

**INVESTIGATION OF CLIMATE RELEVANT PROPERTIES OF
AEROSOL AND CONTRIBUTION OF SOURCES IN ARID REGION,
BIKANER, INDIA**

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**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JULY 2023**

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by

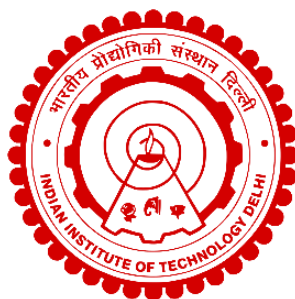
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Submitted

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to the



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CERTIFICATE

This is to certify that the thesis entitled “**Investigation of climate relevant properties of aerosol and contribution of sources in arid region, Bikaner, India**” being submitted by **Ms. Sayantee Roy** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** is a record of the original bonafide research work carried out by her under my guidance and supervision. The thesis work, to the best of my knowledge, has reached the requisite standards fulfilling the requirement for the Degree of Doctor of Philosophy.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.



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Sayantee Roy

ABSTRACT

The concern of deteriorating air quality and the problem of climate change has been linked to dynamics of atmosphere aerosols (or particulate matter, PM). Due to the ubiquitous presence and dynamic nature of aerosols from source to sink, large uncertainties arise in their assessment related to regional and global climate impacts and health effects. As the behaviour are sensitive to a combination of factors like source and meteorology that determines its residence time and transformations in the atmosphere, detailed study in topographically and climatologically distinct regions of the world, and the inclusion of the findings in climate models is sensed useful to reduce prediction uncertainties. Moreover, strategic planning for policy making in order to address local air quality requires baseline understanding of emission sources and impacts. Therefore, this research work is the first set of measurements designed to study the variations, interactions and interrelations of aerosol properties in a typical arid area in the western region of India, where local and regional pollution mixes with natural crustal components. To achieve the designed objectives a top-down approach for identification of probable source of airborne PM is followed in this study, that includes a continuous particle sampling for a two-year period, and measurement of the suite of chemical constituents (elemental and organic carbon, ions, trace metals), followed by source identification by receptor modelling. To address a comprehensive physico-chemical characterization of aerosols and its effect of optical properties that regulates the local air and regional climate, the period of typically substantial PM load seasons was studied.

Exploration of the chemical constituents of PM_{2.5} revealed strong seasonality for PM_{2.5} and its constituents. Highest OC and EC concentrations ($\mu\text{g m}^{-3}$) were found during post-monsoon (15 ± 17 and 5 ± 3) and winter (15 ± 10 and 6 ± 4), respectively, and lowest (2 ± 1 and 0.5 ± 0.9), respectively, in the monsoon. The study site located in an arid region mixed with urban establishment. The favourable atmosphere (temperature $>30^\circ\text{C}$ and humidity $\sim 50\%$) during monsoon and availability of precursors to instigate photooxidation through OH radicals led to transformation of highly volatile organic fractions (OC1) to less volatile higher molecular weight organic fractions and increased the water solubility of OC to form WSOC i.e water-soluble organic carbon (66% of OC). The production of water soluble inorganic ions ($\mu\text{g m}^{-3}$) through aqueous phase chemistry governed PM_{2.5} mass in winter (45.4 ± 31.8 ; 51%) and post-monsoon (32.3 ± 18.5 ; 42%). Another interesting finding is the chemical neutralization during dust prone seasons were regulated by cations of crustal origin, whilst, in colder seasons by NH_4^+ . Majorly, an ammonia-rich environment was

prevalent in winters and post-monsoon, when likely formations of ammonium salts were seen. On contrary, compounds of crustal origin were prevalent at ammonium-poor conditions (warmer months). Saline soil and playa lakes of Thar desert has been a consistent natural source of NaCl and Na₂SO₄. Overall mean concentrations ($\mu\text{g m}^{-3}$) of major (Mg, S, Si, Al, Cl, Ca, Fe and K) and minor trace metals were found as 19 ± 17 and 0.5 ± 0.4 respectively. Non-water-soluble Ca and Mg existed as CaCO₃, MgO and Mg(OH)₂. Inhibited photochemical dissociation causing elevated ambient HNO₃ during colder days facilitated the formation of highly soluble and hygroscopic Ca(NO₃)₂, which is deliquescent at >10% RH, and could catalyse CCN and denser haze formations.

