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Nanoparticles in boreal forest and coastal environment: a comparison of observations and implications of the nucleation mechanism

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Abstract

The detailed mechanism of secondary new particle formation in the atmosphere is still under debate. It is proposed that particle formation happens via activation of 1–2 nm atmospheric neutral molecular clusters and/or large molecules. Since traditional instrumentation does not reach these sizes, the hypothesis has not yet been verified. By directly measuring particle size distributions down to mobility diameters of about 1.3 nm with a pulse-height CPC we provide evidence of the nucleation mechanism in coastal environment (Mace Head, Ireland) and in boreal forest (Hyytiälä, Finland). In both places neutral sub-3 nm condensation nuclei (nano-CN) were continuously present, even when no new particle formation was detected. In Mace Head, however, the concentration of the nano-CN was far too low to account for the particle formation rates during particle bursts. Thus the results imply that on coastal sites new particle formation initiates, as proposed earlier, via homogenous nucleation from biogenic iodine vapors. In contrary, activation of pre-existing nano-CN remains a possible explanation in the boreal forest, but the observed concentrations are not the limiting factor for the particle formation events.

1 Introduction

Aerosol particles deteriorate air quality, atmospheric visibility and human health. Additionally, particles affect the climate both directly by scattering and absorbing solar radiation, and indirectly via cloud processes. Atmospheric aerosols have both natural and anthropogenic sources. Natural new particle formation by gas-to-particle conversion has been frequently observed around the world (Kulmala et al., 2004). Condensational growth in the atmosphere can make the newly formed particles large enough to act as cloud condensation nuclei (e.g., O'Dowd, 2001; Laaksonen et al., 2005). According to model simulations these particle formation events affect the particle budget significantly both on regional and global scale (Spracklen et al., 2006). Nevertheless,

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the IPCC assigns the biggest uncertainty ranges in the radiative forcing estimates to aerosols (IPCC, 2007). Hence, molecular level understanding of nucleation is needed for incorporate the secondary particle formation to the climate models.

Particles can nucleate homogeneously from one or several precursor vapors if the vapor concentrations are high enough. Generally lower supersaturations are needed, when particles form heterogeneously on a pre-existing surface (e.g., Kulmala et al., 2007b). Heterogeneous nucleation on a 1–2 nm molecular clusters, also known as activation of clusters, is proposed as an explanation to particle formation events (Kulmala et al., 2000, 2006). Charged cluster ions are long known to exist in the atmosphere (e.g., Hõrrak et al., 1998), and their recombination could produce electrically neutral particles (Turco et al., 1998). Nucleation on a charged cluster is called ion induced nucleation (Yu and Turco, 2000), and the vapor concentrations required for activation of ions are lower than for neutral particles (Winkler et al., 2008). There is no consensus of how big fraction of atmospheric new particle formation is ion-induced or ion-mediated. Some studies have underlined the crucial role of ions (Yu et al., 2008; Yu and Turco 2008), whereas the conclusions of several other experiments show that the ion concentrations are too low to explain the observed particle formation rates in the boundary layer (e.g., Laakso et al., 2004; Iida et al., 2006; Gagné et al., 2008; Kulmala et al., 2007a).

Different particle formation mechanisms might be prevailing in different environmental conditions. Here we compare measurements from two very distinct environments: the boreal forest in Hyytiälä, southern Finland, and the coast of the North Atlantic Ocean, in Mace Head, Ireland. In Hyytiälä new particle formation is observed on about 25% of days, most frequently in spring time (Dal Maso et al., 2005). However, particles grow the fastest in the summer indicating that particle formation and growth are two separate processes (Hirsikko et al., 2005). In Mace Head strong particle formation bursts are frequently observed in daytime during low tide, probably due to biogenic emission of iodine vapors (O'Dowd et al., 2002c; Yoon et al., 2006). Several laboratory experiments have demonstrated particle formation from the oxidation products of these

iodine-compounds (Hoffmann et al., 2001; Jimenez et al., 2003).

