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Impact of Emission Standards on Fine Particulate Matter Toxicity: A Long-Term Analysis in Los Angeles

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Abstract: This study examines long-term trends in fine particulate matter (PM_{2.5}) composition and oxidative potential in Los Angeles based on data from the University of Southern California's Particle Instrumentation Unit, with chemical composition retrieved from the EPA's Air Quality System (AQS). While regulatory interventions have reduced PM_{2.5} mass concentration and primary combustion-related components, our findings reveal a more complex toxicity pattern. From 2001 to 2008, the PM_{2.5} oxidative potential, measured via the dithiothreitol (DTT) assay, declined from ~0.84 to ~0.16 nmol/min/m³ under stringent tailpipe controls. However, after this initial decline, PM_{2.5} DTT stabilized and gradually increased from ~0.35 in 2012 to ~0.97 nmol/min/m³ by 2024, reflecting the growing influence of non-tailpipe emissions such as brake/tire wear. Metals, such as iron (Fe, ~150 ng/m³) and zinc (Zn, ~10 ng/m³), remained relatively stable as organic and elemental carbon (OC and EC) declined, resulting in non-tailpipe contributions dominating PM_{2.5} toxicity. Although PM_{2.5} mass concentrations were effectively reduced, the growing contribution of non-tailpipe emissions (e.g., brake/tire wear and secondary organic aerosols) underscores the limitations of mass-based standards and tailpipe-focused strategies. Our findings emphasize the need to broaden regulatory strategies, targeting emerging sources that shape PM_{2.5} composition and toxicity and ensuring more improvements in public health outcomes.



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1. Introduction

Ambient particulate matter (PM) is a critical environmental health concern globally, associated with many adverse health effects, including respiratory and cardiovascular diseases, lung cancer, and increased mortality rates [1,2]. PM is categorized based on aerodynamic diameter into coarse (PM_{2.5-10}, 2.5 μm ≤ d_p ≤ 10 μm), fine (PM_{2.5}, d_p ≤ 2.5 μm), and ultrafine particles (UFPs, d_p < 0.1 μm) [3,4]. PM_{2.5} poses significant health risks due to its ability to penetrate deep into the lungs, depositing in the alveolar sacs and triggering inflammation and systemic oxidative stress [1,5,6]. Deposited particles translocate into the bloodstream and reach other organs, potentially causing cardiovascular and neurological disorders [7–9]. Studies have demonstrated that residents in urban environments where vehicular emissions are the primary source of PM, such as Los Angeles, experience higher incidences of asthma, lung cancer, and cardiovascular diseases compared to those in less polluted areas [10–14]. In the early 2000s, Los Angeles was often subject to frequent air quality alerts, raising concerns among health professionals about the escalating rates of

respiratory illnesses, especially among vulnerable populations like children and the elderly [15–17]. This public health crisis incited efforts to implement stringent regulatory actions aimed at reducing PM emissions from vehicular and industrial sources [18–20].

Over the past decades, a comprehensive set of federal and state-level air quality measures have substantially improved air quality in Los Angeles and across California [20–22]. At the federal level, the U.S. Environmental Protection Agency (U.S. EPA) introduced the National Ambient Air Quality Standard (NAAQS) for PM_{2.5} in 1987, aiming to reduce ambient concentrations of PM_{2.5} [23,24]. At the state level, the California Air Resources Board (CARB) introduced stringent vehicular emissions programs with the Low Emission Vehicle I (LEV I) initiative in 1990, later followed by LEV II, LEV III, and the Zero-Emission Vehicle (ZEV) program, each tightening emissions limits on non-methane organic gases (NMOGs), carbon monoxide (CO), nitrogen oxides (NO_x), and PM [25–27]. Additional actions included the Diesel Risk Reduction Plan (2000), financial incentives for replacing high-polluting vehicles (1998–2012), such as the Cleaner Port Truck (CPT) program (2007), Drayage Truck Regulation (2008), and At-Berth Regulation (2010), targeting diesel PM and NO_x emissions from freight and maritime activities [28–31]. In 2013, the Low-Carbon Fuel Standard (LCFS) further encouraged the adoption of cleaner fuels, cutting both particulate and greenhouse gas emissions [32,33]. Hasheminassab et al. (2014) [34] conducted a comprehensive analysis of ambient PM_{2.5} in the Los Angeles Basin from 2002 to 2012, finding a notable reduction in PM_{2.5} concentrations, largely attributed to decreased vehicular emissions resulting from the CARB's regulations. Similarly, Lurmann et al. (2015) [20] highlighted a 21% reduction in PM_{2.5} and significant decreases in NO_x and volatile organic compounds (VOCs) over two decades. These improvements underscore the effectiveness of regulatory measures in mitigating air pollution. However, despite these successes, recent studies indicate that the particle number concentration (PNC) of UFPs has not decreased proportionally and may have plateaued from 2016 onwards [22], suggesting that existing regulations may not sufficiently address UFP emissions, potentially due to the complex nature of UFP sources and formation mechanisms, such as secondary formation and non-tailpipe emissions [35,36]. Moreover, PM comprises a diverse mix of chemical components, including organic compounds, metals, and biological materials, with varying levels of toxicity [37–40]. Transition metals and polycyclic aromatic hydrocarbons from combustion processes have been associated with higher oxidative potential, posing greater health risks even as overall PM mass declines [41]. Consequently, PM mass concentration alone may not adequately reflect the health impacts, emphasizing the need to consider PM composition and toxicity [42–44].

