Absorption by airborne and deposited particles in the 8–13 micrometer range

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ABSTRACT

The absorption of radiation by natural aerosol particles was measured in the 8–13 micrometer wavelength interval. A comparison was made between an in situ method and measurements of particles of deposited form. The results are in agreement to about 30 percent. The main feature of aerosol absorption within the infrared window is a strong absorption peak near 9 micrometers caused by sulfate or quartz particles present in all continental aerosol types. Consequences for the atmospheric heat balance are clear sky cooling rates growing from about 2 per cent in the tropics to about 20 per cent of the total cooling in arctic regions under normal conditions, additionally increasing with increasing relative humidity.

1. Introduction

During recent years attention has been increasingly focused on possible change of local and global climate caused by particulate matter ejected in excess by human industrial activity into the atmosphere. The major mass of particulate matter consists of particles of radii between 0.1 and 10 μm being suspended in the air and strongly interacting with solar and terrestrial radiation. Radiant energy is scattered and absorbed by aerosol particles.

The part that the absorption of radiation by aerosol particles plays in the atmospheric radiation budget is unrevealed as yet partly due to the prediction that the optical depth of atmospheric aerosol particles is exceeded by that one of the atmospheric gases by some orders of magnitude. However, investigations in the atmospheric window regions have pointed out disagreements between measured and computed values of sky radiation suggesting the presence of an additional absorber being comparable in strength to the known absorbers like H_2O, O_3, O_2, N_2O, CO_2 and CO (Hinzpeter, 1957; Roach, 1958; Robinson, 1963; Leupolt, 1966; Quenzel, 1967; Cox, 1969).

Consequently, it has been demonstrated that aerosol particles are composed of chemical substances like soot that are of considerable absorption (Forster & Horwarth, 1968). Similar results are reported by application of the KBr method to mineral dust (Hoidale & Blanco, 1968) and to residues of precipitation (Volz, 1972, 1973). Furthermore, there are measurements of absorption performed on films of aerosol particles collected by jet impactors (Fischer, 1970, 1973, 1974).

Unfortunately these methods are hardly compatible with each other because of the different experimental techniques. However, for the infrared window Grassl (1973*a*) has reported a procedure that yields evaluations of the absorption index of aerosol particles of in situ status by measuring the sky emission and separating the different atmospheric absorbers.

In this paper—for the first time—a comparison is presented between the properties of absorption of aerosol particles suspended in the air by contrast with the absorption of a deposited fraction of those particles, i.e.: for the analysis according to Grassl the sky emission has been measured, while simultaneously aerosol particles have been collected by a jet impactor for the determination of absorption according to Fischer (1974).

The investigations of absorption are confined to the 8–13 μm wavelength interval. In this

range long wave radiative transfer is most intense in the lower atmosphere. Furthermore absorption by aerosol particles can be of the same order of magnitude as water vapour absorption. Only in the tropics water vapor contribution to sky emission is so strong, that particle effects can be neglected.

2. In situ measurements

The absorption of airborne particles was successfully separated from different other absorbers at 4 wavelengths in the 8–13 micron window (Grassl, 1973*a*). In confirmation of the particle absorption found from a set of 78 measurements in Mainz, West Germany, during March to November 1972 the nearly unchanged value of particle absorption should be mentioned along with strongly changing dependence on water vapour of all the other water vapour absorption types. The different absorption types of water vapor are due to water vapor lines, wings of distant lines and a new type of absorption depending on water vapor pressure e besides water vapor mass, in the literature referred to as e-type absorption. The values obtained (optical depth) from these sky emission measurements have to be made comparable to values of the mass absorption index measured on deposited samples. The following assumptions were necessary:

(1) The aerosol particle size distribution was chosen to be a power law distribution of the form $n(r) \sim r^{-4}$. As it was shown by Bergstrom (1973*b*) the particle absorption is only slightly depending on the size distribution and is linearly depending on the imaginary part of the refractive index in the infrared, provided that the imaginary part does not surmount a certain value. Therefore the above assumed particle size distribution is probably of no influence on the results of the conversion.