A reason for the lack of knowledge about the nucleation process has been the incapability to detect or chemically identify the initial clusters. Recent development of measurement techniques (e.g., Mirme et al., 2007; Sipilä et al., 2009) has provided us with tools to reach molecular sizes. Already Weber et al. (1995) detected molecular clusters when ultrafine particles were present. Continuous existence of a neutral cluster pool below 3 nm was first discovered in Hyytiälä by Kulmala et al. (2007a). The applicability of condensation particle counters (CPCs) to detect clusters was further studied by Sipilä et al. (2008). However, CPC measurements alone can not resolve if the activated nanometer-size condensation nuclei (nano-CN) are nucleated particles, molecular clusters or large molecules. In many former articles, they were simply called clusters.

In this article we look for similarities and differences in the characteristics of nano-CN concentrations between boreal forest and coastal environment. Since an analysis of the nano-CN in Hyytiälä has already been published by Lehtipalo et al. (2009) the focus will be on describing the first nano-CN measurements in Mace Head using a pulse-height CPC. We compare the concentrations measured with different instruments to theoretical calculations and to each other. Thus we aim at resolving the possible nucleation mechanism and estimating the importance of clusters to new particle formation on both sites.

2 Materials and methods

2.1 Site description

Hyytiälä SMEAR II-station (61°51′ N, 24°17′ E) is situated in southern Finland about 60 km north-east from the city of Tampere. The nearest village with some industrial activity is ca. 10 km away, and the nearest buildings are by a small lake 500 m away from the measurement station. The station is surrounded by coniferous Scots pine

dominated forest. All the measurements discussed in this article were done inside the forest canopy. The station is equipped with extensive meteorological and aerosol instrumentation. For a more detailed site description see Hari and Kulmala (2005).

The Mace Head atmospheric research station (54°19′ N, 9°54′ W) is a GAW super-site situated on the west coast of Ireland facing North Atlantic ocean. The station is located 100 m from the coastline surrounded by bare land (rocks, grass and peat bog) with no forest or trees in the surroundings. Few scattered single houses are located at the distance of 1 km or greater. The nearest city (Galway, 80 000 inhabitants) is located 60 km to the east/south-east of the station. The site is well exposed to clean marine westerly air masses associated with low pressure systems accounting for nearly 50% of occurrences. Pollution outbreaks are related to high pressure synoptic scale conditions bringing polluted air from UK and continental Europe.

2.2 Instruments and measurements

Particle size distribution from ∼1.3 nm to 5 nm in mobility diameter was measured in Hyytiälä 1–31 May 2008 and in Mace Head 13 June–25 August 2008 by applying pulse-height analysis method (e.g., Saros et al., 1996) to a condensation particle counter (CPC). Pulse height analysis method has formerly been used in size distribution measurements between 3 and 10 nm (Weber et al., 1995), as well as to determine the composition of freshly nucleated nanoparticles (O'Dowd et al., 2002a).

The pulse-height CPC (PH-CPC) consists of a TSI 3025 CPC with modified optics (Dick et al., 2000) and a multi-channel analyzer. The temperature difference between the CPC condenser and saturator was increased until homogenous nucleation of condensing liquid, i.e. butanol occurred. The pulse-height analysis method allows distinction between activation of nano-CN and homogenous nucleation (Sipilä et al., 2008). Every other measurement was made through a diffusion tube, which enabled subtraction of the pulses from homogenous nucleation. Ions were filtered away by applying a voltage to an ion trap. The PH-CPC is capable of detecting particles down to ∼1.3 nm in mobility diameter with a detection efficiency of a few percents (Sipilä et al., 2008), but

the exact size scale and detection efficiency depends on particle composition, charge and background aerosol concentration (O'Dowd, 2004; Sipilä et al., 2009). The data inversion to resolve particle size distribution between 1.3 and 5 nm is based on experimental calibrations with positive silver and Am241-charger generated ions. Detailed description of performance of the instrument and data inversion is presented in Sipilä et al. (2009).

