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Variations of trace gases, meteorological parameters, and their connection with aerosol formation in boreal forests

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[1] The data of observations at Hyytiälä background station in 1997 – 2003 are analyzed for investigating the possible links between physical, chemical, and meteorological parameters for event and nonevent days for different seasons. The seasonal patterns of average trace gases concentrations (O_3, H_2O, NO_x= NO + NO_2, SO_2), UV-A irradiation, temperature, relative humidity, condensational sinks are established and used for evaluating their influence on the seasonal dependence of formation and growth rates of particles in the nucleation mode. The condensational sinks are shown to play a crucial role in the chemical dynamics of the gaseous precursors and the aerosol particles. The variations of the sinks are mainly attributed to the humidification of the preexisting aerosol and thus strongly depend on the relative humidity. *INDEX TERMS:* 0300 Atmospheric Composition and Structure; 0305 Atmospheric Composition and Structure: Aerosols and particles; 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; *KEYWORDS:* trace gases, nucleation, seasonal variation, atmospheric nanoaerosols.

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Introduction

[2] Recent observations have provided impressive evidences that the particle formation processes and their further growth can be detected in different geographic locations and in absolutely diverse conditions. Long term data set on particle formation at a continental forest site (Hyytiälä, Southern Finland) display a strong seasonal variation on the number of occurrences of these events with a maximum during spring time and a minimum in midsummer. Annual variations of the particle growth rate during nucleation events in forest and rural locations also show a strong seasonal trend [*Kulmala et al.,* 2004] with maximal and minimal particle growth rate 4 –17 nm/h (summer time) and 0.5 – 2 nm/h (winter time) respectively.

[3] The particle formation in the atmosphere is a dynamic process. The combination of chemical, physical, and meteorological processes define the production rate of non-volatile substances that can then either nucleate or condense onto the surfaces of foreign particles. Because the chemical composition of newly born particles with the sizes 3 – 10 nm is still unknown, an information on the mechanisms, the sources, and the actual conditions of the particle formation can be only derived from the studies on correlations of various factors and the attempts of their subsequent classification.

[4] The major goal of this presentation is to analyze the diurnal variations in different seasons and the long-term behavior of the trace gases concentrations (SO_2, NO, NO_x), ozone level, relative and absolute humidity, and the meteorological parameters for examining the influence of these seasonal dependence on the aerosol concentration, the formation and growth rates of the particles in the nucleation mode.

[5] Our analysis uses the data set on the parameters obtained during the period 1996 – 2003 at the Hyytiälä station. The station is located in the extended area of Scots pines dominant forests with the conditions typical for a background location. The hour average values of the studied concentrations were calculated for different seasons of each year and for the whole period of measurements. The average concentrations of trace gases, SO_2, NO_x, water vapor, ozone, and short wavelength irradiance UV-A (320–400 nm) as well as all necessary meteorological parameters were determined as averages over different periods for all days of observations and separately, for event and nonevent days.

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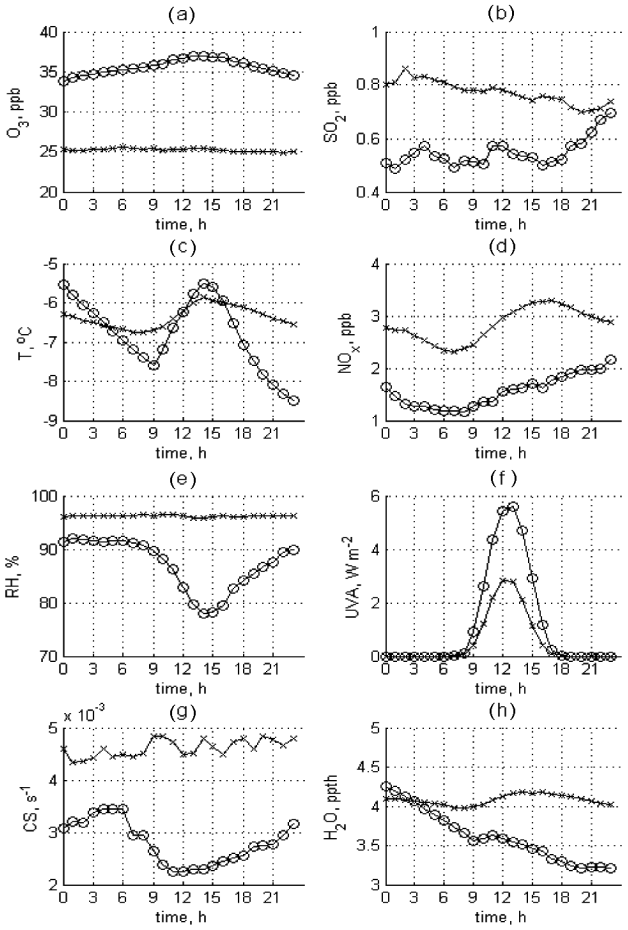

Figure 1. Winter. Mean diurnal profiles of atmospheric parameters for whole period of 1997 – 2003 for event (empty circles) and nonevent days (crosses): a – concentration of O_3, b – concentration of SO_2, c – temperature, d – concentration of NO_x=NO+NO_2, e – relative humidity RH, f – short-wave irradiation UV-A (320 – 400nm), g – condensational sink CS, h – concentration of water vapor H_2O.