One of the primary mechanisms underlying the adverse health effects of PM exposure is the induction of oxidative stress resulting from interactions with biological systems [45,46]. Oxidative stress occurs when the generation of reactive oxygen species (ROS) exceeds the body's antioxidant defenses, leading to cellular damage, inflammation, and exacerbation of respiratory and cardiovascular diseases [47,48]. To quantify the oxidative potential of PM, several assays have been developed, with the dithiothreitol (DTT) assay being one of the most widely used [49–52]. The DTT assay measures the capacity of PM to catalyze electron transfer from DTT to oxygen, simulating redox reactions in biological systems. The rate of DTT consumption correlates with the particle's ability to generate ROS, serving as an indicator of oxidative potential [53,54]. Studies utilizing the DTT assay have provided valuable insights into the relationship between PM composition and toxicity. Verma et al. (2015) [54] demonstrated that organic aerosols and transition metals significantly contribute to the oxidative potential of PM_{2.5}. Despite reductions in PM mass concentrations in Los Angeles, the oxidative potential of PM may not have

decreased proportionally, possibly due to shifts in PM composition towards more toxic constituents [21].

The disconnect between trends of PM mass concentration and toxicity underscores an urgent need to reevaluate air quality metrics and regulatory strategies [4,42,43,55]. Relying solely on mass-based standards may not fully consider the increased health risks posed by the oxidative potential of PM. This study aims to investigate the long-term temporal trends in PM toxicity, focusing on the oxidative potential of PM_{2.5} as measured by the DTT assay in Los Angeles, potentially resulting from PM emission regulations. By examining data spanning the last two decades, we sought to understand the influence of regulatory measures on oxidative potential, considering that none of the regulations specifically targets PM toxicity. This analysis fills a critical knowledge gap and provides insights for policymakers, enabling them to adapt and enhance current and future strategies aimed at improving air quality and public health. By focusing on both PM mass and toxicity, we can develop a more comprehensive understanding of the health impacts of air pollution and devise more effective regulatory interventions.

2. Methods

2.1. Data Collection

Data for PM_{2.5} oxidative potential were collected through a comprehensive review of studies conducted over the past two decades [48,50,56–67]. The initially reported DTT data were presented in different units by various studies (i.e., some as activity per mass of PM, others per volume of air) and were converted between these units using the respective PM mass and sampling duration measurements, ensuring that all DTT data could be directly compared on a consistent basis. Moreover, DTT activity per volume was presented in the main text as it more directly reflects inhalation exposure scenarios, providing a more relevant metric of aerosol oxidative potential for environmental and public health assessments compared to mass-normalized values [68]. Table S1 outlines the sampling campaigns and datasets. Most of these studies were carried out using samplers with consistent protocols for measuring PM oxidative potential [48,50,56–67,69,70]. Detailed information on measurement methods, equipment calibration, instrument specifications, and uncertainties can be found in the original publications cited in Table S1. Most of the DTT data were sourced from the particle instrumentation unit (PIU) of the University of Southern California (USC), which is located in an urban area near downtown Los Angeles, 150 m downwind of a major freeway (I-110). Additionally, the trends of different chemical species such as metals (i.e., barium (Ba), copper (Cu), manganese (Mn), zinc (Zn), chromium (Cr), nickel (Ni), cadmium (Cd), and iron (Fe)) as well as inorganic ions (i.e., sulfate (SO₄^{2−}) and nitrate (NO₃[−]) were obtained from the North Main Street monitoring station, operated by the U.S. EPA as part of the Air Quality System (AQS) and Chemical Speciation Network (CSN) [71]. These trends correspond to the sampling periods of the reviewed DTT studies. It should be noted that these trends were only available from 2005 to 2024, as the CSN did not provide data prior to 2005, and no metals data were available in 2005.

2.2. Additional Sampling, Instrumentation, and Analysis in 2024

The sampling campaigns for PM_{2.5} were conducted at the PIU of the USC during January and February 2024. For PM_{2.5} collection, pre-baked quartz filters (SKC Inc., Eighty-Four, PA, USA) were used in Sioutas Personal Cascade Impactor Samplers (PCISs, SKC Inc., Eighty-Four, PA, USA), operating with a flow rate set at 9 L per minute [72], to ensure accurate mass measurements. This additional sampling during January–February 2024 was conducted to evaluate contemporary conditions under the latest regulatory environment, using the same DTT measurement protocols as earlier datasets, enabling a comparison with

historical trends and highlighting any emerging shifts in PM_{2.5} toxicity. The interpretation of our findings should be contextualized by the temporal limitations of the two-month sampling period, ensuring that conclusions drawn account for potential seasonal variability not captured in this snapshot.