Ambient ion size distribution was measured in Hyytiälä with a Balanced Scanning Mobility Analyzer (BSMA; Tammet et al., 2006), and in Mace Head with a Neutral Cluster and Air Ion Spectrometer (NAIS; Mirme et al., 2007; Manninen et al., 2009b). The mobility range of the BSMA is 0.032–3.2 $cm^2\,V^{-1}\,s^{-1}$ (corresponding to ~0.8–7.5 nm in mobility diameter), and the NAIS 0.0013–3.2 $cm^2\,V^{-1}\,s^{-1}$ (~0.8–40 nm). The NAIS has two operation modes: one for naturally charged ions, and one for neutral particles, which are charged by corona charger before mobility classification. The charging sets the lower detection limit for neutral particles to about 2 nm depending on polarity and concentration (Asmi et al., 2009). Aerosol size distribution between 3 and 500 nm was measured using a twin-DMPS (Aalto et al., 2001) in Hyytiälä and a Scanning Mobility Particle Sizer (SMPS) in Mace Head.

2.3 Data analysis

For air mass analysis 24 h back-trajectories were calculated with a HYSPLIT model (Draxler and Rolph, 2003) to Mace Head at 500 m altitude. Based on these trajectories, the data set from Mace Head was divided into air masses coming directly from the ocean (south to north-west sector) representing clean marine air, and air masses that had been over land area over the past 24 h.

The recombination products, a maximum estimate for the steady-state concentration of neutral particles produced by recombination of ion clusters, was calculated from

$$N_{\mathrm{n,rec}} = \frac{\gamma \alpha N_{\mathrm{i}}^{+} N_{\mathrm{i}}^{-}}{\mathrm{CoagS}(N_{\mathrm{n,rec}})} \quad (1)$$

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where the subscript n refers to neutral clusters and i to ion clusters. γ is the fraction of stable recombination products and α the ion-ion recombination coefficient. For α we used a value of 1.6×10^{-6} cm^3 s^{-1} (Tammet and Kulmala, 2005), and to obtain a maximum estimate, γ was set to unity. The ion cluster concentrations were taken from ion spectrometer data so that only collisions between ions large enough to produce particles about 1.5–3 nm in diameter were accounted for. The coagulation sink (CoagS) was calculated for 2 nm particles from DMPS/SMPS data as in e.g. Dal Maso et al. (2002).

3 Results

3.1 Concentrations

Measurements with a pulse-height CPC was performed at Hyytiälä in May 2008 and at Mace Head in summer 2008 as a part of the EUCAARI campaign (Kulmala et al., 2009). Hereafter we refer as nano-CN concentration to the sum of neutral particles smaller than 3 nm in mobility diameter measured with the PH-CPC. At Hyytiälä, the concentration of nano-CN exceeded 10^3 cm^{-3} almost constantly, sometimes reaching values of 10^5 cm^{-3} (Fig. 1a). The highest concentrations were often measured shortly after sunset. A nighttime maximum was observed on 19 of 30 d in May, and the cluster ion concentration and mean size grew simultaneously. No growth to larger sizes was, however, observed in the nighttime. The average diurnal behavior of the nano-CN concentration was remarkably similar regardless of whether or not the new particle formation events were observed (Lehtipalo et al., 2009).

At Mace Head the nano-CN concentrations varied mostly between 10^2 and 10^4 cm^{-3} (Fig. 1b). During the day the overall concentration was lower by a factor of two and during the night almost one order of magnitude lower at Mace Head than in Hyytiälä. Small clusters and particles are effectively lost by coagulational scavenging (Kerminen et al., 2001). The reason for higher nano-CN concentrations in Hyytiälä compared

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to Mace Head cannot, however, be explained solely by differences in the coagulation sink, as demonstrated by Fig. 2. It should be noted that we tend to underestimate the coagulation sink, especially in Mace Head, as the super-micron particles were not measured and thus lack from the calculated value. Nevertheless, the coagulation sink is generally lower in coastal conditions than in the forest (e.g., Dal Maso et al., 2002), and definitely not high enough to explain an order of magnitude difference in concentrations. This leads to the conclusion that the production rate of nano-CN needs to be higher in Hyytiälä.