(2) The measurements at Mainz were performed at a mean relative humidity of 60 percent. The particle growth with relative humidity should therefore be included. Fortunately one can use values of—for example—an aerosol sampled at Mainz as given by Hänel (1972).

(3) As to the density of aerosol particles the value of 2.5 g/cm^3 was chosen according to Hänel (1972).

(4) The absorption of airborne particles can only be determined for a set of measurements because of a statistical evaluation. Therefore only mean values can be compared. Thus a comparison of different years including all variations of air masses seems reliable. The mean value for airborne particles was determined from measurements in 1972, and for deposited particles from measurements in 1973/74.

Comparative measurements were also performed at Mitzpeh Ramon, High Negev desert, Israel, in May 1973. Considering the results from Israel, however, some reservation is advisable because of a slightly different evaluation: The variation of water vapour content and turbidity necessary for a separation of different absorbers was too small. Therefore the water vapour absorption—mainly e-type absorption—was introduced as determined by measurements at Mainz, and the residue obtained is the particle absorption. That means, a fixed absorption by water vapour was adopted.

3. Measurements on deposited particles

The absorption index which was evaluated by the measurement of the sky emission is compared with the absorption of radiation determined by the transmittance of films of closely packed aerosol particles. The aerosol particles were deposited by an automatic jet impactor (Hänel, 1968). Rolled AgCl monocrystals were used as transparent substrates.

By correct adjustment of the impactor and owing to their natural size distribution the vast majority of aerosol particles deposited are of radii $r \leqslant 1$ μm. Thus to a good approximation the collections by the impactor yield representations of those collectives of aerosol particles which—due to their concentration and size distribution—mostly participate in the radiative transfer in the atmosphere.

The optical measurement and the evaluation of the absorption index is described elsewhere (Fischer, 1974), so it will only be mentioned that—essentially—the absorption of infrared radiation is determined by the difference in transmittance of two samples of slightly different thickness consisting of particles of identical collectives.

The quantity of absorption is presented in terms of the so-called mass absorption index

k/ϱ, i.e. the imaginary part k of the complex refractive index $\hat{n}$ related to the bulk density ϱ of aerosol particles. The density is determined by a separate procedure. According to Hänel (1972) $\varrho = 2.5$ g/cm³ is a realistic mean value of aerosol particles collected at Mainz (this value is related to the relative humidity of about 50 %). The density of the desert particles has not been determined as yet, but in this case $\varrho = 2.5$ g/cm³ seems to be a reasonable assumption, too, particularly because the density of quartz and further significant clay minerals is approximately of this value (Weast, ed., 1973).

4. Sites of measurements

Measurements of the radiative sky emission and simultaneous collections of aerosol particles were arranged near Mainz city which is situated in a heavily industrialized region. The combined experiment was also performed in uncontaminated air at the remote site of Mitzpeh-Ramon in southern Negev, Israel, for (1) any prediction concerning the development of the disturbed atmosphere must be based on the understanding of the conditions of the undisturbed atmosphere, and (2) aerosol particles of desert origin are considered to be an important factor in global radiative transfer, particularly as great desert areas, e.g. the Sahara, are sources of continual long range transport of mineral dust in the atmosphere (Carlson et al., 1972; Jaenicke et al., 1971).

5. Results

In Fig. 1 there is presented the mean mass absorption index of Mainz aerosol particles in the 7–12 μm wavelength interval according to the two independent methods. The triangles stand for the results obtained from the evaluation of the sky emission measurements. They are related to a density of $\varrho = 2.5$ g/cm³ of the aerosol particles. Furthermore, the mean mass absorption index is plotted, which is determined by measuring the transmittance of films of aerosol particles. The values obtained by both methods are in good agreement.