To identify the source contributions based on the chemical composition USEPA-PMF5.0 was run and the analysis resolved eight factors which represents eight sources identified by their chemical profiles together with tracer species. The sources resolved were: Secondary sulphate (25.2%), resuspended dust (23.6%), residential cookstove (13.4%), smelter and non-tail-pipe emissions (11.3%), vehicular emissions (10.8%), lake and sea salt (8.5%), secondary nitrate (4.8%), and brick kilns (2.2%). Winter and post-monsoon PM concentrations in the region were majorly regulated by secondary sulphate and residential cookstove emissions, contributing to 22% and 22-27%, respectively. Dust storms prevalent in the region during pre-monsoon and monsoon have resulted in higher resuspended dust contribution (30-43%) from crustal sources during these seasons. Salt lakes in the region have influenced the fine PM mass with its effect aggravated during the monsoon by the sea-salts from the Arabian Sea. PM_{2.5} mass has been impacted by salt lakes in the area, which is exacerbated during the monsoon by sea-salts from the Arabian Sea. Smelters, non-tailpipe emissions, and vehicular emissions were substantial contributors to moderately polluted to poor conditions (PM_{2.5} mass >60 $\mu\text{g m}^{-3}$). Furthermore, highest PM_{2.5} loading (>90 $\mu\text{g m}^{-3}$) marking the very poor conditions in the region was contributed by residential cookstove emissions and secondary sulphate. Vehicular emissions and numerous smelters from northern states had potential influence on PM mass. The prominent seasonality in the source contributions observed in this study is particularly suggestive of substantial influence of meteorology on PM loading in the region.

The inter-relation between physiochemical and optical characteristics of aerosols during the post-monsoon (Oct, Nov, Dec) and winter (Jan-2021) were inspected by categorizing the days of these seasons into clear (37%), light (33%) and high (31%) pollution periods based on horizontal visibility and measured PM_{2.5} concentrations. Elemental and organic carbon

($50 \pm 15 \mu \text{g m}^{-3}$; 31%) and secondary inorganics ($53 \pm 21 \mu \text{g m}^{-3}$; 33%) dominated the $\text{PM}_{2.5}$ mass ($160 \pm 4 \mu \text{g m}^{-3}$) during high pollution period with low dust ($14 \pm 7 \mu \text{g m}^{-3}$; 8%) content. Interestingly, the clear pollution period was also influenced by carbonaceous fraction ($19 \pm 8 \mu \text{g m}^{-3}$; 32%) and secondary inorganics ($19 \pm 5 \mu \text{g m}^{-3}$; 32%), but the $\text{PM}_{2.5}$ concentrations ($59 \pm 9 \mu \text{g m}^{-3}$) were $\sim$ one-third as compared to high pollution period. High scattering coefficients were observed which were comparable to highly polluted Indian city like Delhi. An exponential increase in non-absorbing material was observed and showed a clear influence on light absorption capacity of EC and dust due to coating/mixing. Higher absorption Ångström exponent (AAE) > 0.6 was observed for substantial BrC (Brown carbon), BC (Black carbon) and dust while increase in non-absorbing to absorbing components ratio > 4 and low amount of EC ($< 4\%$) and BrC reduces AAE below 0.4. Higher mass absorption cross-section ($> 30 \text{ m}^2 \text{g}^{-1}$ of EC) was observed when 4-10% EC fraction of $\text{PM}_{2.5}$ associated with 2.5-3.5 times non-absorbing components to total absorbing components. Likewise, absorption enhanced by three to five-fold compared to uncoated EC for low EC fraction (3-6%) in $\text{PM}_{2.5}$, but for high non-absorbing to absorbing component ratio (> 2.5). Interestingly, absorption was minimally amplified for nominal coating fraction associated with significant core materials or vice-versa. These findings have implications not only in regional climate assessment but also for other regions with comparable geography and source-mixes.

Overall, the study puts forward a complete understanding of the chemical composition and source contribution of fine particulate matter in an arid desert region, with urban influences. Distinct aerosol properties in the region revealed from the study emphasizes the importance to include region specific aerosol properties in the climate models to reduce uncertainties. The results of this work are expected to serve as database to address global climate change in response to long-range transport to and from a desert region with urban influence. Additionally, this work is expected to provide a valuable understanding for researchers, and climate modellers to incorporate the inputs exclusive to similar regions in climate models to obtain more accurate region-specific predictions of future climate change.

