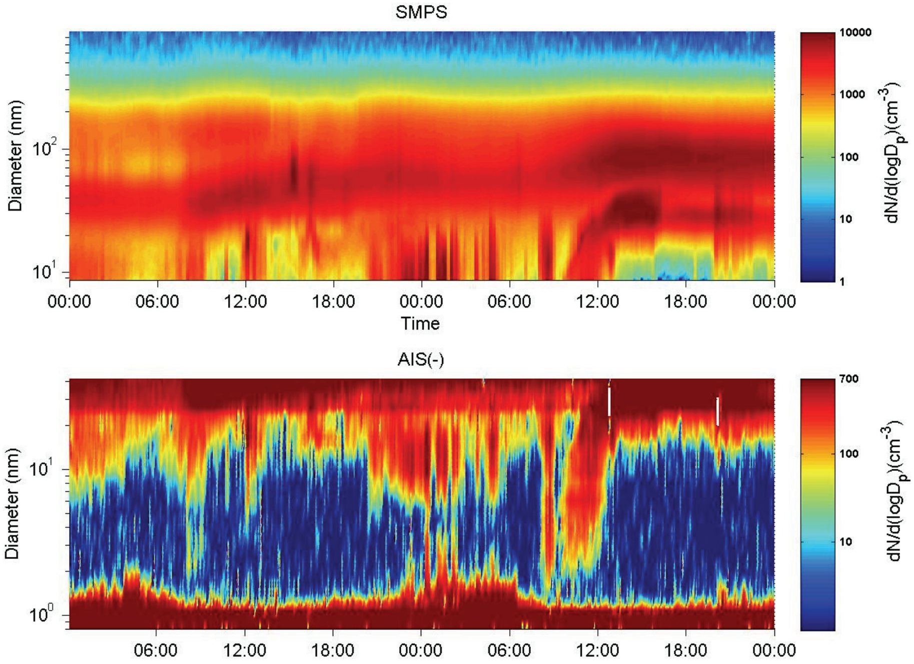

Fig. 6. Aerosol particles size distribution in the size range 8–900 nm (upper panel) and atmospheric ions size distribution in the size range 0.8–42 nm (lower panel) for the period 6–7 October 2008. New particle formation observed on 7 October as recorded by SMPS and AIS for negative polarity. The night before, new ions were formed and grew sufficiently to be recorded by the SMPS.

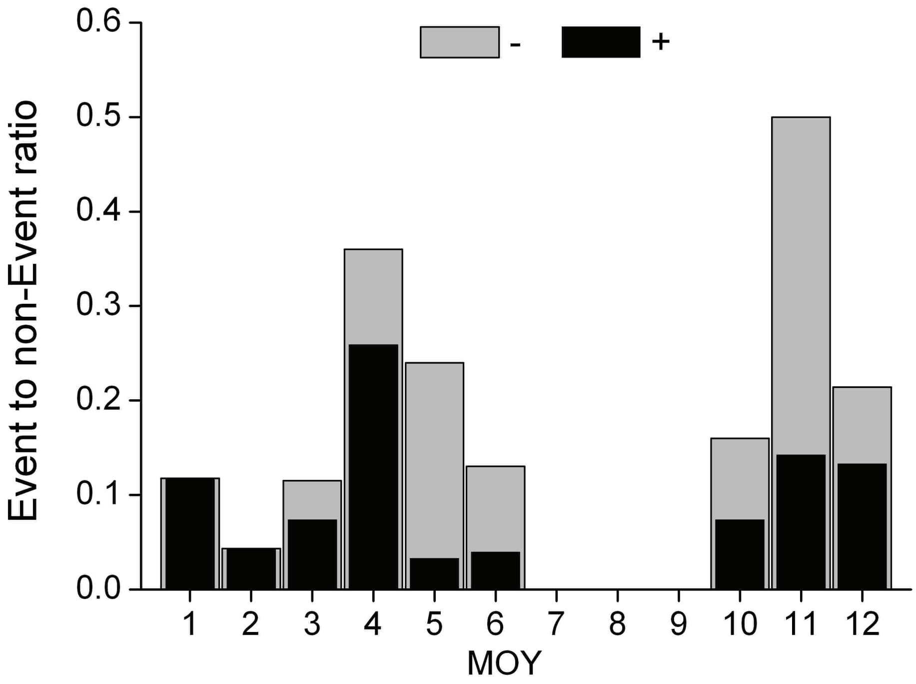

Fig. 7. Monthly event to non-event ratio for negative (grey bars) and positive (black bars) ions.