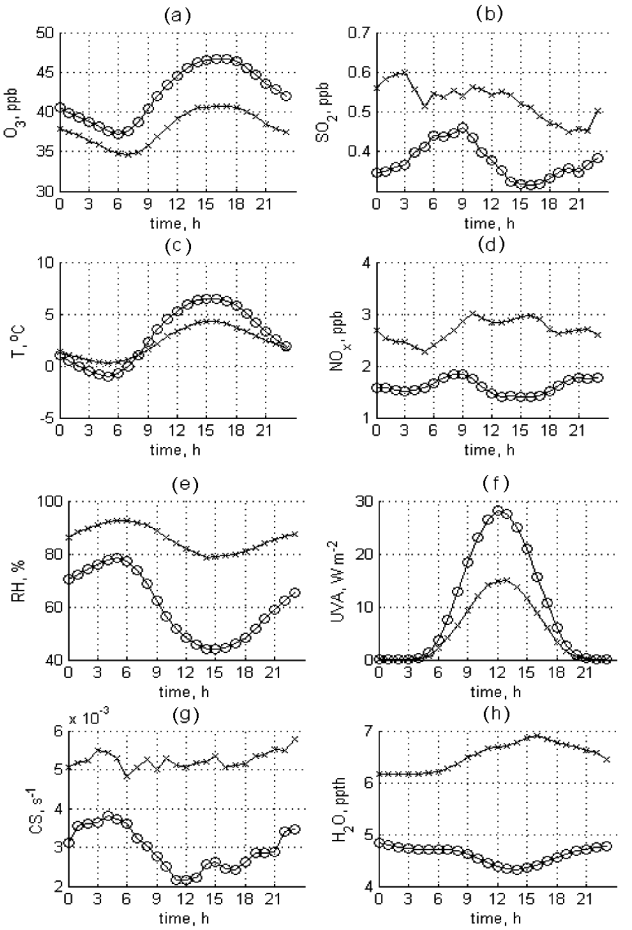

Figure 2. Spring. Mean diurnal profiles of atmospheric parameters for whole period of 1997 – 2003 for event (empty circles) and nonevent days (crosses): a – concentration of O_3, b – concentration of SO_2, c – temperature, d – concentration of NOx=NO+NO2, e – relative humidity RH, f – short-wave irradiation UV-A (320 – 400 nm), g – condensational sink CS, h – concentration of water vapor H_2O.

Results and Discussion

[6] The results of our analysis are presented in Figures 1, 2, and 3 for three seasons (winter, spring, and summer). Shown are the mean diurnal profiles of hour average concentrations of O_3, SO_2, NO_x=NO+NO_2, temperature, relative humidity RH, short-wave irradiation UV-A, condensational sink CS, and concentration of water vapor H_2O for event and nonevent days in Hyytiälä.

Winter

- [7] In winter period the maximal levels of the trace gases concentrations were [SO_2]=0.6 – 0.9ppb, [NO_x]= 1.5 – 3.5 ppb, RH=80 – 100%, [O_3]=25 – 35 ppb, at negative temperatures, minimal absolute humidity, and minimal levels of UV-A.

- [8] A small amount of winter nucleation events is likely related to a deficiency of UV-A and O_3 necessary for the formation of hydroxyl radicals, although the concentration of SO_2 is normally very high.

- [9] The particle formation processes are observed in increasing [O_3] by 30%, decreasing [NO_x], increasing UV-A, and at very small values of the condensation sinks (0.0004 1/s, see [*Mäkela et al.,* 2000]).

- [10] The diurnal dynamics of [SO_2] regularly appears in the event days, with a minimum in [SO_2] at 15 h, which well correlates with the maximums in UV-A, and T and a minimum in RH (80%).

- [11] The particle formation process is often accompanied with the ozone consumption.

Spring

- [12] The maximal frequency of event days is observed in spring time, with the growth rate being 2 – 5 nm/h.
- [13] Maximal concentrations of O_3 ([O_3]=35 –47 ppb) are typical for spring time as well as substantial enhancement in T, UV-A.
- [14] The emission of volatile organic carbon grows due to the spring plant recovery and the beginning of the photosynthetic process. The relation between [SO_2] and VOC changes due to increasing in the bioactivity of trees.
- [15] The formation of nucleation mode is accompanied with a decrease in [SO_2] and [NO_x]. The maximal consumption of these gases are noticed at 14 – 16 h when a minimum in RH(43%) and a maximum in [O_3] (47 ppb) are observed.
- [16] The average concentration levels of trace gases are much lower for event days, whereas the levels of O_3, temperature, UV-A, are considerably higher than for nonevent days.
- [17] A sharp difference is noticed between the daily variations to RH for the event days and those in nonevent days (respective minimal RH are 40% and 80 – 90%) For nonevent days high relative humidity stimulates hygroscopic growth of pre-existing aerosol particles which leads to their surface growth and thus the condensation sink which prevent the formation of the nucleation mode. For event days RH decreases during the day from 75% down to 40%, with the condensation sinks decreasing by the order-of-magnitude, from $(4-5)\times10^{-3}s^{-1}$ to $(4-5)\times10^{-4}s^{-1}$, whereas in nonevent days the condensation sink varies within (2 –3)$\times10^{-3}s^{-1}$ – (2–3)$\times10^{-2}s^{-1}$ [*Kulmala et al.,* 2004].