DTT activity serves as a proxy for the oxidative capacity of ambient particles, which may initiate or exacerbate inflammatory processes in humans, and multiple studies have linked higher oxidative potential to elevated cardiopulmonary risks [73,74]. The oxidative potential of collected PM_{2.5} samples was assessed using the DTT assay following established protocols [50,75]. Briefly, PM extracts were incubated with a DTT solution, and the rate of DTT consumption was measured spectrophotometrically, which serves as an indicator of the particle's capacity to generate ROS. All assays were performed in triplicate and under controlled laboratory conditions to ensure consistency and reliability of the results. While consistent protocols were used to reduce uncertainties, the DTT assay has limitations that may not fully capture all pathways of particle-induced oxidative stress due to factors like incomplete extraction, measurement interferences, and sensitivity to specific species [76]. It should be noted that the DTT data provided for PM_{2.5} DTT in 2008 were obtained using the same methodology as described by Verma et al. (2009) [65]. Pearson correlation analyses ($p < 0.05$) were performed to evaluate associations between DTT activity and chemical species concentrations such as OC/EC and metals. All statistical operations were conducted in Python (version 3.12.0) using the numpy (version 1.26.0) and pandas (version 2.1.1) libraries for data handling and analysis.

3. Results and Discussions

3.1. Long-Term Trends in PM_{2.5} Composition

This section presents the yearly averaged concentrations of various PM_{2.5} species based on data retrieved from the AQS, as shown in Figures 1–3, which illustrate long-term trends in PM_{2.5} components in Los Angeles. Additionally, discrete sampling data were also retrieved from the AQS but were limited to the specific dates provided by prior studies for DTT measurements. These discrete sampling data are presented in the Supplementary Information (Figures S1–S3), providing further context on the evolving PM_{2.5} composition and insights into the specific dates when DTT activity was measured.

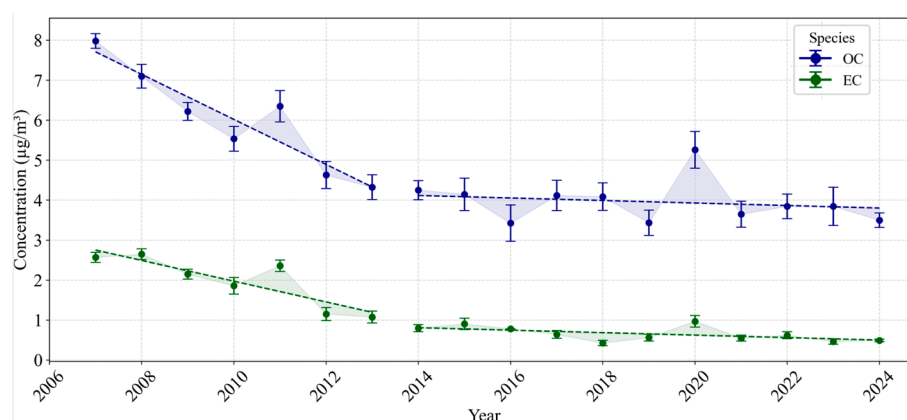


Figure 1. Yearly averaged long-term PM_{2.5} concentrations of OC and EC in Los Angeles (2007–2024).

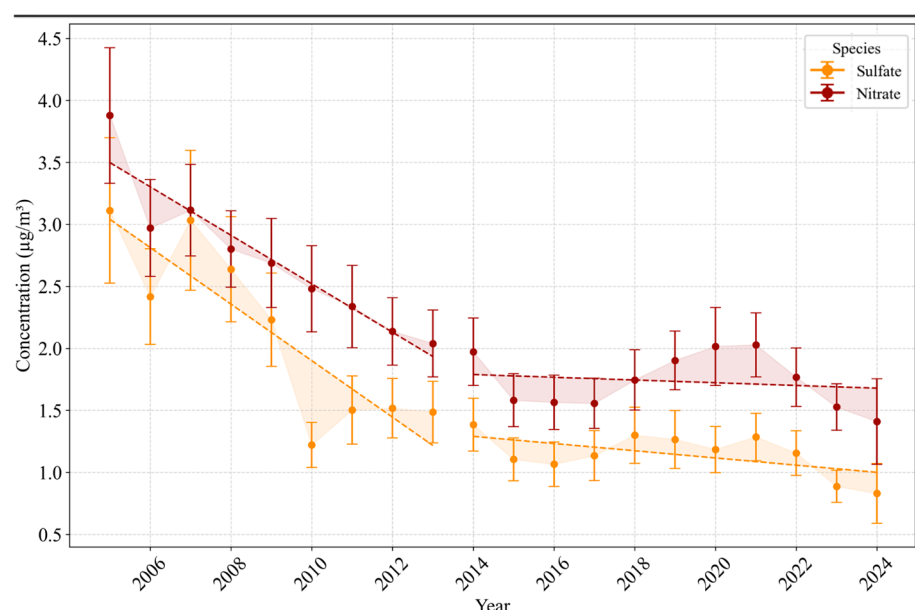


Figure 2. Yearly averaged long-term PM_{2.5} concentrations of sulfate and nitrate in Los Angeles (2005–2024).