The broad absorption band, centered at 9.2 μm, is—in correlation with an intense band at 16.4 μm (see Fig. 2)—assigned to the stretching

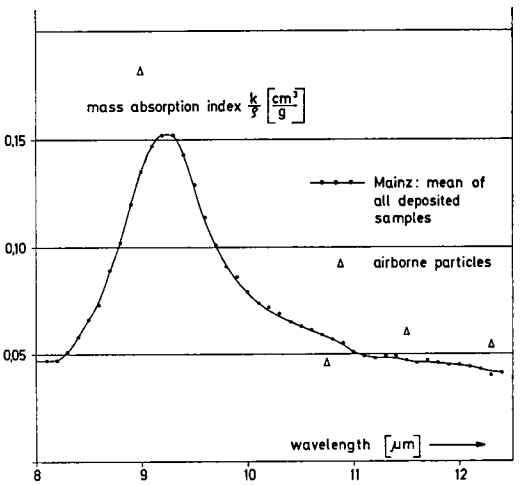

Fig. 1. Mean mass absorption index k/ϱ vs. wavelength of aerosol particles at Mainz as determined on deposited samples ·—·—· and by measurement of the sky emission and computational separation according to the different atmospheric absorbers △. The samples by impactor were taken during the years 1973/74, the "in situ" plot refers to 78 measurements between March and November 1972.

vibration of $(SO_4)^{-2}$ ions, although it should be mentioned that this broad band may cover bands of the C–O and C–N stretching vibrations (Weast, ed., 1973).

In Fig. 2 the mass absorption index measured on deposited aerosol particles is plotted for a set of single days as an example of possible variations of the absorption band at 9.2 μm due to the actually prevailing type of aerosol particles.

In Fig. 3 there is recorded the mass absorption index of aerosol particles that were collected during a dust storm (sharav) indicating a marked content of quartz-like substances due to the typical dublett at 8.8 and 9.4 μm. In this case the corresponding in situ measurement was not feasible. The second plot of Fig. 3 refers to particles which were collected during a set of days of similar weather conditions (subsidence). The doublet of quartz can be distinguished, too, but further bands, e.g. of $(SO_4)^{-2}$ ions, are superimposed. With regard to the necessary precautions discussed in chapter 2 the values obtained by the measurement of the sky emission can be considered to be in agreement with the absorption index of deposited particles.

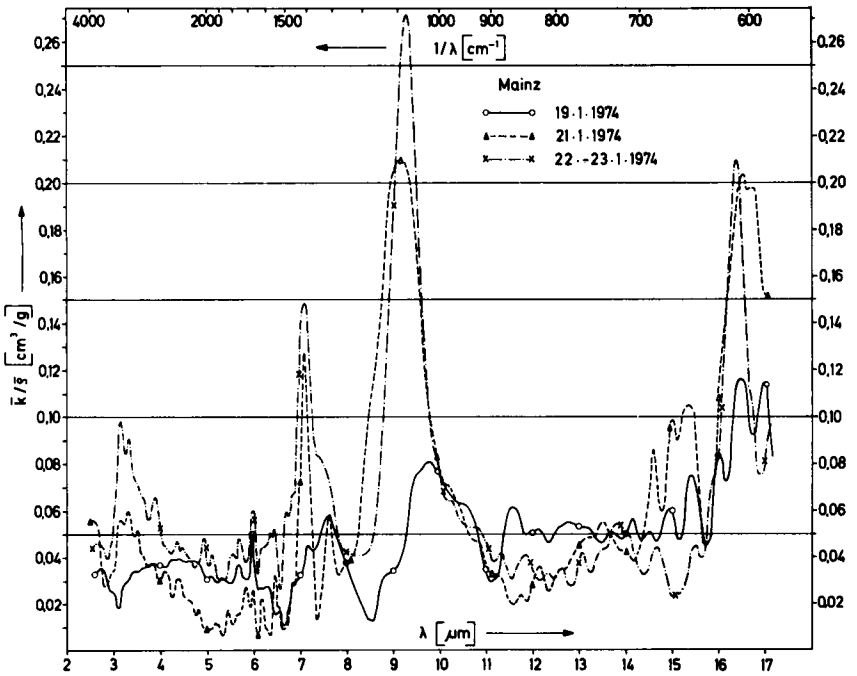

Fig. 2. Mass absorption index k/ϱ vs. wavelength of aerosol particles sampled by impactor at Mainz during a set of days of different prevailing wind condition as a demonstration of possible variation of the absorption index.