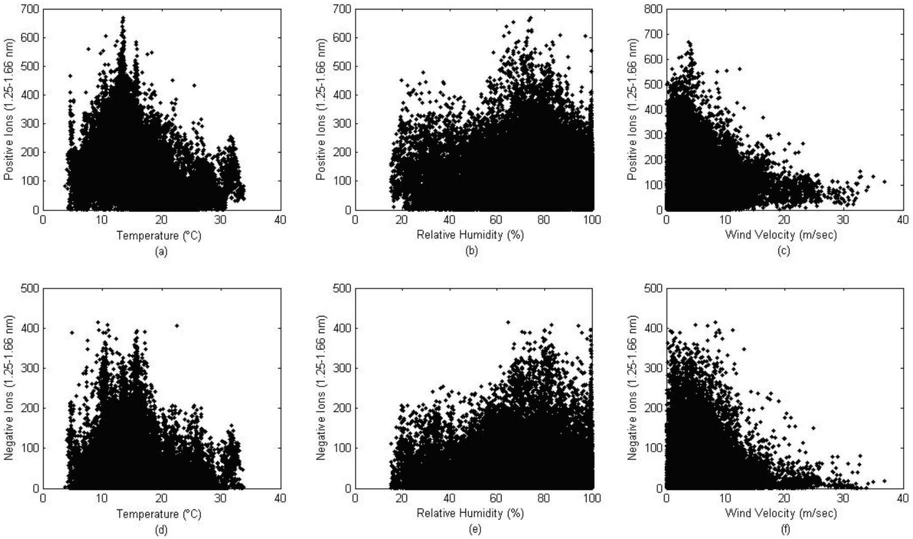

Fig. 8. Variability of atmospheric cluster concentrations in the size range 1.25–1.66 nm depending on temperature, ambient relative humidity and wind velocity for positive **(a–c)** and negative charges **(d–f)**, respectively.

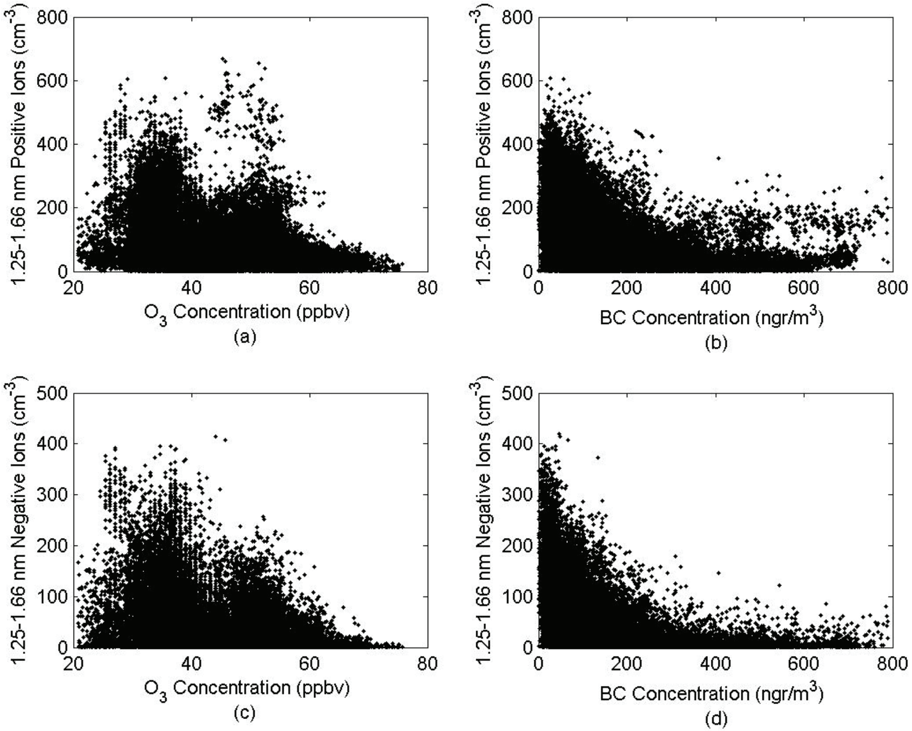

Fig. 9. Variability of atmospheric cluster concentrations at the size range 1.25–1.66 nm depending on ozone and BC concentration for positive **(a, b)** and negative charges **(c, d)**, respectively.