Figure 3 presents a 4-day time series (13–16 June) of total particle concentration between 1.5–3 nm and 3–5 nm. The measurements with the PH-CPC and the NAIS correspond well in both size classes. The 3–5 nm particles are mostly associated with particle formation bursts, and were thus observed in high quantities at daytime low tides. The 1.5–3 nm particles, however, had not a clear relation to the tidal cycle. Another type of divider was found: When the air mass trajectories originated directly from the ocean, i.e. from the clean sector without much of anthropogenic influence, the nano-CN concentration was very low during the night, but peaked around noon (Fig. 4). These daytime maxima were not observed by the NAIS, indicating that the CN are very small and thus disguised by the charger ions in the NAIS. When the air mass advecting to the site had passed over land, no clear diurnal cycle could be distinguished. Especially the nighttime values were much higher than in the marine air masses. On a few days a nighttime maxima were observed, but not as strong or as frequently as in Hyytiälä. The ion cluster concentrations in the same size range were pretty stable throughout the day, but, as also pointed out by Vana et al. (2008), their concentration is much higher in air masses from the land sector, probably due to radon, which is one of the main sources of small ions (the other being cosmic radiation, which should be independent of the air mass origin).

The charged fraction in the size class 1.3–3 nm calculated from the ion spectrometer and PH-CPC measurements was on average about 1% in Hyytiälä, and 18% in Mace Head. The maximum estimate of the ion-ion recombination products falling into

the same size range accounted on average for only a few percents of neutral nano-CN in Hyytiälä, but more than a half of the measured concentration in Mace Head. The diurnal variation of both the ion ratio and the recombination ratio (Fig. 5) showed a minimum in the evening for Hyytiälä and around midday in Mace Head. The ratios were a bit higher in Mace Head during clean, marine air masses. All in all, the contribution of ions varied a lot from day to day in both places, but it seems that the ions have a much bigger contribution to the nano-particle concentration in Mace Head than in Hyytiälä.

Table 1 summarizes the characteristics of the measured concentrations in Hyytiälä and Mace Head during the EUCAARI campaign.

3.2 Particle formation

At Mace Head new particle formation usually occurs as strong bursts of nucleation mode particles during low tide (e.g., O'Dowd, 2002b; Vana et al., 2008). Figure 6 presents an example of PH-CPC data with two distinct particle formation bursts occurring at 12:30 and 15:30 LT, while tidal minima were around 03:30 and 16:00 LT. On the first particle burst most particles have grown to sizes over 3.5 nm before reaching our measurement location, and to sizes over 2 nm on the second burst. No increase can be seen in the smallest size range prior or during the particle burst. However, a rapid change in total number concentration challenges our measurement technique as the supersaturation decreases in the PH-CPC due to vapor depletion and thus limits the reliability of measurements during intensive particle formation.

The formation rate of 1 nm particles during particle formation events in Mace Head has been estimated to be as high as 300–10 000 $cm^{-3}\,s^{-1}$, corresponding to cluster concentrations of 4×10^{4}–$7\times10^{6}\,cm^{-3}$ (Dal Maso et al., 2002). Clearly, the measured concentrations, both neutral and charged, are too low for explaining these kind of particle bursts. In Hyytiälä, the observed formation rate of 2–3 nm particles varies between 0.22–3.9 $cm^{-3}\,s^{-1}$ (Manninen et al., 2009a), and the estimated neutral cluster concentration between 7000–50 000 cm^{-3} (Kulmala et al., 2007a), which is close to the measured nano-CN values.

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4 Discussion and conclusions

Both in Hyytiälä and Mace Head neutral nanometer-size CN were observed continuously with a pulse-height CPC, even when no particle formation was detected with traditional instrumentation, like the DMPS/SMPS with a cut-off size at 3 nm. These clusters or molecules seemed to be more abundant in Hyytiälä, especially at nighttime. The differences in diurnal variation and in charged fraction indicate that they have different sources and therefore different chemical composition in Hyytiälä than in Mace Head.