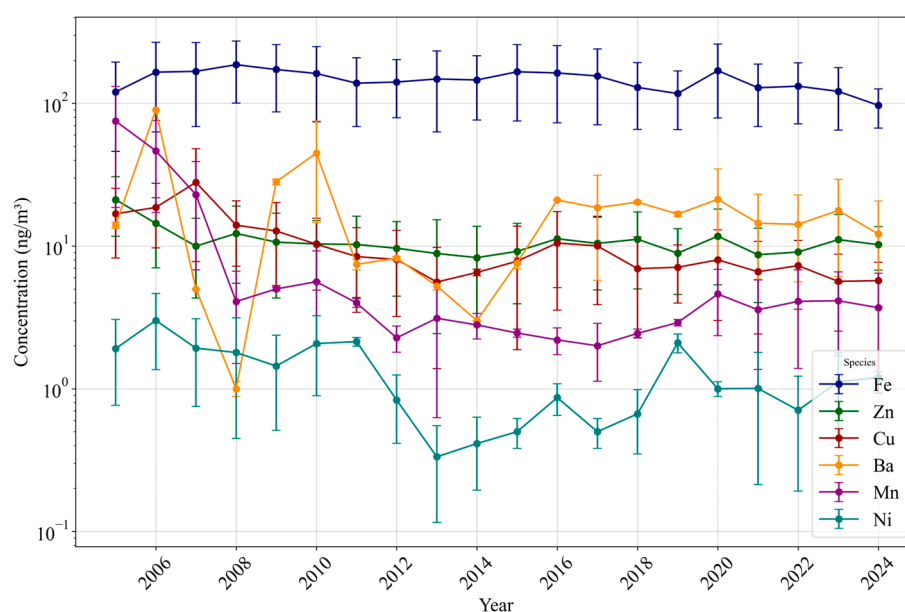


Figure 3. Yearly averaged long-term concentrations of metals in Los Angeles (2007–2024).

3.1.1. Carbonaceous Species: Organic Carbon and Elemental Carbon

Figure 1 presents the yearly averaged concentrations of OC and EC in Los Angeles from 2007 to 2024, revealing two distinct subperiods for both species. During the first subperiod (2007–2016), OC overall decreased from $7.98 \mu\text{g}/\text{m}^3$ in 2007 to $3.43 \mu\text{g}/\text{m}^3$ by 2016. Despite a brief increase to $6.35 \mu\text{g}/\text{m}^3$ in 2011, these marked reductions align with regulatory actions focused on reducing tailpipe emissions [26,30]. This trend aligns with the results of Badami et al. (2024) [22], noting that pollutant reductions were more pronounced during earlier years (2007–2015) due to impactful regulatory efforts targeting primary tailpipe emissions. In contrast, the second subperiod (2017–2024) is characterized by a plateau in OC, varying between approximately $3.43 \mu\text{g}/\text{m}^3$ in 2019 and $5.26 \mu\text{g}/\text{m}^3$ in 2020 before settling around $3.50 \mu\text{g}/\text{m}^3$ in 2024. This stabilization, coupled with intermittent spikes (e.g., the notable increase in 2020 possibly linked to wildfires, including the Bobcat wildfire [77]), suggests

that while tailpipe emissions have been effectively controlled, ongoing contributions from non-tailpipe and secondary aerosol sources continue to influence ambient OC levels [78,79]. This trend is consistent with the findings of Badami et al. (2024) [22], who demonstrated a similar plateau in primary pollutant levels since 2016, underscoring the diminished impact of current regulatory measures and the need for stricter standards. Discrete sampling data corresponding to DTT activity, illustrated in Figure S1, generally align with the overall decreasing trends but also reveal shorter-term variations possibly driven by meteorological factors and transient emission episodes, such as wildfires.

EC exhibits a similar two-phase trend over the same period, with concentrations declining significantly from $2.57 \mu\text{g}/\text{m}^3$ in 2007 to $0.78 \mu\text{g}/\text{m}^3$ in 2016 during the first phase. This marked reduction highlights the success of diesel-specific regulations and fleet modernization in curbing combustion-derived $\text{PM}_{2.5}$ emissions [30]. However, beginning in 2017, EC levels stabilized below $1 \mu\text{g}/\text{m}^3$ without a consistent downward trend, fluctuating between $0.43 \mu\text{g}/\text{m}^3$ in 2018 and $0.97 \mu\text{g}/\text{m}^3$ in 2020 before settling in the range of $0.46\text{--}0.62 \mu\text{g}/\text{m}^3$ by 2024. These findings suggest that residual combustion sources continue to contribute to EC levels, highlighting the need for additional regulatory measures to address these emissions [26]. This trend aligns with observations from Badami et al. (2024) [22], which emphasize the initial effectiveness of regulations followed by a plateau in pollutant levels, underscoring the limitations of existing controls. The concurrent EC measurements corresponding to DTT activity (Figure S1) further support these trends, revealing episodic surges that highlight the interplay between effective tailpipe regulations and transient emission sources. Collectively, the two-phase evolution observed for both OC and EC indicates a sustained decline in primary tailpipe emissions during the earlier years, followed by stabilization in recent years.

