01 Jan 1990

Physical Properties Of Coarse Aerosol Particles And Haze Elements In Polluted Urban-marine Environment

Josef Podzimek
Missouri University of Science and Technology

Recommended Citation

J. Podzimek, "Physical Properties Of Coarse Aerosol Particles And Haze Elements In Polluted Urban-marine Environment," *Journal of Aerosol Science*, vol. 21, no. 2, pp. 299 - 308, Elsevier, Jan 1990.
The definitive version is available at https://doi.org/10.1016/0021-8502(90)90012-M

J. Aerosol Sci., Vol. 21. No. 2, pp. 299–308, 1990.
Printed in Great Britain.

0021–8502/90 \$3.00+0.00

PHYSICAL PROPERTIES OF COARSE AEROSOL PARTICLES AND HAZE ELEMENTS IN POLLUTED URBAN–MARINE ENVIRONMENT

JOSEF PODZIMEK

Department of Mechanical and Aerospace Engineering and Graduate Center for Cloud Physics Research,
University of Missouri, Rolla, MO 65401, U.S.A.

(*Received* 13 *February* 1989; *and in final form* 29 *August* 1989)

Abstract—Measurements of coarse particles (with $r \geq 1.0\ \mu$m) with the aid of a cascade impactor and of particle (droplet) identification in sensitized gelatine layers reveal their mean concentration of about 1.5 cm^{-3} during the months of May and June 20 km west from Napoli in Italy. Haze particles (droplets) are usually featured by insoluble core and many small particles deposited on their surface. Sea salt aerosol does not play a dominant role in the haze element formation at this site of measurement.

INTRODUCTION

The main aim of the cooperation of the Instituto di Meteorologia i Oceanografia of the Instituto Universitario Navale, Napoli (IUNN), the Laboratoire de la Physique des Precipitations of the Université Scientifique, Technologique et Medicale, Grenoble (USTMG) and the Graduate Center for Cloud Physics Research of the University of Missouri-Rolla (GCCPR-UMR) was to study the properties of interacting marine and urban (industrial) aerosols. The program, named Marine-Urban-Napoli-Aerosol Project (MUNAP), included the aerosol climatology, the physical properties of sampled aerosol (e.g. particle size and volume spectra, particle morphology), gravimetric analysis and chemical analysis of filter aerosol samples.

The instruments for aerosol sampling and the field meteorological station were located in Monte di Procida, a small town 20 km west of Napoli. Most of the measurements in the summer of 1987, which are described in this study, were taken on the terrace of a house located 57 m above sea level and fully exposed to the winds blowing from the sea. For several days, comparative measurements and aerosol samples were taken at the mole of the local harbor, approximately 3 m above the breaking sea waves and 350 m west of the main station at the terrace.

Special attention was paid to the haze (fog) occurrence. In this case starting at 8:00 a.m., the measurements and observations were made every 2 h or more frequently. Most of the measurements were terminated at 18:00 p.m., however, comparative measurements were made also at night.

Because the concentration and size distribution of small particles and their relationship to the main meteorological parameters has been described in a special report (Podzimek, 1987), the summary of which is currently prepared for publication, this study concentrates on the coarse particle concentration, their size distribution and morphology.

METHODOLOGY

The mean concentration and size distribution of particles with radii larger than 1.0 μm was determined from cascade impactor air samples. In addition to these parameters the number of particles containing chloride ions was obtained with the aid of a chemical spot test method. This so called Liesegang circle technique has been developed and applied by many authors since the early fifties (survey, see e.g. Yue and Podzimek, 1980). Its advantage is its simplicity, but it does impose time consuming evaluation and uncertainty while evaluating mixed nuclei at different relative humidities. The latter factors might cause larger errors in determining the 'magnification factor' which converts the observed circular spot (Liesegang circle) in the sensitized layer into the spherical salt solution droplet in the atmosphere (e.g. Preining *et al.*, 1976; Yue and Podzimek, 1980; Gerard *et al.*, 1987). The evaluation of 72 samples from Mte di Procida summer measurements reveals the shape of the insoluble particles and particle positions in the haze element or fog droplet.