The composition of nanoparticles is hard to measure directly, and is therefore not known. Proposed candidates for forming clusters include oxidation products of volatile organic compounds (e.g., Bonn and Moortgat, 2003). For example monoterpenes and their oxidation products exhibit a similar diurnal variation in Hyytiälä than the measured nano-CN (Rinne et al., 2005; Sellegri et al., 2005). The fact, that the nano-CN concentration follows solar radiation in Mace Head when air masses come form the ocean, implies that their formation includes some photochemical reactions. When the air masses have passed over land area, VOCs emitted from the vegetation or anthropogenic emissions might explain the higher and more varying concentrations. At least the nano-CN seem not to consist of the same biogenic iodine compounds that make the nucleation mode particles, as they do not exhibit similar tidal cycle than the particle formation events. The exact chemical composition of the nano-CN remains to be solved in future studies.

A much bigger fraction of clusters can be explained solely by the ions in Mace Head than in Hyytiälä. The minimum in ion fraction at nighttime in Hyytiälä gives a reason to assume that we have a source of neutral nano-CN near ground. One should, however be careful when comparing the measurements with a CPC and an ion spectrometer, since the size is determined with different methods, which might lead to discrepancies in the smallest sizes.

It can be concluded that in Hyytiälä we have a constant resource of seed-embryos

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for new particle formation. The measured nano-CN concentrations are easily large enough to explain particle formation events via activation of the clusters. The nano-CN concentration does not, however, seem to be the critical factor determining whether a nucleation event occurs. The main process limiting particle formation is probably the competition between growth of particles and their loss by scavenging, rather than the production of initial clusters (Riipinen et al., 2007). Maybe sulphuric acid, which is often connected to first steps of new particle formation (e.g., Weber et al., 1996; Sihto et al., 2006; Petäjä et al., 2009; Nieminen et al., 2009) or some other vapor is needed for activation and/or growth of particles. The start of the particle formation is also related to meteorological conditions and boundary layer dynamics (Nilsson et al., 2001a,b; Sogacheva et al., 2008). In Mace Head the concentrations of the nano-CN and the cluster ions, even together, are too small to account for the observed formation rate of the nucleation mode particles. Thus it seems that the particles are formed by homogenous nucleation of the same vapor(s), which make them grow to sizes of a few nanometers before reaching our measurement location.

The apparently different nucleation mechanisms behind the new particle formation at Mace Head and Hyytiälä suggest that also in other environments, where the nucleation rate is high (over some tens in $cm^{-3}\,s^{-1}$) new particle formation happens via homogeneous nucleation, and the activation type nucleation is probably dominating in places where the formation rate is of the order of unity.

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Table 1. Characteristics of nano-CN concentrations in Hyytiälä and Mace Head (MH). Recombination ratio is the maximum estimate of recombination products divided with neutral nano-CN. Ion ratio is the fraction of ions from all particles between 1.3–3 nm.

	Hyytiälä	MH (all data)	MH (clean sector)
Nano-CN			
– daytime (cm^{-3})	1000–40 000	500–20 000	500–10 000
– nighttime (cm^{-3})	1000–100 000	100–10 000	100–1000
Recombination ratio	3%	54%	62%
Ion ratio	1%	18%	19%

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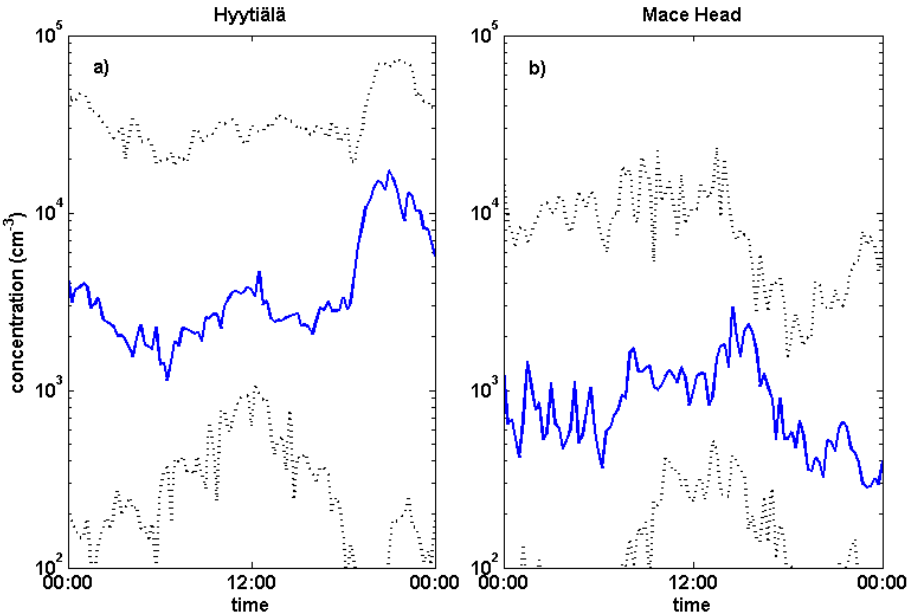

