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AEROSOL EVOLUTION AND METAMORPHOSIS DURING AND AFTER
HAZE (FOG) FORMATION OVER THE BAY OF NAPLES

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INTRODUCTION

The cooperative program of Marine-Urban-Napoli-Aerosol Project (MUNAP) included the aerosol climatology in summer and winter period in 1987, the study of physical properties of interacting marine and urban (industrial) aerosols and some information about the chemical composition of aerosol particles deposited on filters. The instrumentation enabling to characterize evolution during the MUNAP summer measurements included : GE Condensation Nuclei Counter with TSI Diffusion battery, Gardner AN Counter ASAS 300A and FSSP-100 aerosol spectrometers PMS, TSI MassMonitor and Electrostatic Precipitator and inertial impactors UNICO and CASELLA. This covered the whole particle size range from 0.004 μm to 50 μm . The meteorological parameters were obtained from the measurement of wind vector and its fluctuation by Gill Anemometer (R.M. Young Comp., Traverse City) and from the measurement of mean wind speed and direction by the SIAP recording anemometer. The hygrometric unit, MBW Electronics, recorded the dry and dew-point air temperatures and the solar radiation was measured by Differential Pyrradiometer Couzet, F.E.M.. Most of the meteorological data and data from FSSP-100 were plotted by Exorset 30 and 1000 units.

This study covers the major part of summer measurements made between May 15 and June 16, 1987 at Mte di Procida, a little town located approximately 20 km west of Naples. During this time two measuring sites were used : On the terrace of the house, where the field laboratory and the evaluation center were located, and at the mole of the Mte di Procida harbor approximately 350 m westwards. The terrace of the house at an elevation of 57 m above sea level was fully exposed to the winds blowing from the sea (S, SW, W and NW). For comparison, several few measurements from Napoli will be also presented. Because the general description of summer measurements and of the aerosol climatology was published elsewhere (Podzimek, 1987 ; Ianniruberto, 1988) we will concentrate in this study on aerosol evolution and transformation during and after haze formation. At these situations usually more measurements have been performed than what was required by the standard program (aerosol measurements every hour between 7:00 a.m. and 21:00 p.m. and several few measurements and samplings at night).

RESULTS OF THE MEASUREMENTS

Two questions have to be answered first before analysing the possible effect of haze formation : How much the different sampling site affects the counts and how much influence has the wider environment on the measurements ? Table I, in which are summarized all measurements during the mentioned time period helps to answer the first question.

Local and more distant sources of small particulates affect considerably the measurements of AN. For comparison, in the pure maritime air we measured only 2070 AN cm^{-3} . Larger particulates are apparently not affected much by the local sources excepting several few cases of the observed heavy local pollution (construction work at the mole and trash burning) . The winds from NE and N are

TABLE I.

Mean Aerosol Concentration (in parantheses is the number of measurements)

Aerosol Measurement	Mole	Mean Concentration { N cm ⁻³ }		for Total
		Terrace	Calm	
Gardner Counter AN (d < 0.2 μm)	6274 (83)	9181 (167)	8430 (9)	8178 (259)
ASAS-300 A				
R-4 (0.16-0.34 μm)	553.6 (76)	562.1 (127)	646.4 (9)	562.7 (212)
R-3 (0.28-0.75 μm)	122.2 (63)	119.0 (103)	190.4 (6)	122.6 (172)
R-2 (0.31-1.16 μm)	50.8 (56)	51.5 (145)	82.0 (9)	52.6 (210)
R-1 (0.64-3.00 μm)	12.8 (76)	12.8 (128)	15.7 (9)	12.9 (213)
PMS-FSSP-100				
(0.5-8.0 μm)	1.58 (42)	1.36 (100)	1.84 (6)	1.44 (148)
(1.0-16.0 μm)	0.49 (42)	0.36 (99)	0.48 (3)	0.40 (144)

featured by higher counts of AN. In the same direction is the center of the town and the center of heavy industry around Pozzuoli and Bagnoli (8 to 15 km NW) .

Very interesting is the evolution of the aerosol size spectrum at high relative humidity and the haze formation. A numerical model has been developed (Ianniruberto, 1988) which includes the data from the aerosol spectrometer ASAS-300A with the most sensitive size domain of interacting marine-urban aerosol particles. The size distribution curve is approximated by a nine order polynomial which indicates the accumulation mode and the mean concentration of particulates in different size ranges. Usually in the morning hours there was a high humidity with visibility smaller than 2 km (e.g. May 15 and June 2 and 11, 1988) . The size distribution curves were featured by one or two secondary maxima indicating clearly at high relative humidity the location of the accumulation mode and its shifting toward larger particles sizes. A typical example is presented in Fig.1 which was taken from the series of measurements made in the downtown of Naples in September. In the morning hours (7:00a.m.) at high relative humidity, the accumulation mode was at 1.6 μm particle radius; at 9:00 a.m. at 1.5 μm and at 1:00 p.m. the accumulation mode was almost not existing at relative humidity 51%. There is also a considerable decrease of particle concentration almost in all size ranges (except the largest one) at relative humidity lower than 70%. The only explanation we have now is the formation of larger aggregates on evaporating droplets and the aggregation of originally individual particles on the droplet surface.