The standard technique for sampling and slide preparation was used (see e.g. Yue and Podzimek, 1980): a 10% silver nitrate solution was added to a hydrosol of 8% laboratory grade gelatin in the volume ratio 1:20. After drying the slides in vertical position the slides were stored in containers which protected them against light and contamination. Usually, slides were exposed in the inertial impactor (UNICO or Casella) for 15 min at an air flow rate of 17.5 l min^{-1}. Exposed slides were illuminated for 15 min by u.v. lamp (Pen-ray Quartz Lamp, Ultra Violet Products, Inc.) before photographing the circular brown-reddish spots (nuclei containing chloride ions), insoluble particulates and haze elements. The photographs were usually taken at a magnification around 500 × at the central part under the impactor slots. After processing the film was projected on a screen with a scale or the magnified pictures evaluated in Zeiss TGZ3 particle evaluator.

Due to the very low coarse particle concentration (sometimes less than 1.0 particle cm^{-3}) the standard deviation of plotted values in the diagrams varied between 10 and 20% for particles with radii near 1.0 μm. For particle radii 5.0 μm, the standard deviation of plotted values often surpassed 50%.

RESULTS OF MEASUREMENTS

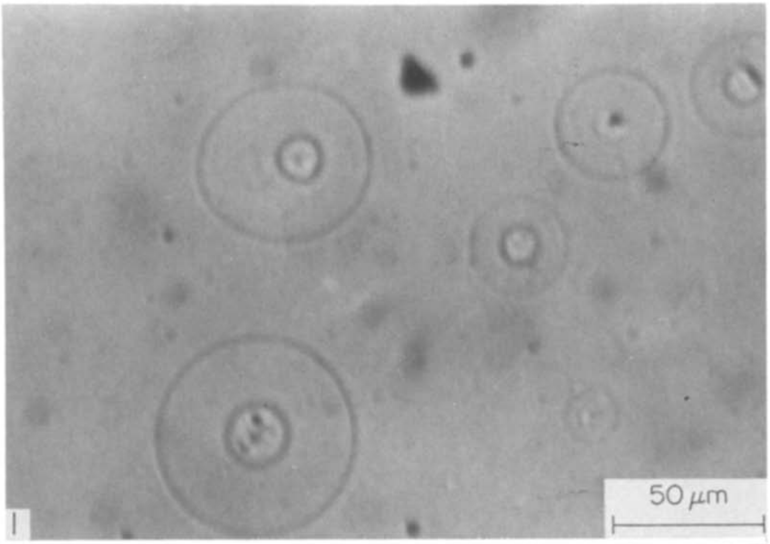
(*a*) *Morphology of coarse particles at the Bay of Napoli*

The summer sampling at Mte di Procida can be divided into several specific groups characterized by: (i) high relative humidity (haze or fog formation); (ii) by advection of highly polluted industrial air from the region to the east around Pozzuoli and Bagnoli, and (iii) by pure maritime air from the northwest.

The haze situation is featured by many Liesegang circles (Fig. 1) which, however, have not in their majority the typical brown-reddish color of sea salt nuclei. Often they contain many particles with $r < 3.0$ μm around an inner circle revealing the particle scavenging and deposition on the surface of haze elements. Most of the insoluble particles were presumably soot or carbonaceous material with some mineral component. Many of the insoluble particles were coated by a highly hygroscopic substance such as sulfuric acid. These rings are quite different in size and structure from the regular haze particles (compare Fig. 2 with Fig. 1). Although it is sometimes very difficult making the distinction between regular Liesegang circles with a clearly formed inner dark reddish ring (of diameter D_{LCI}) and coated particles with insoluble core (of diameter D_{CPI}), we can find the mean difference between the corresponding outer and inner ring ratios ($D_{\mathrm{LCO}}/D_{\mathrm{LCI}}$ and $D_{\mathrm{CPO}}/D_{\mathrm{CPI}}$). This is demonstrated in Fig. 3 where the samples taken at relative humidity higher than 70% are evaluated. This finding seems to be quite relevant to the potential impact of haze particles on the transfer of radiative energy.