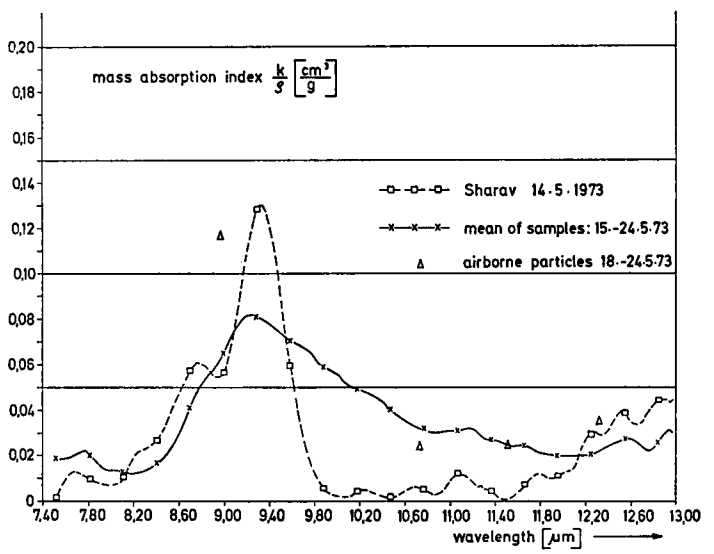

Fig. 3. Mean mass absorption index k/ϱ vs. wave length of aerosol particles at Mitzpeh Ramon, Israel. Measurement of collected samples ×—× in comparison to results obtained by the "in situ" method Δ. Additionally the mass absorption index of particles of dust storm (Sharav) origin is plotted.

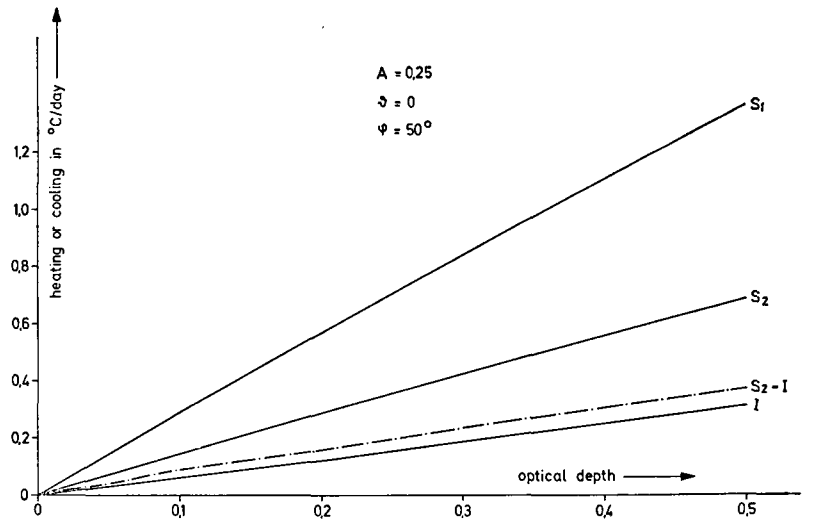

Fig. 4. Heating (S_1 for $k = 0.02$ and S_2 for $k = 0.01$) and cooling I (for US standard atmosphere and absorption indices according to Grassl (1973*a*)) in dependence of the optical depth of the aerosol in the visible region at the equinox at 50° latitude, and at a surface albedo of $A = 0.25$. The plot of $S_2 - I$ presents the net effect due to aerosol particles.

Attention is attracted to the relatively poor agreement at 9 μm that deserves further discussion. According to Bergstrom (1973*b*) the MIE absorption coefficient in the infrared is not a strong function of the size distribution of the particles. So the modification which the size distribution of airborne particles—mainly with regard to radii $r < 0.15$ μm—undergoes during the collection process in the impactor should be of no effect. The MIE absorption coefficient is linear with the absorption index up to about $k = 1.25$. However, it is not determined as yet, if the mean absorption index obtained from deposited particles can be transferred to all particles or if it is due to a few highly absorbing particles along with a non-absorbing residue. In this case the linearity between MIE absorption coefficient and absorption index fails, and the evaluation of the absorption index even may not be single valued (Bergstrom, 1973*a*).