3.1.2. Inorganic Ions: Nitrate and Sulfate

Figure 2 illustrates yearly averaged sulfate and nitrate concentrations in Los Angeles from 2005 to 2024, revealing two subperiods consistent with the broader regulatory timeline. During the first subperiod (2005–2016), sulfate decreased from approximately $3.11 \mu\text{g}/\text{m}^3$ in 2005 to $1.06 \mu\text{g}/\text{m}^3$ in 2016, while nitrate similarly declined from $3.88 \mu\text{g}/\text{m}^3$ in 2005 to $1.55 \mu\text{g}/\text{m}^3$ by 2016. This substantial reduction aligns with progressively stricter sulfur and nitrogen oxide controls, which target on-road and off-road sources of NO_x and SO_x [64,80]. In the second subperiod (2016–2024), both sulfate and nitrate remain below their mid-2000s levels but exhibit minor variability. For instance, sulfate concentrations stabilized around $1.50 \mu\text{g}/\text{m}^3$ during 2011–2015, followed by a gradual decline to $0.78 \mu\text{g}/\text{m}^3$ by 2024. Nitrate similarly stabilizes to values near $1.5\text{--}2.0 \mu\text{g}/\text{m}^3$ after 2016, with modest variability across the later years. These plateaus suggest that while tailpipe regulations and fuel improvements have significantly curtailed sulfate and nitrate formation pathways, other factors—including regional atmospheric chemistry, wildfires, and potential contributions from stationary sources—can produce episodic elevations [34,65,81].

Additionally, sulfate and nitrate exhibit broadly consistent downward trends in both the annual AQS dataset (Figure 2) and the discrete sampling intervals used in previous DTT-focused studies (Figure S2). This consistency possibly stems from stronger and more direct controls on sulfur content in fuels and NO_x emissions from on-road and off-road engines, resulting in relatively stable, long-term reductions in these inorganic ions [82]. In contrast, OC and EC levels display more pronounced fluctuations between the annual and discrete datasets. A significant decrease ($p < 0.05$) in OC, EC, nitrate, and sulfate concentrations was observed during the first subperiod (2007–2014), followed by a plateau from 2014 onwards. This trend mirrors total $\text{PM}_{2.5}$ changes in Los Angeles, as corroborated by the work of Badami et al. (2024), affirming that early regulatory efforts were highly

effective, with subsequent gains being more modest [22]. The difference arises because EC and especially OC are influenced by a broader range of sources—beyond tailpipe emissions—including mechanical abrasion (e.g., brake and tire wear), secondary organic aerosol formation VOCs, and re-suspended dust [21,83,84]. These non-tailpipe processes are not as directly constrained by existing regulations, leading to less uniform and at times divergent trends when comparing annual means to snapshots aligned with DTT sampling. As a result, even though EC and OC exhibit predominant declines from early regulatory efforts, their more diverse and evolving source profiles yield significant year-to-year variability not seen in the comparatively steadier trajectories of sulfate and nitrate. Moreover, the maritime sector also emits precursors—often referred to as ‘delayed primary organics’—that transform into secondary organic aerosols, boosting oxidative potential even as sulfur-related emissions decline under stricter fuel regulations [85]. Previous studies have demonstrated that port activities, including ships, locomotives, and heavy-duty vehicles, can substantially affect coastal neighborhoods, contributing to elevated OC levels and reinforcing the role of non-tailpipe sources in driving PM_{2.5} toxicity [85,86].

3.1.3. Trace Elements and Metals

Figure 3 illustrates the yearly trends of key trace elements and metal species in Los Angeles between 2005 and 2024, indicating a comparatively stable pattern over this interval. While OC and EC exhibit clear subperiods of decline, the concentrations of metals such as Ba, Cr, Cu, Fe, Mn, Ni, Ti, and Zn remain relatively constant or fluctuate, reflecting non-tailpipe and largely unregulated sources (e.g., brake/tire wear, resuspended road dust, and industrial emissions) [63,87,88]. In particular, Fe shows the highest concentrations, ranging from approximately 100 to 170 ng/m³, with an average of almost 150 ng/m³ during this period, and occasional spikes, such as ~210 ng/m³ in 2020. Other metals, including Ba, Zn, and Cu, exhibit concentrations around 10–20 ng/m³, consistent with previous findings in the literature [61,87].

These metals do not exhibit the sustained downward trends observed for combustion-related species, indicating that stricter tailpipe regulations have reduced OC and EC emissions, and metals might have emerged as more important contributors to PM_{2.5} toxicity [64]. Concurrent sampling intervals corresponding to reported DTT activities (Figure S3) support this observation, showing that metal concentrations remain substantial even when OC and EC levels are comparatively low. The stable concentrations of metals, combined with the declining trends of tailpipe emission tracers (e.g., OC and EC), suggest an increasing relative contribution of non-tailpipe metal sources to PM_{2.5} oxidative potential as their proportion in PM_{2.5} mass concentrations continues to grow, which is explored in greater detail in the following sections.