(*b*) *Number and volume size distribution of coarse particles*

The results of the investigation into the concentration and size distribution of insoluble particles is plotted in Fig. 4. Besides the total number of particles per interval of logarithm of radii, the number of unattached (interstitial) particles (IP), insoluble particles found in the core (L.C.C.) and attached on the surface (A.P.) of haze elements and the particles found in the core of coated particles (C.P.I.) are plotted as a function of particle radii [$dN/d(\log r) = f(r)$]. The majority of particles with $r = 2.0$ μm is deposited on the surface of haze particles (attached particles). The concentration of all insoluble attached particles of this size is comparable with the number of unattached particles moving freely in the air. This finding stresses the importance of particle scavenging by haze or fog elements. Individual



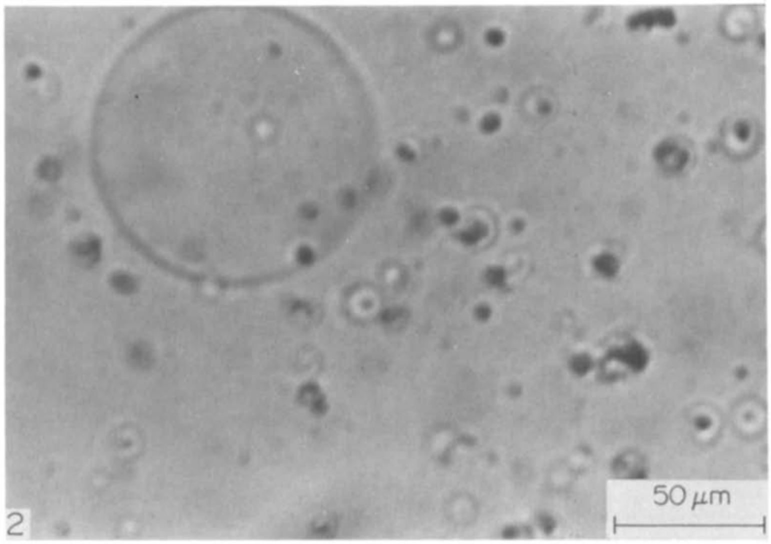


Fig. 1. Impactor sample of haze particles forming Liesegang circles with solid particles inside. Sample was taken at Mte di Procida, 7:12 p.m., 19 May 1987, at r.h. = 85% and W-NW wind of 5.0 m s^{-1}.

Fig. 2. Impactor sample in highly polluted air in Mte di Procida. Sample was taken 10:04 a.m., 20 May 1987, at r.h. = 79%.

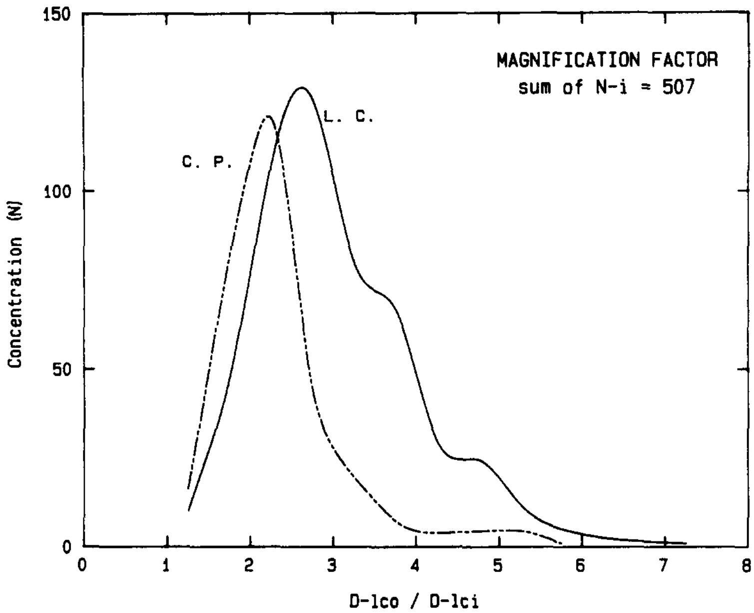


Fig. 3. Ratio between the diameter of outer and inner ring (or inner 'spherical' solid particle, D_{CPI}) for regular Liesegang circles, D_{LCO}/D_{LCI}, and for coated solid particle in the core, D_{CPO}/D_{CPI}. Total number of evaluated Liesegang circle ratios was 507; total number of coated particle ratios was 300.

