Effect of aging with pollution on the complex refractive index of pure submicron clay particles

Sarla^{1, 2} and S. K. Mishra^{*1, 2}

¹CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi-110012, India ²Academy of Scientific and Innovative Research (AcSIR), Ghaziabad- 201002, India (*E-mail of the corresponding author: mishrask@nplindia.org)

Abstract

Modelling the optical and radiative properties of atmospheric particles is governed by one of the key input parameters i.e. refractive index of aerosols. Availability of the region-specific refractive index data of aerosol is major challenge for atmospheric community. The refractive index of aerosol is function of their physico-chemical properties. Uncertainty in the computation of the spectral refractive indices of the aerosol leads to erroneous assessment of their optical and radiative properties.

In present work, refractive index of pure clay (Kaolinite and Illite and their variable mixtures) and polluted clay [clay polluted with anthropogenic hematite, AH (0.10 to 1.48%), black carbon, BC (2 to 10%), ammonium sulphate, AS (13%) and ammonium nitrate, AN (8%)] submicron particles have been computed for the wavelength range 0.38 to 21.5 μ m. Anthropogenic hematite enhanced the overall absorption in the UV and Visible range with maximum absorption at lower wavelength (less than 0.55 μ m). Aging of the pure submicron clay particles with pollutants (AH, BC, AS, AN) significantly enhanced the imaginary part of the refractive index (k) in near infrared window (0.86 to 21.5 μ m) of the solar radiation. Clay aged with pollution mixture of 1.48% AH and 10% BC shows maximum absorption in the ultraviolet region. Highest "k"value (1.2) was observed corresponding to 21.5 μ m wavelength.

Keywords: Complex refractive index, Submicron pure clay, Kaolinite, Illite, polluted clay

Introduction

Fine clay particles are natural aerosols present in the atmospheres. Mineralogical composition of the parental surface influenced the aerosol composition [1]. Submicron clay particles interact with anthropogenic species during long range transport which alters the optical and radiative behaviour of particles. The physico-chemical (morphology and composition) properties of aerosol govern its absorption and scattering behaviour [2-5]. Spectral refractive

index is one of the key parameters in regulating the optical properties of aerosol [3, 6-7]. Refractive indexis composed of real and imaginary part. Real part of refractive index responsible for scattering behaviour of the aerosol, while absorbing nature is determined by the imaginary part [8-9].

For assessment of optical and radiative properties of aerosol, it's necessary to understand the complex refractive index of aerosol. Unfortunately, the computation of complex refractive index leadsto erroneous assessment of particle optical and radiative properties in lack of region-specific refractive index data. In the present work, effect on the spectral refractive index of pure clay aged with the pollution species (AH, BC, AS, AN) has been studied.

Methodology

The fine aerosol samples were collected in Delhi at CSIR-NPL (28.70°N, 77.10°E) using Envirotech sampler (model: APM 550). Elemental analysis reveals occurrence of Aluminosilicates [Kaolinite (K) and Illite (I)] which is evidenced by earlier studies [10-11].Based on the aforesaid findings, five probable submicron pure clay mixtureswere considered [100% K, 100% I, (20% K+80% I), (50% K+50% I), (80% K+20% I)]. Now, these pure clay mixtures were aged with pollution species (AH, BC, AS, AN) with varying composition of anthropogenic hematite [AH] (0.10% to 1.48%), black carbon [BC] (2-10%), Ammonium Nitrate [AN] (8%) and Ammonium Sulphate [AS] (13%). Effective refractive index was calculated using volume mixing rule.

Result and Discussion

Studies reported black carbon 6-10% variation for Indian environment [15] and urban environment like Delhi reported 10% BC, 8% AN and 13% AS. Studies show that the anthropogenic iron emitting from biomass burning and other combustion sources ranges from 0.10% to 1.48%. Figure 1 shows the spectral refractive index of submicron aged clay (i.e. pure clay mixtures aged with AH) for aforementioned AH percentages i.e. 0.10% and 1.48%. Aging with AH, increased the overall k value of refractive index in UV, visible and NIR wavelength. Maximum enhancement was observed at 0.38 μ m wavelength. Hematite acts as strong absorber of incoming solar radiation especially at short wavelength in blue spectral region [2, 12-14]. AH enhances the absorption of submicron clay particles with maximum enhancement observed at wavelength -0.55um. Mixing of AH with pure submicron clay

particles shows negligible effects on absorption of incoming solar radiation in Infrared region.

