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Title: DEVELOPMENT OF NANOPHOTOCHEMICALS FOR AGRI-BIOMASS DERIVED LIGNIN VALORIZATION AND PHOTODYNAMIC APPLICATIONS

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Publisher: IISER Mohali Abstract:

ndia is currently experiencing significant indoor and outdoor air pollution from urbanization, industry, and population increase. Because of its harmful effects on the lungs and respiratory system, air pollution is one of the main causes of morbidity and early mortality. 17.8% of India's all-cause mortality in 2019 was attributable to hazardous gases and suspended particulate matter in the air. The environmental impacts of urban development are generally believed to follow a Kuznets inverted U-curve. According to the hypothesis, environmental contamination increases during the early stages of economic expansion, but when higher income levels are reached, the environment improves. Globally several developed countries have passed the inflection point of the Kuznets curve, and have a well-organized urban air quality management system. However, in India, urbanization has been unbalanced and focused on a limited set of megacities to which people are migrating in search of better income options. These megacities are becoming regional air pollution hotspots. Tree plantation, a short-term intervention measure, was always promoted as a mitigation strategy to reduce air pollution in India. Trees absorb gaseous air pollutants through leaf stomata, sequester particulate matter and gases via dry deposition on their surface. Thus, urban green areas may help to improve urban air quality. However, during photosynthesis, many trees release volatile organic compounds (VOCs) known as biogenic volatile organic compounds (BVOCs). In cities with high NOx levels, VOCs are precursors that fuel the production of secondary pollutants such as tropospheric ozone and secondary organic aerosol. Therefore, planting unsuitable high BVOC emitting species in such areas may worsen regional air quality rather than improve it. Urban sites are high-stress environments, and different biotic and abiotic factors impede a tree's growth and cause tree mortality, making it difficult for vegetation to flourish in such an environment. Due to this at present the air pollution tolerance index (APTI) is given a high weightage when selecting species for urban plantations. Also, because of land constraints, urban plantations only contain minor patches of woods and semi-natural ecosystems. Hence, choosing the most suitable species is crucial to maximizing the advantages of a small amount of greenery. My research focused on how vegetation reduce air pollution, specifically on how to identify the most suitable tree species to plant and how to measure the impact of urban vegetation on air quality quantitatively and reliably. My research outcome proposes a new index to assess the air quality impact of trees in an urban environment termed: The Air Quality Impact Index (AQII). This index provides better criteria for evaluating a species for urban plantation based on factors like aerodynamic properties, leaf structure, pollution uptake potential, pollution tolerance, ozone and aerosol precursor emissions, and pollen allergy impact. I also discuss and compare the drawbacks of existing tree selection methods for urban plantation schemes that are employed in India namely: The air pollution tolerance index (APTI) and the Anticipated performance index (API). The argument for a better index was justified by contrasting the urban air impact of two equally recommended species as per API score, namely Mangifera indica (API = 5.9 ± 0.9) and Polyalthia longifolia (API = 4.8 ± 1.0). Mangifera indica is a high isoprene and moderate monoterpene emitter, whereas Polyalthia longifolia is a non-isoprene emitter and a low monoterpene emitter. Both are equally recommended for urban plantation at present. The impact of both species on ozone formation differs by two orders of magnitude when these species are planted in a NOx rich roadside environment. Polyalthia longifolia sequesters more ozone through its stomata than can be formed from its precursor emissions even in summer and hence reduces ozone levels both at the site itself and downwind. For Mangifera indica the ozone formation potential of its precursor emission flux is 4 times larger than the stomatal uptake during peak daytime. Hence, the plantation of Mangifera indica would fuel tropospheric ozone production and exceedances both at the plantation site as well as downwind and can aggravate rather than ameliorate ozone exceedance events. I find that the high API of Mangifera indica resulted from its high APTI and its economic value. Whereas pollution tolerance is necessary criteria for selecting trees to be planted in polluted environments it is not sufficient to evaluate the impact of trees on urban air quality. When my newly proposed index is used to evaluate the suitability of both species, Polyalthia longifolia has a score of 22 and is highly recommended for urban plantations. Mangifera Indica, has a score of 11 owing to its high ozone and SOA formation potential. Species with a score of 11-16 should only be planted after conducting a sitespecific impact assessment, which in this case would rule out plantation in environments where ozone production is VOC limited. Further, I reviewed 149 globally known urban species for their isoprene and monoterpene emission potential, pollen allergy potential, stomatal conductance, and morphological characteristics and calculated the new AQII for 98 species. For 52 species with API rank reported in the literature, the AQII was also compared with the API score. Next in terms of process based understanding, I investigated whether vegetation can be helpful in sequestering pollutants that are primarily emitted at night through stomatal uptake. To this end I conducted field work and found several species have a non-zero nighttime stomatal conductance. I compared two fundamental approaches to estimate the stomatal flux potential of trees and stomatal conductance as a function of various environmental factors, to see which model is able to capture the observed behavior better. Among the two methods namely multiplicative and photosynthetic, the former is believed to be a better approach for leaf-level and regional-level applications. However, through my results, I demonstrated the superiority of the photosynthetic approach. I optimized and ran the DO3SE (Deposition of Ozone for Stomatal Exchange) dry deposition model for four years (2018-2021) with input data and compared the model output with the field measurements on Mangifera indica. The multiplicative model overestimates the daytime stomatal conductance when compared with measured stomatal conductance and prescribes zero conductance at night, while measurements show an average conductance of 100 mmol (H2O) m-2s-1 between 9 p.m. and 4 a.m. However, the photosynthetic model, which incorporates the overnight stomatal opening during respiration, can replicate the observed night-time stomatal conductance. Further results show the nocturnal flux contributes 64%, 39%, 46%, and 88% of the total for NO2 uptake in winter, summer, monsoon, and postmonsoon, respectively. For SO2, nocturnal uptake amounts to 35%, 28%, 28%, and 44% in winter, summer, monsoon, and post-monsoon, respectively, while for ozone, the night-time uptake contributes 30%, 17%, 18%, and 29% of the total stomatal uptake in winter, summer, monsoon, and post-monsoon, respectively. I also propose strategies to improve the DO3SE photosynthetic and multiplicative models in the future. My thesis also showed that studying the environmental response functions of tropical tree species yields amazing new insights. In Mangifera indica I found an exceptional tolerance to hot and dry air. The tree is capable of maintaining maximum stomatal conductance till a vapor pressure deficit (VPDmax) of 8 kPa. This is more than double the highest VPDmax observed for any other tropical tree species so far studied. This may be a peculiar adaptation of plant species that evolved to flower and fruit during the drought that precedes the onset of the rainy season in tropical winter dry climates. The high cooling potential of mango orchards during the hottest season of the year which is accompanied by high pollution tolerance may indeed be one of the key reasons why urban planners favour such plantations despite the fact that they fuel tropospheric ozone formation.

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