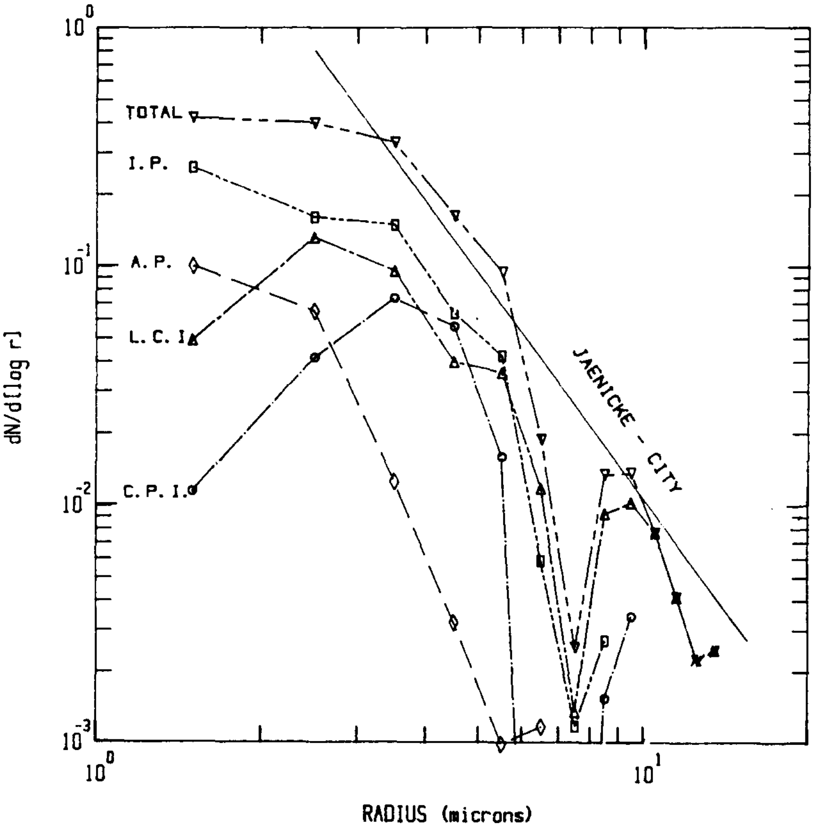


Fig. 4. Insoluble particle size distribution at Mte di Procida. May–June 1987. A.P., attached particles; I.P., interstitial; L.C.I., in the core of L.C.; C.P.I., inside of coated particle. Total number of particles: 2559.

coated particles with radii larger than 1.0 μm show size distribution curves different from those for unattached particles. At this time we have no definite explanation of the second modus in the size distribution in Fig. 4. It was typical for all samples from Mte di Procida. One cannot exclude specific conditions of particle sampling in the UNICO impactor (transition from one stage into another). For comparison, a curve representing a mean 'city' (anthropogenic and industrial) aerosol size distribution (Jaenicke, 1984, p. 20) is plotted in the same figure. (Concentrations, N, refer to 1 cm^3.)

The corresponding volume distribution curves reflect the insoluble particle distribution with maximal values for total particle volumes corresponding to radii between 3 and 5 μm. The curve for volume distribution of attached particles has a different shape, with a maximum value of $dV/d(\log r) \cong 2.0 \times 10^{-12}$ at $r = 1.9$ μm.

The pure 'water' droplets made no brown-reddish rings typical of solution droplets containing chloride ions. Most of the rings contained small insoluble particles in the core or around the core (Fig. 1). This reveals the size of the original haze droplets before the liquid starts to diffuse into the gelatine layer. The ring's outer zone reveals often more complicated structure due to the evolution of periodic precipitation of diffusing ions. During our measurements we found more Liesegang circles with inner rings than without any internal circles, as shown in Fig. 5.

In order to demonstrate the role of sea salt in haze droplet formations, all measurements were divided into two groups: one at r.h. $>73\%$ with two subgroups for Liesegang circles (L.C.) (diameters of inner ring) and coated particles by some liquid solution (C.P.—diameter of outer ring). The second group was formed by all measurements at r.h. $<73\%$ and with the same subgroups as in the previous case. The curves in Fig. 6 are plotted in relative units (normalized with respect to the total particle counts in each group). One would expect that, if the majority of nuclei were to be formed of sodium chloride particles, a markable difference should be found between size distribution of Liesegang rings around salt containing particles for humidities larger and smaller than 73%. Because that was not the case, we can hypothesize that our hygroscopic particles (giving origin to Liesegang circles) were composed in their majority of substances activated at relative humidity below 73%.