Fig. 1. Diurnal variation of nano-CN (1.3–3 nm) concentration in Hyytiälä and Mace Head. The line is at median of 15 min mean concentrations during the whole measurement period, and the dashed lines indicate 5%- and 95%-percentiles.

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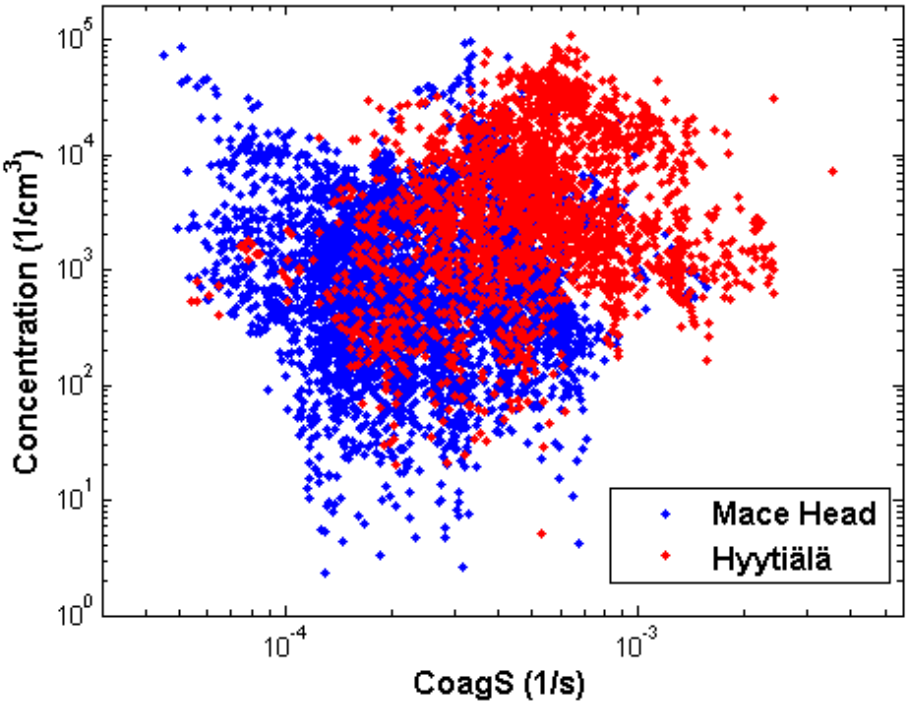

Fig. 2. Measured nano-CN concentration as a function of coagulation sink (CoagS) calculated for 2 nm particle from DMPS/SMPS data.