सारांश

बिगड़ती वायु गुणवत्ता की चिंता और जलवायु परिवर्तन की समस्या को वायुमंडल के एरोसोल (या पार्टिकुलेट मैटर, पीएम/PM) की गतिकी से जोड़ा गया है। स्रोत से सिंक तक एरोसोल की सर्वव्यापी उपस्थिति और गतिशील प्रकृति के कारण, क्षेत्रीय और वैश्विक जलवायु प्रभावों और स्वास्थ्य प्रभावों से संबंधित उनके मूल्यांकन में बड़ी अनिश्चितताएं पैदा होती हैं। चूंकि व्यवहार स्रोत और मौसम विज्ञान जैसे कारकों के संयोजन के प्रति संवेदनशील होता है जो इसके निवास समय और वातावरण में परिवर्तन को निर्धारित करता है, दुनिया के स्थलाकृतिक और जलवायु संबंधी रूप से अलग-अलग क्षेत्रों में विस्तृत अध्ययन, और जलवायु मॉडल में निष्कर्षों को शामिल करना भविष्यवाणी अनिश्चितताओं को कम करने के लिए उपयोगी माना जाता है। इसके अलावा, स्थानीय वायु गुणवत्ता को संबोधित करने के लिए नीति निर्माण की रणनीतिक योजना के लिए उत्सर्जन स्रोतों और प्रभावों की आधारभूत समझ की आवश्यकता होती है। इसलिए, यह शोध कार्य भारत के पश्चिमी क्षेत्र के एक विशिष्ट शुष्क क्षेत्र में एरोसोल गुणों की विविधताओं, अंतःक्रियाओं और अंतर्संबंधों का अध्ययन करने के लिए पहला परीक्षण डिज़ाइन किया गया है, जहां स्थानीय और क्षेत्रीय प्रदूषण प्राकृतिक भूपर्पटी घटकों के साथ मिश्रित होता है। डिज़ाइन किए गए उद्देश्यों को प्राप्त करने के लिए इस अध्ययन में वायुजनित पीएम के संभावित स्रोत की पहचान के लिए एक टॉप-डाउन दृष्टिकोण का पालन किया गया है, जिसमें दो साल की अवधि के लिए निरंतर कण नमूनाकरण, और रासायनिक घटकों (एलमेन्टल और ऑर्गेनिक कार्बन, आयनों, ट्रेस धातुओं) के समूह का माप शामिल है, इसके बाद रिसेप्टर मॉडलिंग द्वारा स्रोत की पहचान की गई है। एरोसोल के व्यापक भौतिक-रासायनिक लक्षण जाँच-पड़ताल करने के लिए और स्थानीय वायु और क्षेत्रीय जलवायु को नियंत्रित करने वाले ऑप्टिकल गुणों के प्रभाव को संबोधित करने के लिए, आमतौर पर पर्याप्त पीएम लोड सीज़न की अवधि का अध्ययन किया गया था।

PM_{2.5} के रासायनिक घटकों की खोज से PM_{2.5} और उसके घटकों के लिए मजबूत मौसमी स्थिति का पता चला। उच्चतम OC और EC सांद्रता ($\mu\text{g m}^{-3}$) क्रमशः मानसून के बाद (15 ± 17 और 5 ± 3) और सर्दियों (15 ± 10 और 6 ± 4) के दौरान पाई गई, और सबसे कम (मानसून में क्रमशः 2 ± 1 और 0.5 ± 0.9)। अध्ययन स्थल शहरी स्थान के साथ मिश्रित शुष्क क्षेत्र में स्थित है। मानसून के दौरान अनुकूल वातावरण (तापमान $> 30^\circ\text{C}$ और आर्द्रता $\sim 50\%$) और OH रेडिकल्स के माध्यम से फोटोऑक्सीडेशन को प्रेरित करने वाले अग्रदूतों की उपलब्धता के कारण अत्यधिक वाष्पशील कार्बनिक अंशों (OC1) का कम अस्थायी उच्च आणविक भार वाले कार्बनिक अंशों में परिवर्तन हुआ और WSOC बनाने के लिए OC की घुलनशीलता यानी पानी में घुलनशील कार्बनिक कार्बन (OC का 66%) में वृद्धि हुई। जल में घुलनशील अकार्बनिक आयनों का उत्पादन ($\mu\text{g m}^{-3}$) जलीय चरण रसायन विज्ञान के माध्यम से सर्दियों में (45.4 ± 31.8 ; 51%) और मानसून के बाद (32.3 ± 18.5 ; 42%) PM_{2.5} द्रव्यमान को नियंत्रित करता है। एक और दिलचस्प खोज यह है कि धूल वाले मौसमों के दौरान रासायनिक तटस्थता को भूपर्पटी मूल के धनायनों द्वारा नियंत्रित किया जाता था, जबकि ठंडे मौसमों में NH_4^+ द्वारा नियंत्रित किया जाता था। मुख्य रूप से, अमोनिया युक्त वातावरण सर्दियों और मानसून के बाद प्रचलित था, जब अमोनियम लवण के संभावित गठन देखे गए थे। इसके विपरीत, भूपर्पटी मूल के यौगिक