Seven sets of slides exposed at the mole of the harbor Mte di Procida were divided into two groups: three at high wind speed ($v > 5.0$ m s^{-1}) and maritime SW-winds, and four at

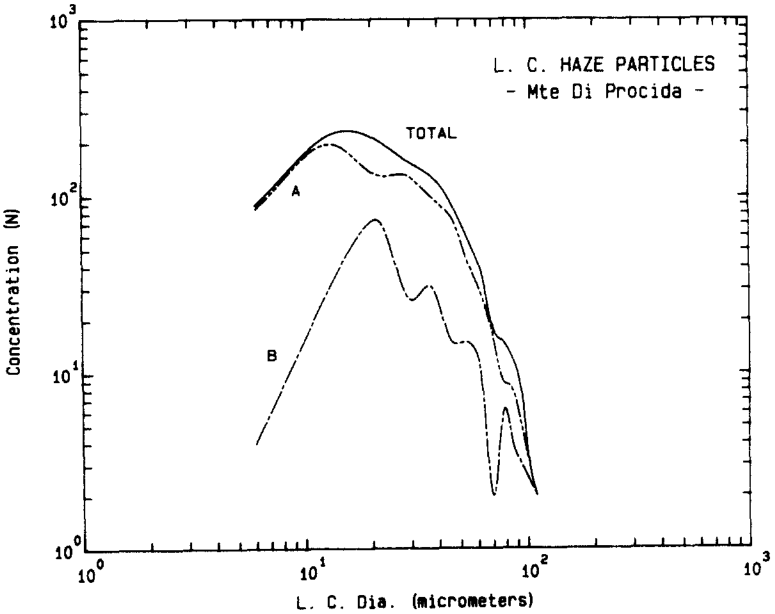


Fig. 5. Haze particles forming Liesegang circles with 'contaminated' inner circle (A) and without inner circle (B). Total number of evaluated particles: 1046.

winds from NW-N-NE sector where large community and heavy industry (at a distance of approximately 7 km) are located. The first group is featured by higher counts of marine aerosol, however, only for the small particle size range ($r<2.75$ μm). One sees also much smaller counts of larger particles if compared to urban and industrial aerosols (Fig. 7). The secondary peak of the marine particle curve at $r=4.0$ μm reveals that a portion of these

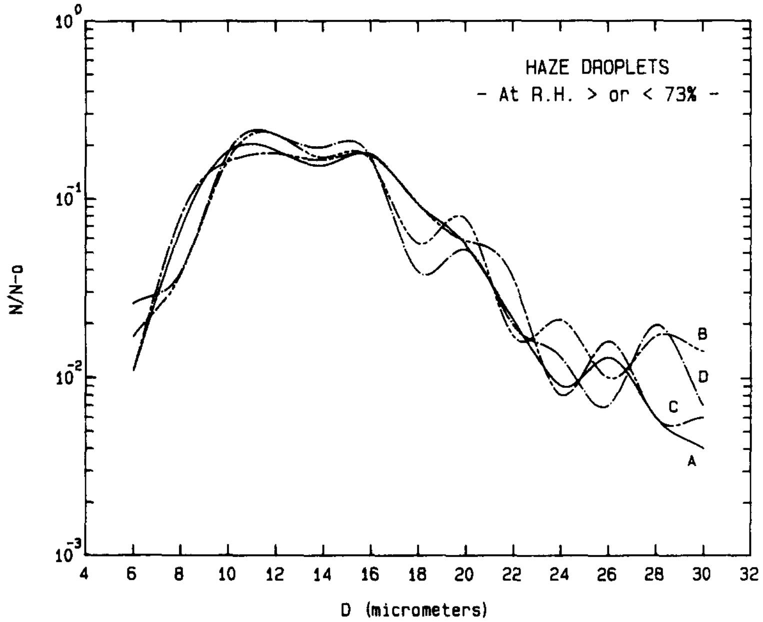


Fig. 6. Haze element formation at different r.h. (greater and smaller than 73%). Curves are plotted in relative units (normalized with reference to the total number, N, in a specific group). A, L.C.I. plus C.P.O. ($N=529$) for r.h. < 73%; B, L.C.I. plus C.P.O. ($N=287$) for r.h. > 73%; C, L.C.I. at r.h. < 73% ($N=367$); D, L.C.I. at r.h. > 73% ($N=153$).