In the domain of coarse particles ($r > 1.0 \mu\text{m}$), we evaluated separately the number of solid insoluble particles deposited in the center of haze elements, on the surface of haze droplets ("satellites") and outside of haze elements (interstitial particles). For the aerosol sampling a simple inertial impactor (UNICO or CASELLA) was used and aerosol particles and haze elements were deposited in sensitized gelatine layers smeared on microscopic slides. This technique (evaluation of Liesegang circles formed by salt ion diffusion in gelatine) was described elsewhere (e.g. Yue and Podzimek, 1980) . In this way, also the concentration of salt particles and their approximate sizes can be evaluated. The results of summer measurements at Mte di Procida are shown in Fig.2.

One sees that the majority of insoluble particles with $r = 1.0 \mu\text{m}$ is deposited on the surface of haze elements ("satellites"). Individual (interstitial) particles and particles coated with a thin soluble layer have the size distribution curves different from "satellites" . At this time, we have no definit explanation of the low counts of insoluble particles at about $r = 1.0 \mu\text{m}$ and of the second modus which was found in most of the samples. One cannot

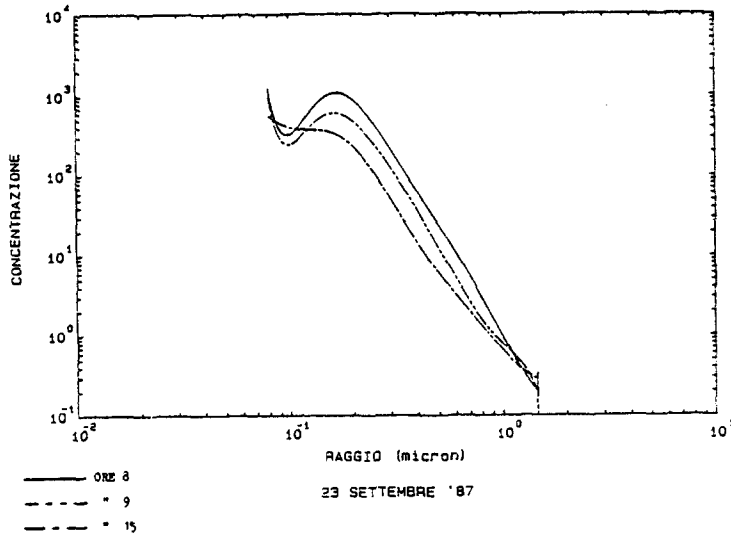


Fig.1. Aerosol size spectrum evolution during and after a haze situation on 23 September 1987 for 8:00 a.m., 9:00 a.m. and 15:00 p.m.

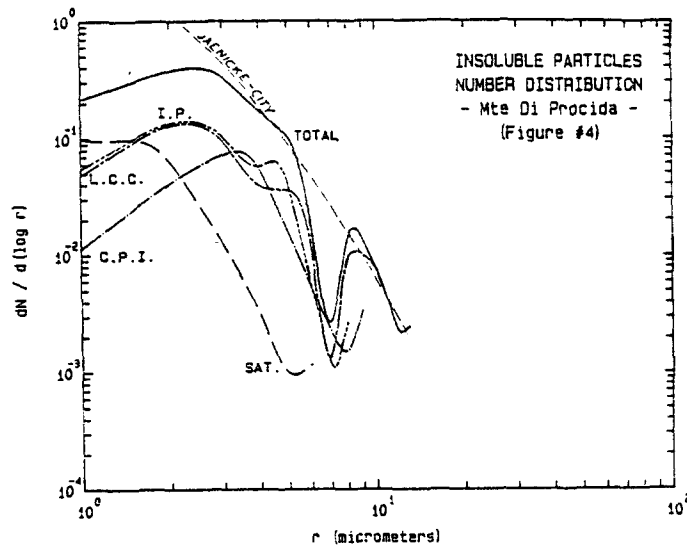


Fig.2. Insoluble particle mean size distribution found during the haze formation at Mte di Procida (summer 1987). I.P. - interstitial particles ; L.C.C. - Particles in the core of a Liesegang circle; C.P.I. - particles in the center of a coated particle aggregate; SAT. - "satellite" particles at the haze droplet surface.

exclude specific sampling conditions in the UNICO impactor. For comparison, an "envelope" curve for city aerosol (Jaenicke, 1984) was drawn in Fig.2. Similar relationships were found in volume distribution curves of aerosol particles.

The results of these studies have been applied to the modeling of particle activation (droplet growth) in the marine environment and to the possible interpretation in the light scattering by inhomogeneous coarse particles. Many times has been observed that particulates deposited in sensitized gelatine layers, at relative humidity lower than 73%, reveal distinct Liesegang circles (halos).

Also, many of the insoluble particles have halos only around one or more active spots on their surface. One has to introduce a more sophisticated correction to the mass increase coefficient which - besides the mass fraction of the soluble material in the particle - would take into account the absorption of ions on the insoluble part of the nucleus.

The structure of the coarse particulates and haze elements at Monte di Procida indicates its potential impact on light extinction and scattering. Models, similar to those published by Mita (1982), support the idea that - in the domain of coarse particulates - soot or salt mixtures covered by a thin layer of surface active material might have considerable effect on light scattering and visibility. Using as a mean value (deduced from our measurements) of the ratio b/a (radius of the coated particle to the radius of insoluble core) = 1.21 one obtains the real increase of absorption cross section by applying a correction factor, $\sigma/\sigma_0 \approx 1.5$ (σ_0 is the absorption cross section of the uncoated particle of the same size).

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