अमोनियम-खराब परिस्थितियों (गर्म महीनों) में प्रचलित थे। थार रेगिस्तान की लवणीय मिट्टी और खारा झीलें NaCl और Na₂SO₄ का लगातार प्राकृतिक स्रोत रही हैं। प्रमुख (एमजी, एस, सी, अल, सीएल, सीए, फे और के) और लघु ट्रेस धातुओं की कुल औसत सांद्रता ($\mu\text{g m}^{-3}$) क्रमशः 19 ± 17 और 0.5 ± 0.4 पाई गई। Ca और Mg, जो गैर-पानी में घुलनशील है CaCO₃, MgO और Mg(OH)₂ के रूप में मौजूद थे। ठंडे दिनों के दौरान बढ़े हुए HNO₃ के कारण बाधित फोटोकैमिकल पृथक्करण ने अत्यधिक घुलनशील और हीड्रोस्कोपिक Ca(NO₃)₂ के गठन की सुविधा प्रदान की, जो >10% RH पर द्रवित होता है, जो सीसीएन और सघन धुंध संरचनाएँ को उत्प्रेरित कर सकता है।

रासायनिक संरचना के आधार पर स्रोत योगदान की पहचान करने के लिए USEPA-PMF5.0 चलाया गया और विश्लेषण ने आठ कारकों का समाधान दिया जो अनुरेखक प्रजातियों के साथ उनके रासायनिक प्रोफाइल द्वारा पहचाने गए आठ स्रोतों का प्रतिनिधित्व करता है। समाधान किए गए स्रोत थे: द्वितीयक सल्फेट (25.2%), पुनर्निलंबित धूल (23.6%), आवासीय चूल्हा (13.4%), स्मेल्टर और गैर-टेल-पाइप उत्सर्जन (11.3%), वाहन उत्सर्जन (10.8%), झील और समुद्री नमक (8.5%), द्वितीयक नाइट्रेट (4.8%), और ईट भट्टे (2.2%)। क्षेत्र में सर्दियों और मानसून के बाद पीएम सांद्रता को मुख्य रूप से माध्यमिक सल्फेट और आवासीय चूल्हा उत्सर्जन द्वारा नियंत्रित किया गया था, जो क्रमशः 22% और 22-27% का योगदान देता था। प्री-मॉनसून और मॉनसून के दौरान क्षेत्र में चलने वाली धूल भरी आंधियों के परिणामस्वरूप इन मौसमों के दौरान भूपर्पटी स्रोतों से उच्च पुनर्निलंबित धूल का योगदान (30-43%) होता है। क्षेत्र में नमक की झीलों ने सूक्ष्म पीएम द्रव्यमान को प्रभावित किया है, जिसका प्रभाव मानसून के दौरान अरब सागर से निकलने वाले समुद्री नमक के कारण बढ़ गया है। क्षेत्र में नमक की झीलों के कारण सूक्ष्म पीएम द्रव्यमान प्रभावित हुआ है, जो अरब सागर से निकलने वाले समुद्री नमक के कारण मानसून के दौरान और बढ़ जाता है। स्मेल्टर, गैर-टेलपाइप उत्सर्जन, और वाहन उत्सर्जन मध्यम प्रदूषित से खराब स्थिति (PM_{2.5} लोडिंग >60 $\mu\text{g m}^{-3}$) में महत्वपूर्ण योगदानकर्ता थे। इसके अलावा, उच्चतम PM_{2.5} द्रव्यमान (>90 $\mu\text{g m}^{-3}$) जो क्षेत्र में बहुत खराब स्थितियों को दर्शाता है, आवासीय कुकस्टोव उत्सर्जन और द्वितीयक सल्फेट के कारण था। वाहन उत्सर्जन और उत्तरी राज्यों के कई स्मेल्टरों का पीएम द्रव्यमान पर संभावित प्रभाव था। इस अध्ययन में स्रोत योगदान में प्रमुख मौसमीता देखी गयी है जो कि विशेष रूप से क्षेत्र में पीएम लोडिंग पर मौसम का पर्याप्त प्रभाव का संकेत देती है।