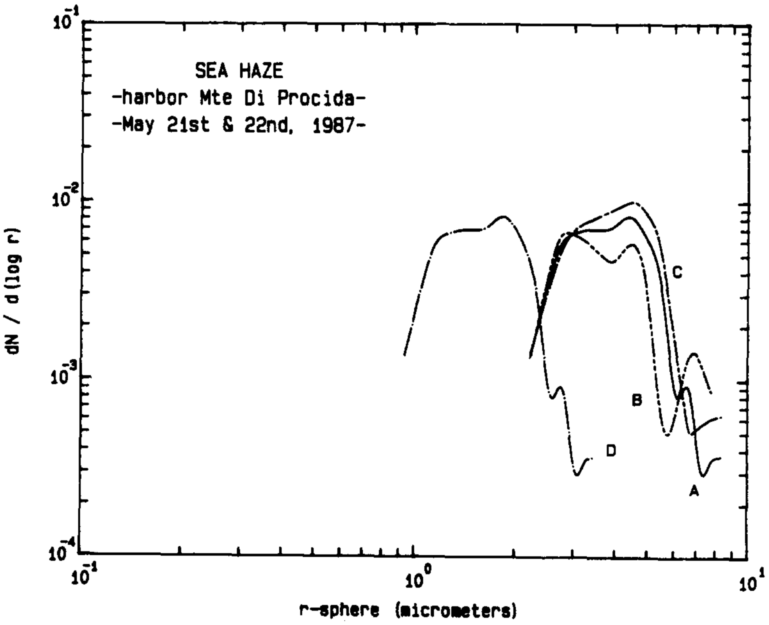


Fig. 7. Haze element size distribution at different surface wind speed and direction. Samples taken at the mole of Mte di Procida harbor. A, total mean size distribution at Magnification Factor = 1.8; B, at SW wind of velocity $v>5$ m s^{-1}; C, at N and NE wind of velocity $v \leq 1.0$ m s^{-1}; D, total mean size distribution assuming the less realistic Magnification factor = 4.3.

particles might be contaminated by local urban aerosol or soil particles. For the evaluation of L.C., a simplistic assumption was made: in mean, the magnification factor for transforming the L.C. or C.P. into a droplet (particle) of radius r was 1.8. A larger magnification factor would lead to smaller calculated r (Yue and Podzimek, 1980).

(c) *Comparison with gravimetric measurements and light scattering instruments*

Our calculation of total volume of coarse insoluble particles and the assumption of mean density of 2.0 $\mathrm{g\,cm^{-3}}$ led to the mean value of the insoluble aerosol mass load at Mte di Procida of 48.2 $\mu\mathrm{g\,m^{-3}}$ during our summer measurements. The total particle deposit on nucleopore filters (S 32393 B) exposed at Mte di Procida was in mean 212 $\mu\mathrm{g\,m^{-3}}$ for samples from 19 to 29 May 1987, 576 $\mu\mathrm{g\,m^{-3}}$ for 21 and 22 May samples, and 490 $\mu\mathrm{g\,m^{-3}}$ for samples taken between 1 and 11 June 1987. The second period of sampling was featured often by strong maritime winds ($v > 7.0\ \mathrm{m\,s^{-1}}$) from the west. The specific filter samples showed a high variability of particle mass load. Values below 20 $\mu\mathrm{g\,m^{-3}}$ were not unusual.

The comparison with light scattering instruments presents several problems which are inherent to coarse mixed particle counting in optical counters (edge effect, calibration of the instrument). In mean, the particle concentration in the particle size range 1.0–16.0 μm of the Knollenberg light-scattering aerosol counter (FSSP-100) was between 0.15 and 0.95 particle $\mathrm{cm^{-3}}$. This, compared to the average concentration measured by impactors, around 1.5 $\mathrm{cm^{-3}}$, might lead to the conclusion that light scattering instruments considerably undercount the coarse particle concentration. However, one has to realize that for our evaluation all particles found in haze droplets were counted separately, and that usually several coarse insoluble particles were deposited on the surface or in the droplet core. Therefore the comparability of the counts by two different techniques is acceptable, except for the uncertainty of light scattering counter calibration (e.g. Gayet, 1976; Pinnick and Auvermann, 1979).

DISCUSSION

The complicated particle morphology prompted a specific approach to the particle size distribution. Curves for insoluble particles (Fig. 4) and haze droplets (Figs 5–7) were plotted separately, as indicated above. When the volume distribution of insoluble particles is added, one sees that the measured concentrations fit better in the 'city' aerosol as presented by Jaenicke (1984) than they do in marine aerosol referring to its characteristics. The specific feature of the aerosol at the Bay of Napoli is the presence of large insoluble particles (even at Mte di Procida, which is not close to the main industrial centers in this area). A preliminary analysis of the aerosol filter samples showed a considerable content of carbon. For example, a sample taken during a haze on 1 June 1987 at Mte di Procida had 1.39 μg of carbon and small amounts of hydrogen and nitrogen in particulate form per $\mathrm{m^3}$ of air (analysed in Perkin Elmer 240C Elementar Analyzer).