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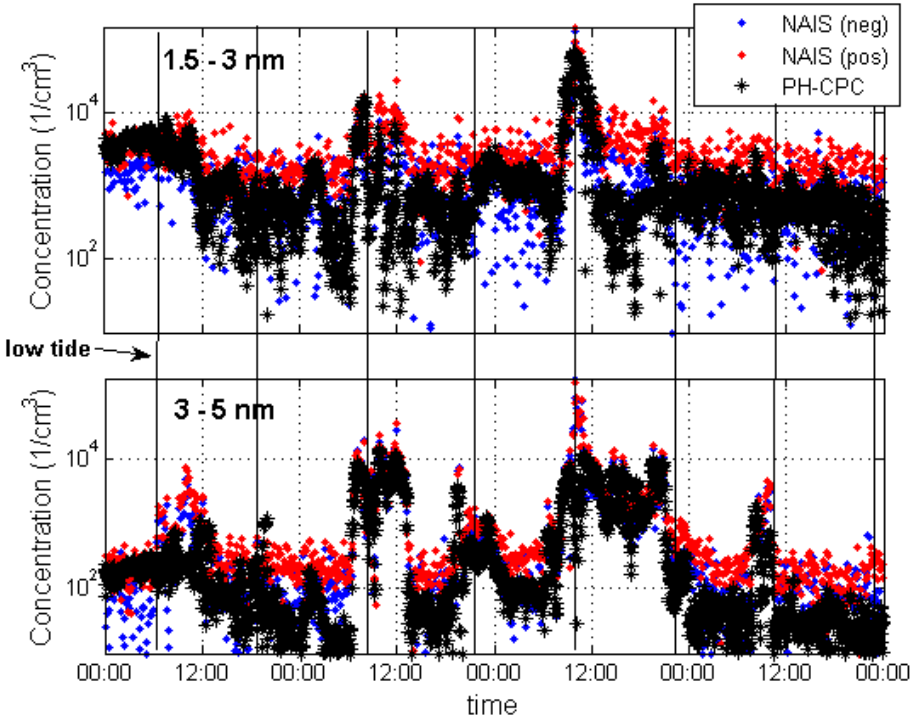

Fig. 3. Total concentration of 1.5–3 nm, and 3–5 nm particles in Mace Head 13–16 June 2008 measured with the PH-CPC (stars) and the NAIS (dots, positive and negative charging polarity of the instrument). Vertical lines indicate the times of low tide.

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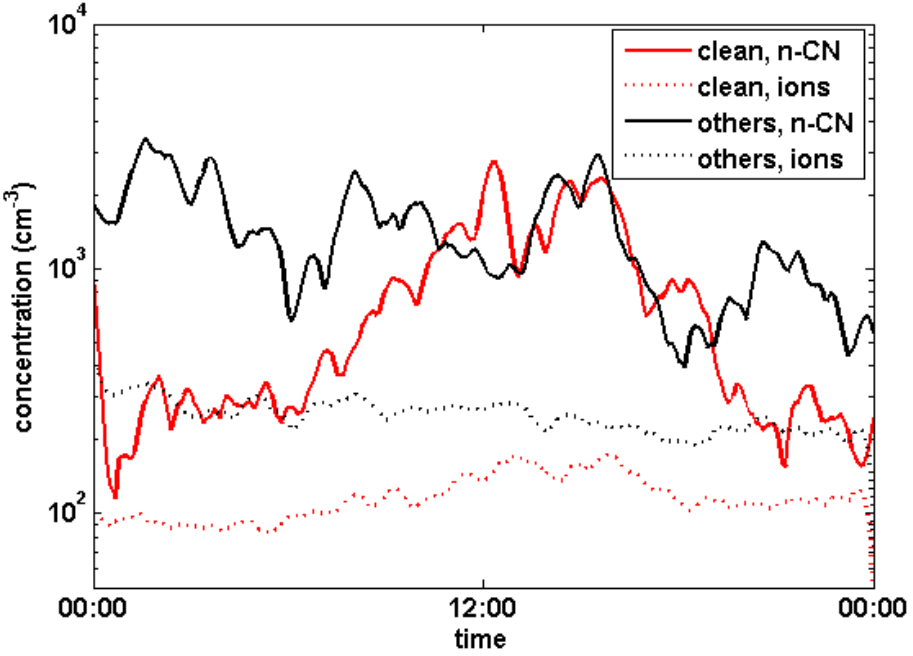

Fig. 4. Diurnal variation of nano-CN and 1.5–3 nm ions (pos+neg) in Mace Head. The data is divided into two fractions depending of whether the air mass trajectories came directly from the ocean (clean, red lines), or if they had passed over land areas (others, black lines).