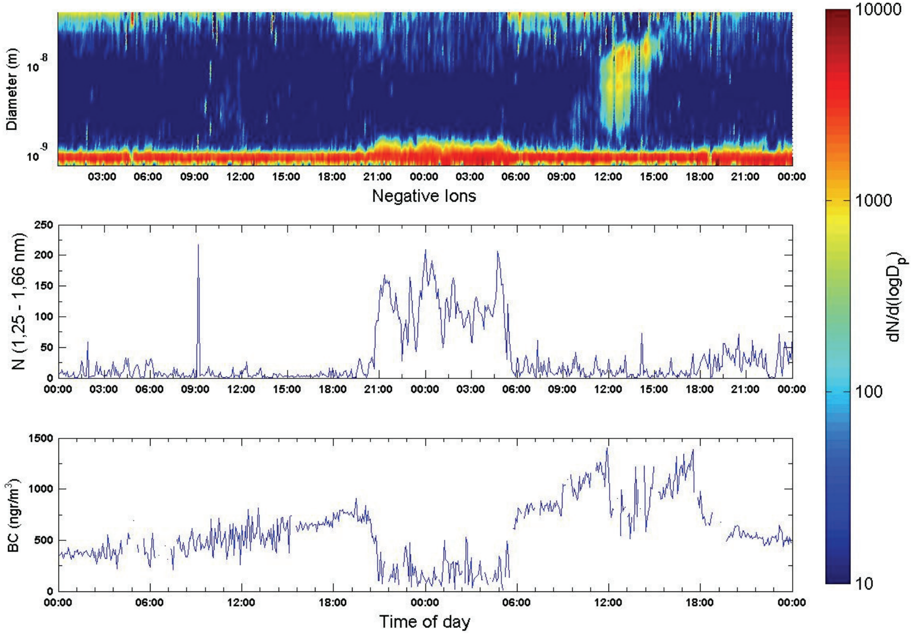

Fig. 10. Night-time enhanced ion concentration event observed on 29–30 March 2009 demonstrating a clear case of anti-correlation of small ion cluster concentrations with BC. Upper panel: negative ion number size distribution. Middle panel: negative ion number concentration in the size range 1.25–1.66 nm. Lower panel: BC mass concentration.

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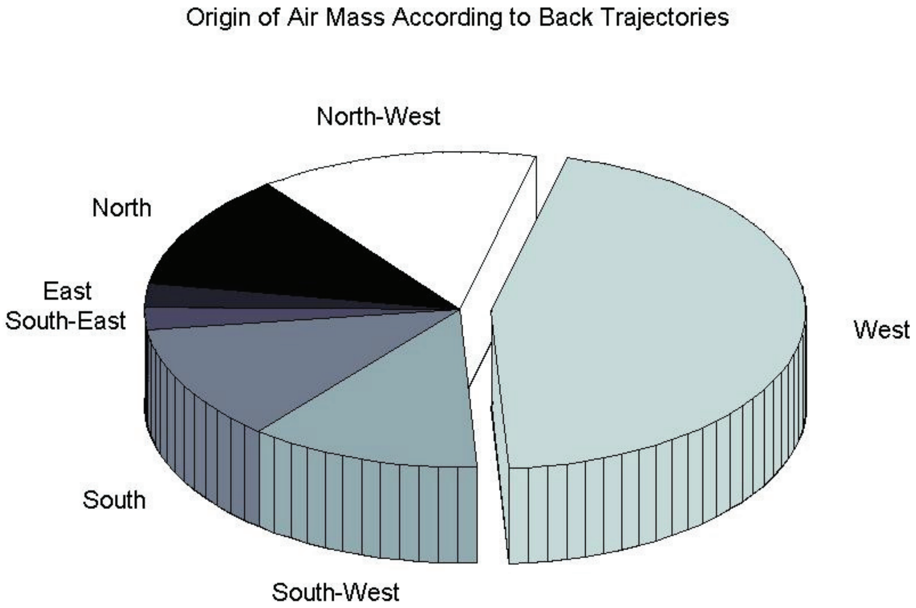

Fig. 11. Distribution of air masses origin at 1000 m (5 days back trajectory) arriving at Finokalia during night-time enhanced ion concentrations events.

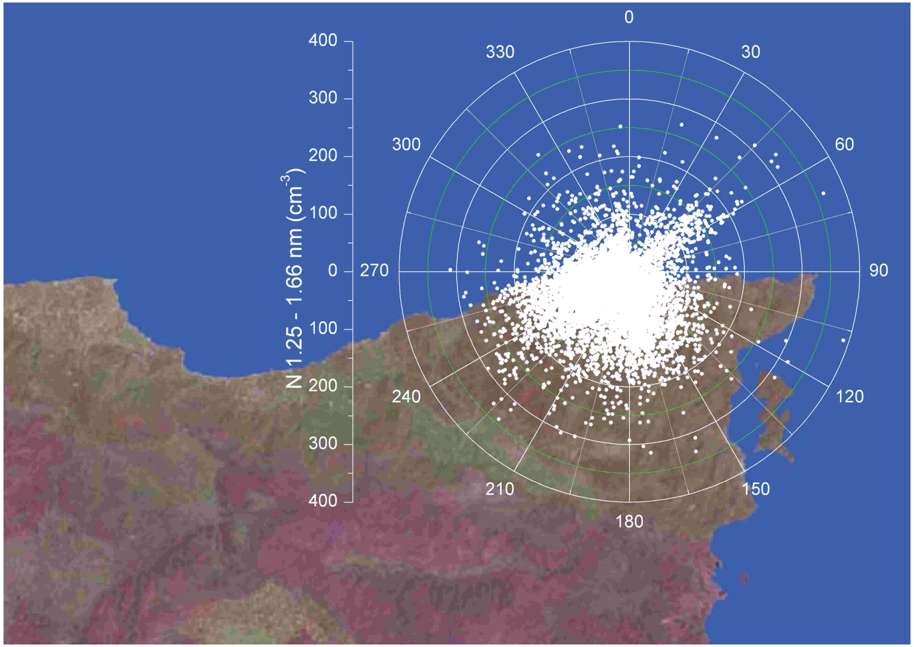

Fig. 12. Dependence of negatively charged atmospheric cluster concentrations at the size range 1.25–1.66 nm on the wind direction.