Even at humidities far below 73% many of the particles sampled at Mte di Procida revealed distinct Liesegang circles (halos) (e.g. 18 May at r.h. = 67 and 56%, 19 May at r.h. = 71%, 21 May at r.h. = 70%, 27 May at r.h. = 67%). Just above sea level, the circles were well-developed at humidities between 65 and 67% (e.g. 22 May 1987). Besides that, many of the insoluble particles had halos only around one or more active spots on their surface.

Several interesting observations can be made concerning the application of the measured coarse aerosol data to the extinction of atmospheric radiation. Very simple models have been deduced for short-term and long-term aerosol radiation attenuators. They are related to particle residence time, atmospheric conditions and physico-chemical properties of atmospheric particles. According to Jaenicke (1984) we assume that the coarse aerosol particles measured at the Bay of Napoli may have residence time ranging from 1 to 14 days. This requires that the most effective attenuator ought to be large enough to have the maximum extinction efficiency factor ($K_E \geq 2$), yet small enough to ensure a long residence. Based on that, Hänel (1984, p. 17) deduced the lower and upper size limits for the most effective long-term attenuators

$$0.482\lambda \leq r \leq 2.89 \times 10^{-4} \text{ cm}.$$

The wavelength of radiation is λ. One can expect that soot or salt mixtures coated with mixed surface active material might have the largest effect on the extinction of atmospheric radiation.

One of the most important parameters seems to be the ratio of the total surface of insoluble coarse particles deposited in the core (LCC) and on the surface of haze droplets (AP). From the total number of almost 500 Liesegang circles sampled at different meteorological situations at the seashore and at the cliffs of the community Mte di Procida we concluded that between 1.45 and 10.11% of the haze droplet surface was taken by the particles in the core of the droplets and between 1.85 and 9.04% by the particles attached to the droplets during nine individual samplings. There is approx. 2:1 ratio in both categories for samples taken at the cliffs in the community and aerosol sampled at the sea (terrace: $\overline{\text{LCC}} = 6.01\%$, $\overline{\text{AP}} = 5.30\%$; sea: $\overline{\text{LCC}} = 2.77\%$, $\overline{\text{AP}} = 2.98\%$). The industrial–urban source of coarse particles is also apparent from the evaluation of the surface coverage dependent on wind direction. Maximum $\overline{\text{LCC}} = 7.29\%$ and $\overline{\text{AP}} = 1.56\%$ was found from the wind direction WNW at the time when construction and other work has been done in this direction. Coverage of haze droplets depends strongly on their mean size which is related, among other factors, to relative humidity. In mean for r.h. > 73% the measured coverage was $\overline{\text{LCC}} = 2.68\%$, $\overline{\text{AP}} = 2.44\%$ and for r.h. < 73, 5.51 and 5.20%. That indicates the importance of our study of coarse aerosols for radiative transfer and visibility measurement (especially if more information on aerosol composition and behavior at different relative humidities is available).

CONCLUSIONS

The study of physical properties of coarse aerosol particles at the Bay of Napoli is based on the application of the old Liesegang circle technique used several decades ago for identifying specific ions in atmospheric aerosol. This technique has been proven to be a very useful tool for studying the morphology of coarse particulates and haze droplets. More realistic models might be suggested for nuclei activation and its role in light extinction and scattering.

The coarse aerosol particles at Mte di Procida represent a typical marine–urban environment with its dramatic changes at different meteorological situations. In mean, the coarse particle concentration in summer is about 1.5 cm^{-3}, with maximum values surpassing 10.0 cm^{-3} (in the case of intense pollutant production in the community, e.g. trash burning, construction work). Several per cent of the coarse particulate matter is composed of carbon with concentrations surpassing $15 \mu\text{g m}^{-3}$ in the air advected from industrial and urban areas. Concentrations of sea salt 'giant nuclei' will surpass only the number of 1 cm^{-3} when at high wind speed 'white caps' formed on the sea surface.