Furthermore, the disagreement at 9 μm could in fact be caused by a misrepresentation of highly absorbing particles in the impactor collections, or may be due to their absence in the sampled ground-near air volume or due to specific physico-chemical properties reducing the adhesion to the collector substrates (Winkler, 1974).

Never-the-less, the results of the investigation of the absorption index of both urban and desert aerosol particles indicate satisfactory agreement with respect to two such completely different methods of measurement. The two methods of evaluating the absorption index—by measuring the sky emission and by investigation of the transmittance of films of deposited particles—can be considered as equivalent. Moreover, the latter method is of more general application because of its independence on favourable weather conditions.

The most remarkable fact found in these investigations is the significance of strong bands of aerosol particles exactly in that part of the infrared region of the spectrum which is named "the atmospheric window". All but marine types of aerosol particles tested so far are of marked absorption in that region (Volz, 1972, 1973; Fischer, 1974). Furthermore, short wave radiation is also absorbed by aerosol particles (Fischer, 1973; Chin-J-Lin et al., 1973; Lindberg et al., 1974).

6. Consequences to the radiation budget

Influences on heating and cooling rates

Any infrared absorbing material is an emitter, too. The atmospheric infrared window from

8–13 micron is the only region where weakly absorbing particles can contribute remarkably to the radiation budget. All particle-loaden layers of the atmosphere will emit radiation and are thus contributing to radiation fluxes and radiative flux divergence. In two recent papers (Grassl, 1973*b*, 1974*a*) the contribution to radiative cooling in the infrared was shown for different climates and for a temperature inversion with all particles trapped below this inversion. For standard atmospheres the aerosol contribution to cooling rates at an optical depth $\tau = 0.2$ at 0.55 micrometer is growing from 2 per cent in the tropics to 20 per cent of the total cooling rate in the arctic regions. Below temperature inversions at high relative humidities the aerosol contribution is comparable to the water vapour contribution.

In the visible and near infrared part of the spectrum absorbing particles lead to a heating of the particle-loaden layers of the atmosphere as it was shown by Eschelbach (1972), Yamamoto & Tanaka (1972), and Grassl (1974*b*) and as it was measured during Caenex by Kondratyev et al. (1973). In the solar and terrestrial part of the spectrum the imaginary part of the refractive index of aerosol particles is strongly depending on relative humidity, however, in an opposite way. Since heating at dry conditions dominates cooling and cooling is stronger at high relative humidities there is always a distinct relative humidity where cooling balances heating.

In Fig. 4 an example is presented for the net effect (plot S_2–I) of heating due to short wave absorption and cooling due to long wave emission. Obviously there are climatological regions where a compensating effect can be expected between the two opposite radiative flux divergences.

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ПОГЛОЩЕНИЕ ВОЗДУШНЫМИ И ОСАЖДЕННЫМИ ЧАСТИЦАМИ В ИНТЕРВАЛЕ 8–13 МИКРОМЕТРОВ

Поглощение радиации частицами естественного аэрозоля измерялось в интервале длин волн 8–13 микрометров. Было произведено сравнение между измерениями in situ и измерениями осажденных частиц. Результаты согласуются между собой в пределах 30 %. Главной особенностью поглощения аэрозоля в инфракрасном окне является сильный пик поглощения вблизи 9 *мкм*, вызываемый сульфатными или кварцевыми частицами, присутствующими во всех типах континентального аэрозоля. Следствием этого для теплового баланса являются скорости выхолаживания при ясном небе, растущие от примерно 2 % в тропиках до примерно 20 % от общей скорости выхолаживания в арктических областях при нормальных условиях с дополнительным увеличением с ростом относительной влажности.