3.1.4. Long-Term Trends of the Ratio of Trace Elements and Metals to Elemental Carbon

To further illustrate the shift from tailpipe to non-tailpipe sources, Figure 4 presents yearly concentration ratios of Fe/EC, Zn/EC, Cu/EC, and Ti/EC from 2007 to 2024, derived from a broad set of annual sampling days rather than only those aligned with DTT measurements. To account for the different scales of mean metals’ concentrations, particularly Fe, compared to others, the ratios were normalized using Shift Z-Score Normalization. This method standardizes the data by subtracting the mean and dividing it by the standard deviation for each metal, ensuring comparability across species. Additionally, a constant equal to the minimum Z-score was added to all normalized values to eliminate negative values.

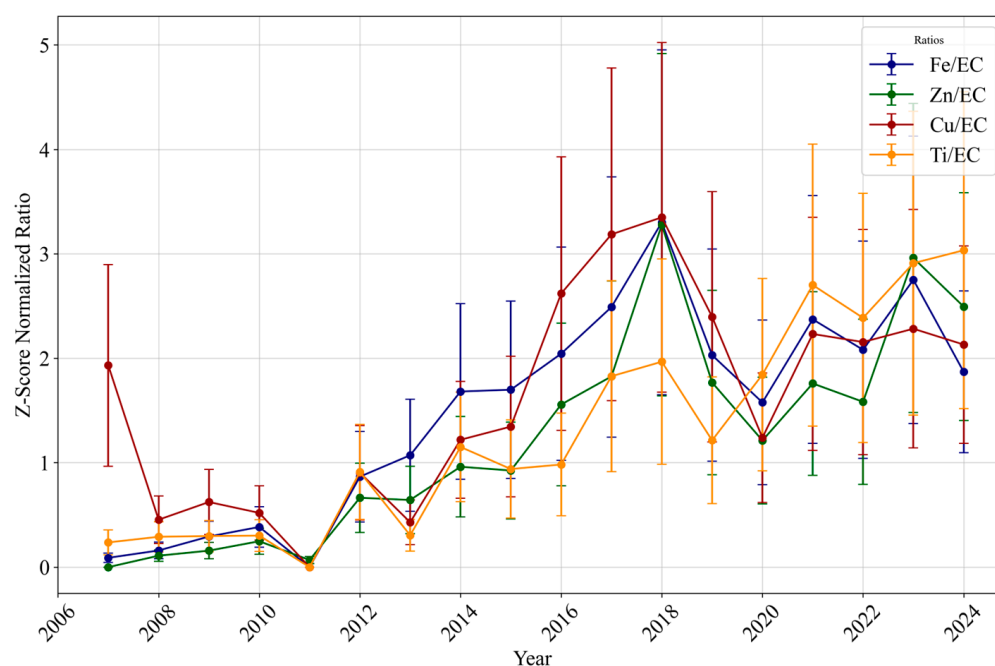


Figure 4. Normalized averaged long-term normalized ratio of specific metals to EC mass in Los Angeles (2007–2024). The error bars represent the standard deviation of the yearly normalized ratios.

The normalized Fe/EC ratio, for example, shows a steady increase from approximately 0.47 in 2007 to 3.65 in 2018, maintaining values around 2.0 in the early 2020s. Similar upward trends are observed for Zn/EC and Cu/EC. The earlier regulatory years exhibit significantly lower metal-to-EC ratios, reflecting the dominant influence of tailpipe emissions during that time. The higher Cu/EC ratio for 2007 can be attributed to comparatively elevated Cu concentrations during that year, as shown in Figure 3, and to the ratio's reliance on Cu data within the Shift Z-Score Normalization process. These rising metal/EC ratios further corroborate the arguments in the previous sections that as regulations effectively reduce tailpipe-related EC emissions in the earlier years, non-tailpipe sources, such as tire and brake wear and re-suspended road dust, contribute an increasing fraction to the PM_{2.5} composition [26,87]. This shift might suggest an increased role of non-tailpipe sources in influencing the oxidative potential of ambient aerosols, as their proportional contribution to PM_{2.5} mass has grown relative to declining tailpipe emissions, which is in agreement with the results reported in the literature [21].

3.2. Trends in DTT Activity and Correlations with Species

3.2.1. Long-Term Trends of Oxidative Potential of PM_{2.5}

Figure 5 presents the long-term oxidative potential of PM_{2.5}, measured by the DTT activity per volume, from 2001 to 2024, revealing two distinct subperiods. The first subperiod (2001–2008) is characterized by a pronounced decline in DTT activity, which decreased from approximately 0.836 nmol/min/m³ in 2001 to 0.163 nmol/min/m³ by 2007. This substantial reduction corresponds to the early phase of tailpipe emissions regulatory actions (initiated in 2000) and the implementation of stricter standards under the U.S. EPA [28,29]. These regulatory actions significantly reduced combustion-derived particulate matter, thereby diminishing the oxidative burden associated with tailpipe emissions.