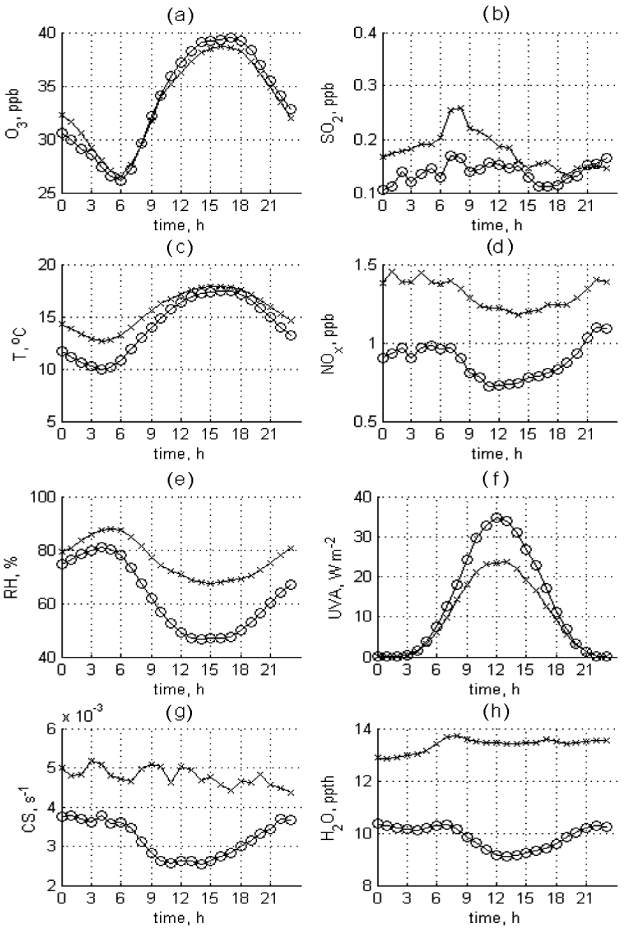

Figure 3. Summer. Mean diurnal profiles of atmospheric parameters for whole period of 1997 – 2003 for event (empty circles) and nonevent days (crosses): a – concentration of O3, b – concentration of SO_2, c – temperature, d – concentration of NO_x=NO+NO_2, e – relative humidity RH, f – short-wave irradiation UV-A (320 – 400 nm), g – condensational sink CS, h – concentration of water vapor H_2O.

Summer

- [18] The number of event days is minimum, maximal particle growth rate reaches 5 – 10 nm/h.
- [19] Very low concentrations of SO_2 (0.2 – 0.1 ppb) NO_x (0.7 – 0.3 ppb) are fixed in summer time, whereas the values of UV-A, T, and RH reach their maxima.
- [20] High temperatures and UV-A substantially enhance the emission VOC, especially isoprene whose maximal emission is observed in June and July. Because maximal emission of VOC coincides with minimal level of SO_2 other correlation links are expected to occur between different parameters.
- [21] Nucleation events occur on dry days which agrees well to the data obtained by *Buzorius et al.,* [2003], where a negative correlation (-0.9) was found between the absolute water content and the particle formation probability in Hyytiälä [*Suni et al.,* 2003]. Likely this anticorrelation is a consequence of a sharp decrease of the particle formation rate due to the ozonolysis exocyclic monoterpenes in increasing the absolute water content [*Bonn et al.,* 2002].
- [22] Increasing the emission of VOC likely explains the maximal values of the particle growth rate up to 8 – 17 nm/h [*Mäkela et al.,* 2000], maximal observed particle diameter (up to 60 nm), the latter being a growing function of T.
- [23] The highest concentrations of VOC and their further conversion to the non-volatile oxidized organic precursors as well as growth of T and UV-A give rise to the particles become able to reach the Aitken or even accumulation size, but the concentration of nucleation particles decreases with strong increase in VOC emission, as supported by model experiments [*Pirjola,* 1999].

Conclusion

[24] Practically all sources and sinks have a seasonal pattern. Seasonal variations of VOC connected with the biological activity of trees and VOC reach a maximum in summer time. Opposite seasonal variation are observed for SO_2. Maximal level of SO_2 is observed in winter and is stipulated by seasonal differences in the wind direction. Sinks of trace gases depend on the meteorological conditions: height of mixing layer (which is maximal in summer), losses on the surfaces (minimal in winter for snow cover), losses in the canopies (maximal in summer time), the influence of RH on the condensation sink. The seasonal variations formation particles is result from a balance of sources and sinks and demand a thorough analysis in future.

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