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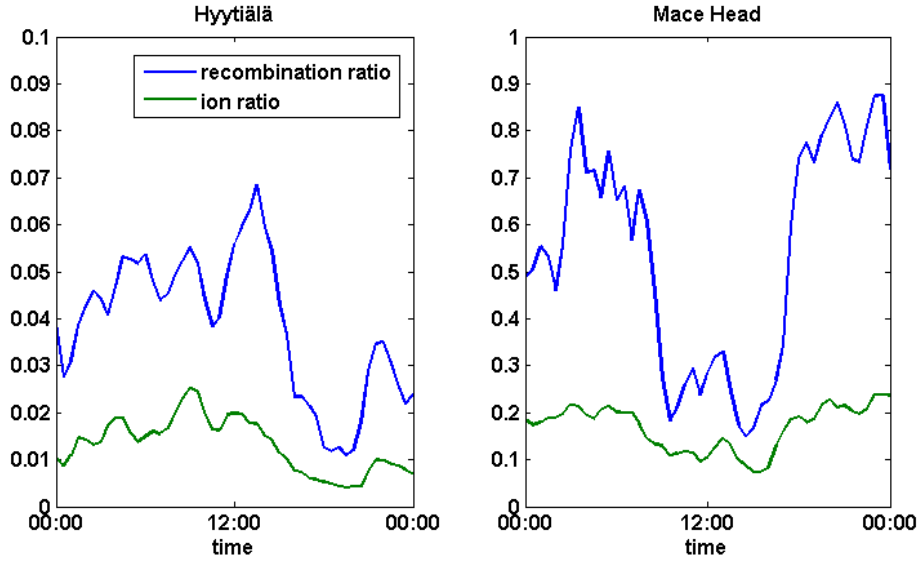

Fig. 5. Median fraction of ions from all measured particles in the size range 1.3–3 nm (ion ratio) and the fraction of recombination products from neutral nano-CN (recombination ratio).

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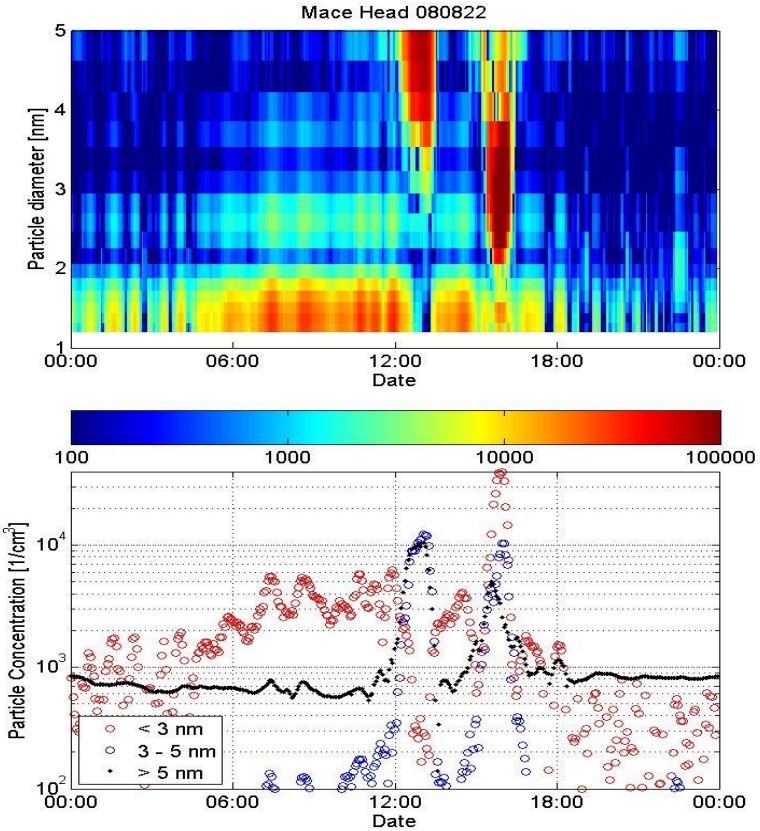

Fig. 6. Size distribution (upper panel) and total concentration (lower panel) measured with PH-CPC in Mace Head 22 August 2008. Low tide occurred at 03:30 and 16:00 LT. Sharp drop in cluster concentration during first particle burst is probably an instrumental artifact.

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