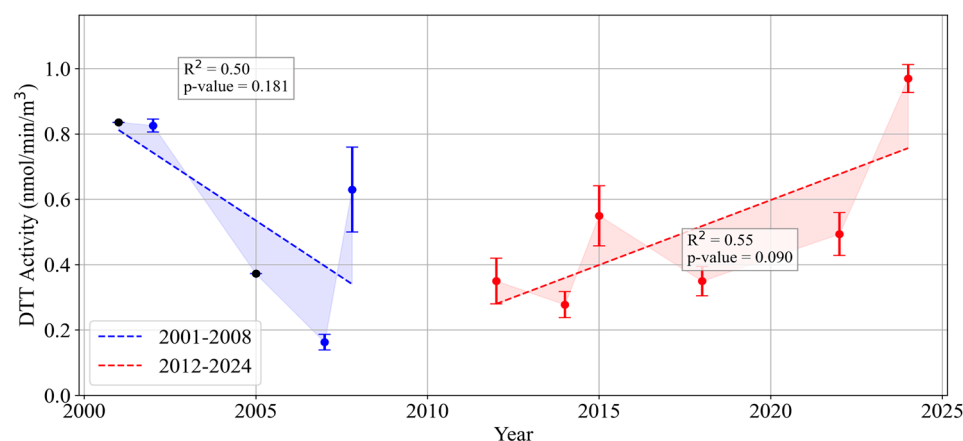


Figure 5. Long-term trends of volumetric DTT activity of PM_{2.5} in Los Angeles (2001–2024).

The second subperiod (2012–2024) reveals a gradual rise in DTT activity, increasing from approximately 0.35 nmol/min/m³ in 2012 to nearly 0.97 nmol/min/m³ by 2024. This trend indicates that while overall PM mass and primary tailpipe tracers such as EC and OC have declined due to ongoing regulatory efforts, alternative sources—particularly non-tailpipe emission tracers (e.g., Fe, Cu, Zn from brake and tire wear) and secondary organic aerosols—have become increasingly significant in influencing PM_{2.5} oxidative potential [61]. These findings align with the concurrent shift in PM composition discussed in Sections 3.1.3 and 3.1.4, where metals and friction-derived emissions emerged as major contributors to ambient toxicity. As older diesel fleets were retrofitted or replaced and advanced emissions controls were implemented, the relative contribution of non-tailpipe sources grew, reflecting a broader transformation in the composition of urban PM in Los Angeles [80,89]. Consequently, the PM_{2.5} DTT activity per volume highlights an evolving toxicity profile increasingly driven by mechanisms and species not directly targeted by traditional tailpipe-focused regulations.

Figure S4 further complements this analysis by presenting the long-term trend of DTT activity per PM_{2.5} mass in Los Angeles. Similar to the per-volume metric, DTT per mass reveals two subperiods, with an initial decline during the early regulatory years, consistent with the success of early tailpipe-focused measures. However, following this initial reduction, DTT per mass exhibits a much slower rate of decrease, approaching a near-stable or very slow decline in later years. This subtle downward trend suggests a gradual rather than pronounced reduction in intrinsic aerosol toxicity over time.

The distinction between per-volume and per-mass trends highlights a shift in PM_{2.5} composition. The initial reduction in DTT activity per volume reflects regulatory success in reducing the overall ambient PM concentration. However, the slower decline in DTT activity per mass suggests that the composition of the remaining PM has shifted toward a higher relative contribution of more toxic components, such as non-tailpipe metals, secondary organic aerosols, and frictional emissions. This compositional shift underscores the growing proportional role of unregulated sources as primary components like sulfates, nitrates, and EC were reduced. These trends suggest that while overall PM_{2.5} mass concentrations declined due to tailpipe emission controls, the oxidative potency of the remaining PM_{2.5} mass remains significant, driven by emerging non-tailpipe and secondary sources, emphasizing the importance of expanding regulatory efforts to address these sources to further mitigate PM_{2.5} toxicity.

3.2.2. Correlations of Species with PM_{2.5} DTT Activity

Figure 6a,b presents long-term trends in the correlations between DTT activity and key PM_{2.5} constituents, including EC, OC, Fe, Zn, Cu, Mn, and Pb, based on data collected in Los Angeles from 2012 to 2024. We examined the correlation between individual chemical species and volumetric DTT activity to highlight the key contributors to PM_{2.5}-induced oxidative stress [90]. Only statistically significant correlations ($p < 0.05$) are shown in the figure. Over time, the correlations between metals (e.g., Fe, Zn, Cu, Mn, and Pb) and DTT activity tend to strengthen, consistent with earlier studies that identified transition metals as major drivers of PM oxidative potential [53,73,91]. By the 2015–2018 period, correlation coefficients for these metals were notably higher, reflecting the increasing contribution of non-tailpipe metal emissions to the oxidative potential of fine PM as tailpipe-related sources diminished under the influence of regulatory measures [87,92]. Although the 2018 dataset [57] included averages from multiple global cities—potentially introducing some variability not solely attributable to local factors—the overall pattern still aligns with the observed decline in combustion-related influences and the growing significance of non-tailpipe sources, such as brake and tire wear, as key contributors to PM_{2.5} toxicity.



Figure 6. Long-term trends of correlation of (a) metals and (b) OC and EC with DTT activity of PM_{2.5} in Los Angeles.