The size and volume distribution of coarse particulates do not deviate much from the typical distributions suggested by other authors. Deviation for $r = 1.0$ and $7.0 \mu\text{m}$ from these model curves might be explained by the deficiency of our impactor (UNICO) sampling technique, and by the fact that both unattached and attached particles to droplets are counted.

Analysis of the haze particle spots in the gelatine layer reveals that (besides the sea salts) a high percentage of hygroscopic substance causing the formation of diffusion rings around a 'carrier' insoluble particle might be of anthropogenic origin. These substances do not form a colored reddish-brown well developed ring like chloride ions, and are frequently found at winds blowing from urban and industrial areas.

One can hypothesize that the structure of the coarse particles at the Bay of Napoli, especially the high number of attached particles found on the surface of the haze droplets, might have considerable impact on light extinction and scattering and its modeling in a similar environment (e.g. Mita, 1982). Finally, this investigation of coarse particles ought to be compared with the results of small particle measurements and with more detailed analysis of meteorological parameters (Podzimek *et al.*, 1987).

Acknowledgements—The assistance of the following personnel during MUNAP field measurements and evaluation of data is highly appreciated: Dr H. Andriambeloma, J. Napolitano and Miss I. Martins from USTM-Grenoble, Mr M. Ianniruberto from IUN-Napoli and Mr G. Stowell, G. Pope and Miss D. Capps from UM-Rolla. Mrs V. Maples and Mr J. Barker from GCCPR-UMR ably helped in preparing this report for publication. The complex scientific evaluation of the MUNAP measurements has been effectively aided by Professors A. De Maio, E. Sansone and G. Spezie from the Instituto di Meteorologia e Oceanografia, IUN-Napoli and by Dr R. Montmory, Director of the Laboratoire de la Physique des Precipitations, USTM-Grenoble.

The financial support for the program came from FORMEZ (Centro di Formazione per il Mezzogiorno), Roma, from National Science Foundation, Washington, D.C. (Grant ATM84-13814), and from the three cooperating Universities mentioned in the Introduction.

REFERENCES

DeMaio, A., Ianniruberto, M., Podzimek, J., Sansone, E. and Spezie, M. (1989) Primi risultati del progetto MUNAP (Marine and Urban Napoli Aerosol Project), *Annali IUN, Napoli*, p. 71–82.

Gayet, J.-F. (1976) Sur les performances d l'ASSP-100 de Knollenberg pour la granulometrie des nuages. *J. Rech. Atmos.* **10**, 105–118.

Gerard, R., Villard, A. and Serpolay, R. (1987) Conditions de reproducibilité du developpement des anneaux de Liesegang produits par un aerosol de chlorure de sodium. *Atmos. Res.* **22**, 335–350.

Hänel, G. (1984) The physical chemistry of atmospheric particles. In *Hygroscopic Aerosol* (Edited by Ruhnke, L. H. and Deepak, A.). pp. 1–20. A. Deepak Publ., Hampton, VA.

Jaenicke, R. (1984) Physical aspects of the atmospheric aerosol. In *Aerosols and their Climatic Effects* (Edited by Gerber, H. E. and Deepak, A.), pp. 7–33. A. Deepak Publ., Hampton, VA.

Mita, A. (1982) Light absorption properties of inhomogeneous spherical aerosol particles. *J. Met. Soc. Jap.* **60**, 765–775.

Pinnick, R. G. and Auvermann, H. J. (1979) Response characteristics of Knollenberg light-scattering aerosol counters. *J. Aerosol Sci.* **10**, 55–74.

Podzimek, J. (1987) *Preliminary Report on Marine-Urban-Napoli Aerosol Project (MUNAP)*, May–June, 1987. p. 44. GCCPR, University of Missouri, Rolla, July.

Podzimek, J., Andriambeloma, H., Ianniruberto, M., DeMaio, A., Montmory, R., Spezie, G. and Stowell, G. (1988) Aerosol evaluation and metamorphosis during and after haze (fog) formation over the Bay of Naples, *Abstracts European Aerosol Conf.*, Lund, 30 August–2 September 1988, p. 143.

Preining, O., Podzimek, J. and Yue, P. C. (1976) The magnification factor for sodium chloride Liesegang circles established with an aerosol centrifuge. *J. Aerosol Sci.* **7**, 351–358.

Yue, P. C. and Podzimek, J. (1980) Potential use of chemical spot test method for submicron aerosol sizing. *Ind. engng Chem. Prod. Res. Dev.* **19**, 42–46.