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Interactive Comment

Interactive comment on "Influence of spectral solar irradiance on the formation of new particles in the continental boundary layer" *by* M. Boy and M. Kulmala

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The paper makes a good attempt to relate the intensity and frequency of new particle formation to particular wavelength ranges of the ambient solar irradiance based on approximately collocated long-term measurements at a boreal forest site. The measurements were carried out using state-of-the-art instrumentation at an appropriate location for this study. Particle nucleation has been extensively studied at the SMEAR II station and this phenomenon is well established and widely reported. Despite the previous studies, the mechanisms and conditions for nucleation are still poorly understood at this location, in common with almost all locations where atmospheric nucleation has been observed. The attempt made by this paper to clarify the relationship between particle formation and ambient irradiance is therefore timely, important and welcome. It builds upon and extends previous work by the authors in aiming to identify the specific wavebands best correlated with particle formation. The analytical methods employed are appropriate and utilise the measured data well. The identification of the short wavelength region as the most important to particle formation is therefore convincing.

The abstract of the paper, however, promises a little more than is delivered. I was eagerly anticipating presentation of the photochemical mechanism probably responsible for the formation of new particles. Whilst it is undoubtedly true that the photolysis of ozone to form singlet-D oxygen atoms is dependent on shorter wavelength radiation, it is only the first stage in a mechanism which is one of a wide variety of short-wavelength initiated photochemical mechanisms potentially responsible for condensable material formation. As stated in the paper, PRIMARY hydroxyl radical production is entirely dependent on singlet-D oxygen formation, but the OH concentration will be additionally controlled by secondary production and losses (this must be mentioned, probably in the summary section where the original statement is made). The singlet-D oxygen production rate alone is unlikely to be a causal indicator of new particle formation. Even the calculations of precursor availability in Coe et al. (2000) saw it necessary to clearly state the assumptions of constant OH losses and no secondary OH production when the hypothesised precursor species and mechanism were explicit. O'Dowd et al. (1999) used measured OH concentration for a similar calculation of precursor production rate. When neither of these studies identified a clear relationship in superficially much simpler environments it is unlikely that a simple calculation of singlet-D production rate will throw any light on a mechanism in the current study. In summary, the difficulty in such an approach lies in the identification of a precursor mechanism and prediction of species concentration in the absence of the postulated species. It is accepted that the precursor is unlikely to be that initially-hypothesised in the two cited papers (H2SO4), but a calculation of singlet-D production rate with no hypothesised condensable material or mechanism is not useful and may be misleading. For example, if oxidation is initiated by ozonolysis and the intermediate further reacts pho-

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tochemically to yield a condensable material, singlet-D oxygen may be uninvolved in particle production but may track the precursor concentration. Indeed, it is identified in section 3.4 that more than one mechanism may be involved, attributing an event with a long production lag time to possible production of condensable material by direct ozonolysis of monoterpenes. No strong case is made for the other events being initiated by, or otherwise directly attributable to, singlet-D oxygen atom production as opposed to any other photochemical reaction requiring uv irradiation. Even if particle formation is initiated by hydroxyl radical attack, the other factors determining its concentration should be mentioned. This will also help explain the non-event days with high singlet-D oxygen production rates - possibly being far more significant than the condensational sink or temperature effects mentioned in section 4. A further potential complication is presented by the daily onset of significant heat flux. This will be related to solar zenith angle and, if turbulent mixing is involved in the particle formation, may appear as a relationship between particle number and solar irradiation. This will not necessarily be at the longer wavelengths since a threshold heat flux may be required, and the threshold will be reached at lower zenith angles than the onset of longer wavelength light.

I therefore feel that the discussion of singlet-D production rate and the mention of a new likely production mechanism in the abstact are misleading and should be amended. It should be presented as an example of how short wavelength irradiation COULD be involved in particle formation. Anything stronger appears not to be well-founded.

In addition to this one major criticism, there are a few minor errors. The heading for section 3.3 is incomplete and there are a number of incorrectly-bracketted references.

As mentioned at the beginning, the measurements and subsequent analysis do convincingly identify irradiance in the waveband 300 to 330 nm as being a driver for new particle formation. This established relationship is sufficient to merit publication of the work.

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