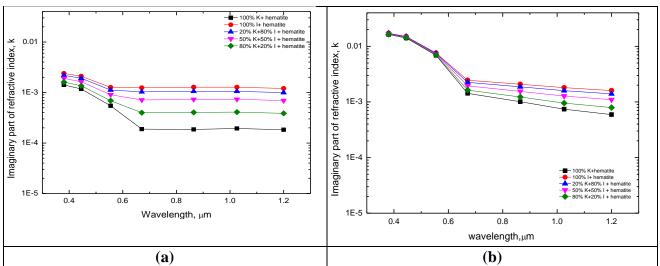


Figure 1: Imaginary part of refractive index of submicron clay particles (variable percentage of illite and kaolinite clay mixtures have been considered) which are polluted with anthropogenic hematite (a) 0.010 % (b) 1.48%.

Conclusion

Complex refractive index of pure submicron clay particlesis influencedbecause of the aging with the considered species. Anthropogenic species like AH, BC enhances the absorption while species like ammonium nitrate and ammonium sulphate tends to decrease the absorption due to their scattering behaviour.

References

[1] I. N. Sokolik and O. B. Toon, Incorporation of mineralogical composition into models of the radiative properties of mineral aerosol from UV to IR wavelengths, JOURNAL OF GEOPHYSICAL RESEARCH, 104 (1999) 9423-9444.

[2] Mishra, S. K., and Tripathi, S. N., Modeling optical properties of mineral dust over the Indian Desert, J. Geophys. Res., 113, (2008), D23201, doi: 10.1029/2008JD010048.

[3] Mishra, S.K.; Agnihotri, R.; Yadav, P.; Singh, S.; Prasad, M.V.S.N.; Praveen, P. S.; Tawale, J. S.; Rashmi; Mishra, N. D.; Arya, B. C.; Sharma, C. Morphology of atmospheric particles over semi-arid region (Japur, Rajasthan) of India: Implication for optical properties. Aerosol and Air Quality Research. (2015), 15:974-984.

[4] Mishra, S. K.; Saha, N.; Singh, S.; Sharma, C.; Prasad, M.V.S.N.; Gautam, S.; Misra, A.; Gaur, A.; Bhattu, D.; Ghosh, S.; Dwivedi, A.; Dalai, R.; Paul, D.; Gupta, T.; Tripathi,S. N.; Kotnala, R.K. Morphology, mineralogy and mixing of individual atmospheric particles over Kanpur (IGP): Relevance of homogenous equivalent sphere approximation in radiative

models. MAPAN-Journal of Metrology Society of India. (2017),DOI 10.1007/s12647-017-0215-7.

[5] Mishra, S. k., Ahlawat, A., Khosla, D., Sharma, C., Prasad, M.V.S.N., Singh, S., Gupta, B., Tulsi, Sethi, D., Sinha, P.R., Ojha, D. K., Wiedensohler, A., Kotnala, and R. K., Experimental investigation of variations in morphology, composition and mixing-state of boundary layer aerosol: A balloon based study over urban environment (New Delhi), Atmospheric Environment, 185, (2018), 243–252

[6] Cappa, C. D., Che, D. L., Kessler, S. H., Kroll, J. H., and Wilson, K. R., Variations in organic aerosol optical and hygroscopic properties upon heterogeneous OH oxidation, J. Geophys. Res.,(2011),116.

[7] Goel, V., Mishra, S. K., Lodhi, N., Singh, S., Ahlawat, A., Gupta, B., Das, R. M., Kotnala, R. K., Physico-chemical characterization of individual Antarctic particles: Implications to aerosol optics, Atmospheric Environment 192 (2018) 173-181.

[8]Bohren, C. F., and Huffman, D. R. Absorption and Scattering of Light by Small Particles, John Willey, Hoboken, N. J,(1983),550 pp.

[9] Seinfeld, J. H., and Pandis, S. N. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley, (2006), Hoboken, N. J.

[10] Soil Survey and Land Use Plan of Delhi Territory (1979), National Bureau of Soil Survey and Land Use Planning.

[11] K. P. Tomar, High-spacing Irregularly Interstratified Layer-silicates in the Alluvial Soil Clays of Meerut, India. Clay Minerals (1985) 20: 115-124.

[12]X. L. Zhang, G. J. Wu, C. L. Zhang, T. L. Xu, and Q. Q. Zhou, What is the real role of iron oxides in the optical properties of dust aerosols?, Atmos. Chem. Phys.(2015) 15: 12159–12177.

[13]D. R. Longtin, E. P. Shettle, J. R. Hummel and J. D. Pryce, A Wind Dependent Desert Aerosol Model: Radiative Properties, Air Force Geophys. Lab., (1988), Air Force Syst. Command Hanscom Air Force Base, Mass, AFGL-TR-88-0112, 115.

[14] Y. Derimian, A. Karnieli, Y. J. Kaufman, M. O. Andreae, T. W. Andreae, O. Dubovik, W. Maenhaut and I. Koren, The role of iron and black carbon in aerosol light absorption, Atmos. Chem. Phys., (2008) 8, 3623–3637.

[15] UNEP (United Nations Environment Programme), 2011. Report. www.unep.org.