For OC and EC, contrasting trends are observed in their correlations with DTT activity. OC exhibits a slight decreasing trend in correlation, which may indicate the reduced role of tailpipe emissions in driving the oxidative potential of fine PM over time [21]. Moreover, OC consistently displays stronger correlations with DTT activity compared to EC, with the exception of one year, in agreement with the previous studies [92]. This suggests that OC has a greater intrinsic role in contributing to oxidative potential. In contrast, EC shows a modest increase in its correlation with DTT activity, a trend possibly driven by its concurrent emissions with non-tailpipe tracers, such as metals, which are strongly correlated with the oxidative potential of fine PM, rather than its own inherent toxicity. The rising correlation of EC with DTT activity may therefore reflect the indirect influence of non-tailpipe sources on oxidative potential. These trends underscore the growing importance of emissions from non-tailpipe emissions and resuspension processes in the modern PM_{2.5} chemical composition in megacities such as Los Angeles [21]. Despite the slight decrease trend of OC levels and its correlations with the oxidative potential of fine PM, it still remains high, highlighting the importance of other sources of OC, such as photochemistry, biomass combustion, and non-tailpipe emissions, in addition to primary emissions that are also part of OC [21].

Moreover, the modern vehicle fleet exhibits shifting patterns of UFP emissions related to emerging technologies and after-treatment systems. While diesel emissions have dropped due to widespread adoption of diesel particulate filters (DPFs), gasoline direct injection (GDI) engines emit greater numbers of UFPs and larger quantities of semi-volatile or intermediate-volatility organic compounds (IVOCs and SVOCs) that foster secondary organic aerosol formation [93]. In diesel vehicles, oxidation catalysts (DOCs) effectively reduce hydrocarbon emissions but also produce sulfuric acid by oxidizing SO₂, which can nucleate with oil-derived organics to form nanoparticles [94]. Although DPFs remove most primary soot, they also reduce certain precursors of secondary organic aerosols [95]. Consequently, modern diesel engines can have reduced PM mass yet still feature nanoparticle formation pathways involving delayed organics—much of which originate from lubricating oil [96]. These organic-rich nanoparticles and associated metal additives likely account for a portion of the residual oxidative potential observed in ambient PM_{2.5}, highlighting the need to address both diesel and gasoline fleets as well as non-tailpipe sources in toxicity-oriented regulatory frameworks.

4. Summary and Conclusions

This study examined long-term trends in both the composition and oxidative potential of PM_{2.5} in Los Angeles over the past two decades, with a particular focus on the DTT assay as an indicator of particle-induced oxidative stress. Our results demonstrate that although mass concentrations of key combustion markers (e.g., OC and EC) have markedly declined—particularly before 2016—there has been a subsequent shift in PM_{2.5} composition toward non-tailpipe emissions tracers. These species, which remained largely unregulated, accounted for a growing fraction of PM_{2.5} toxicity. This transition was reflected in the partial resurgence or plateau of DTT activity per mass between 2012 and 2024 and the increase in the per volume DTT activity of fine PM, as well as the increasing correlation trends. Metals including Fe, Cu, and Zn remained relatively stable or even proportionally increased within the PM_{2.5} composition, underscoring their elevated oxidative potential in a context where traditional tailpipe emissions have already been substantially mitigated. The growing contribution of non-tailpipe emissions and secondary aerosol formation suggests that residual toxicity is increasingly driven by unregulated sources. Furthermore, while DPFs have successfully lowered PM mass, GDI technology and certain diesel after-treatment processes (e.g., oxidation catalysts) promote nanoparticle formation by enabling

the nucleation of sulfuric acid and oil-derived organics. These organic-rich UFPs and associated trace metals, originating partly from lubricating oil, sustain or elevate residual oxidative potential in modern vehicle exhaust, reinforcing the need to regulate both diesel and gasoline sources through toxicity-focused strategies. These findings suggest prioritizing unregulated sources—particularly non-tailpipe metals and secondary organics—will be crucial for further improving air quality and protecting public health. Policymakers could consider integrating toxicity metrics like oxidative potential (e.g., DTT activity) alongside mass concentration limits in future regulatory frameworks to target both total PM mass and its most hazardous chemical components. Our findings suggest that focusing solely on mass-based regulatory standards could overlook toxicologically significant shifts in PM composition, especially the rising influence of metal-rich, non-tailpipe sources. To address these emerging toxicity concerns, policymakers can consider placing tighter limits on metallic additives in brake components, particularly copper and zinc, which continue to appear prominently in PM_{2.5}. More stringent guidelines or incentive-based programs for low-wear brake and tire materials would help reduce the fraction of non-tailpipe emissions driving oxidative stress.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/toxics13020140/s1>, Figure S1: OC and EC concentrations in Los Angeles (2007–2024) on dates corresponding to DTT activity reported in prior studies; Figure S2: Sulfate and Nitrate concentrations in Los Angeles (2007–2024) on dates corresponding to DTT activity reported in prior studies; Figure S3: Metals' concentrations in Los Angeles (2007–2024) on dates corresponding to DTT activity reported in prior studies; Figure S4: Long-term trends of DTT activity per mass of PM_{2.5} in Los Angeles (2001–2024); Table S1: List of studies reporting the DTT activity in Los Angeles from 2001 to 2024; [48,50,56–59,61,63–65].

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