मानसून के बाद (अक्टूबर, नवंबर, दिसंबर) और सर्दियों (जनवरी-2021) के दौरान एरोसोल की भौतिक रासायनिक और ऑप्टिकल विशेषताओं के बीच अंतर-संबंध का निरीक्षण इन मौसमों के दिनों को क्षैतिज दृश्यता के आधार पर स्पष्ट (37%), प्रकाश (33%) और उच्च (31%) प्रदूषण अवधियों में वर्गीकृत करके किया गया और PM_{2.5} सांद्रता को मापा गया। कम धूल ($14\pm 7 \mu\text{g m}^{-3}$; 8%) सामग्री के साथ उच्च प्रदूषण अवधि के दौरान एलमेन्टल और ऑर्गेनिक कार्बन ($50\pm 15 \mu\text{g m}^{-3}$; 31%) और द्वितीयक अकार्बनिक ($53\pm 21 \mu\text{g m}^{-3}$; 33%) PM_{2.5} द्रव्यमान ($160\pm 4 \mu\text{g m}^{-3}$) पर हावी रहे। दिलचस्प बात यह है कि स्पष्ट प्रदूषण अवधि कार्बोनेसियस अंश ($19\pm 8 \mu\text{g m}^{-3}$; 32%) और द्वितीयक अकार्बनिक ($19\pm 5 \mu\text{g m}^{-3}$; 32%) से भी प्रभावित थी, लेकिन उच्च प्रदूषण अवधि की तुलना में PM_{2.5} सांद्रता ($59\pm 9 \mu\text{g m}^{-3}$) एक तिहाई थी। उच्च प्रकीर्णन गुणांक देखे गए जो दिल्ली जैसे अत्यधिक प्रदूषित भारतीय

शहर के बराबर थे। गैर-अवशोषित सामग्री में तेजी से वृद्धि देखी गई और कोटिंग/मिश्रण के कारण EC और धूल की प्रकाश अवशोषण क्षमता पर स्पष्ट प्रभाव देखा गया। BrC (ब्राउन कार्बन), BC (ब्लैक कार्बन) और धूल के लिए उच्च अवशोषण एंगस्ट्रॉम एक्सपोनेंट (AAE) >0.6 देखा गया, जबकि गैर-अवशोषित-अवशोषित घटकों के अनुपात में 4 से अधिक की वृद्धि और EC की कम मात्रा (4% से कम) और BrC AAE को 0.4 से कम कर देता है। उच्च द्रव्यमान अवशोषण क्रॉस-सेक्शन (EC का $30 \text{ m}^2 \text{ g}^{-1}$) तब देखा गया जब $\text{PM}_{2.5}$ का 4-10% EC अंश कुल अवशोषित घटकों के 2.5-3.5 गुना गैर-अवशोषित घटकों से जुड़ा था। इसी तरह, $\text{PM}_{2.5}$ में कम EC अंश (3-6%) और उच्च गैर-अवशोषित-अवशोषित घटक अनुपात (>2.5) के लिए अनकोटेड EC की तुलना में अवशोषण तीन से पांच गुना बढ़ गया। दिलचस्प बात यह है कि महत्वपूर्ण कोर सामग्रियों से जुड़े नाममात्र कोटिंग अंश के लिए अवशोषण को न्यूनतम रूप से बढ़ाया गया था या इसके विपरीत। इन निष्कर्षों का न केवल क्षेत्रीय जलवायु मूल्यांकन पर बल्कि तुलनीय भूगोल और स्रोत-मिश्रण वाले अन्य क्षेत्रों पर भी प्रभाव पड़ता है।

कुल मिलाकर, अध्ययन शहरी प्रभावों के साथ एक शुष्क रेगिस्तानी क्षेत्र में सूक्ष्म कणों की रासायनिक संरचना और स्रोत योगदान की पूरी समझ को सामने रखती है। क्षेत्र में विशिष्ट एयरोसोल गुणों ने अनिश्चितताओं को कम करने के लिए जलवायु मॉडल में क्षेत्र विशिष्ट एयरोसोल गुणों को शामिल करने के महत्व को उजागर किया। इस कार्य के परिणाम शहरी प्रभाव वाले रेगिस्तानी क्षेत्र से लंबी दूरी के स्थानांतरण के जवाब में वैश्विक जलवायु परिवर्तन को संबोधित करने के लिए डेटाबेस के रूप में काम करने की उम्मीद है। इसके अतिरिक्त, इस कार्य से भविष्य के जलवायु परिवर्तन की अधिक सटीक क्षेत्र-विशिष्ट भविष्यवाणियां प्राप्त करने के लिए जलवायु मॉडल में समान क्षेत्रों के विशेष इनपुट को शामिल करने के लिए शोधकर्ताओं और जलवायु मॉडलर्स को एक मूल्यवान समझ प्रदान करने की उम्मीद है।

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