Goldschmidt 2024 Abstract
https://doi.org/10.46247/gold2024.23033

Nitrated Aromatic Compounds in atmosphere: emissions, secondary formation and potential health risks

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Nitrated aromatic compounds (NACs), encompassing nitro groups (-NO_2) adorned aromatic rings or a polyaromatic hydrocarbons (PAHs), serve diverse industrial roles. Beyond industrial use, NACs emit from combustion sources like biomass burning and vehicle emission, and they can also form secondarily in the atmosphere. Despite their trace levels in ambient particulate matter (PM), NACs raise health and climate concerns due to their toxicity and light-absorbing characteristics. Here we first characterized emissions of PM-bound NACs, especially nitrated polycyclic aromatic hydrocarbons (NPAHs) and nitrophenols (NPs), from on-road fleets based on tests in an urban tunnel frequented by over 30,000 vehicles daily. Through regression analysis, we determined average emission factors for diesel and gasoline vehicles, identifying diesel vehicles as the dominant NAC sources. Although the emission factors of 7 toxic NACs were around 3% those for the 16 USEPA priority PAHs, their benzo(a)pyrene toxic equivalence quotients (TEQ_{BaP}) approached over 25% that of the PAHs. Remarkably, 6-nitrochrysene, predominantly from diesel vehicles, contributed 93% of the total NAC TEQ_{BaP}. Further, we explored PM-bound NACs from agricultural waste combustion, using corn straw burning as a case study. Among the detected NPAHs, 1,6-dinitropyrene emerged as the most prevalent, while 4-nitrocatechol was the dominant NP. Notably, 2-nitropyrene, often associated with secondary NPAH formation, ranked as the second most abundant NPAH sourced from corn straw combustion. The levels of nine toxic NACs were under one-third of those for the 16 USEPA priority PAHs, yet their TEQBaP was roughly tenfold higher. In a final phase, we performed field measurements of $PM_{2.5}$-bound NACs in Guangzhou, China, revealing that the TEQ_{BaP} of NACs were comparable to or exceeding that of PAHs, with significant secondary formation suggested by receptor modeling and molecular markers. This secondary formation was corroborated by smog chamber experiments conducted under various conditions of light, darkness, and relative humidity.