URBAN AIR QUALITY

Tracking pollutant emissions

Progress in the post-combustion treatment of diesel vehicle exhaust has led to shifting proportions of the constituents of nitrogen oxides. Observations from 61 European cities suggest that the outlook on attaining NO_2 standards is more optimistic than expected.

Drew R. Gentner and Fulizi Xiong

The composition and impacts of air pollutant emissions from motor vehicles have evolved dramatically over the past several decades. Key advances have been made in engine design and technology, fuel composition and the post-combustion treatment of exhaust[1,2]. Comprehensive air-quality management plans necessitate knowledge regarding the evolving composition of emissions across diverse geographical regions. Writing in *Nature Geoscience*, Grange and colleagues[3] have made strides to improve our understanding of changes in nitrogen oxide (NO_x) emissions from the diesel-heavy European motor-vehicle fleet. They find that the fraction of NO_x emissions comprised of primary nitrogen dioxide (NO_2) emissions is lower than that expected in policy projections.

NO_2 is a regulated air pollutant owing to its direct effects on human health. NO_2 and nitric oxide (NO) are together referred to as NO_x, and both play key roles in urban and regional air quality, such as in the formation of ozone and secondary particulate matter. Approximately 90% of NO_x in uncontrolled diesel exhaust is emitted as NO and then later oxidized into secondary NO_2 (ref. [1]). If more NO_2 is emitted in place of NO, this change has significant health effects, especially for near- or on-road exposure, where NO_2 concentrations exceed standards[4,5].

NO_x emissions from the European motor-vehicle fleet have drawn public attention with recent scandals. Auto manufacturers cheated in emission tests to bring diesel-powered vehicles to market that exceeded the total NO_x emission standard under normal driving modes. This has fuelled ongoing important policy debates over the use of gasoline- versus diesel-powered vehicles in Europe. Starting in the 1990s, diesel vehicles have been favoured because of their better fuel efficiency, but disadvantages in terms of NO_x and primary particulate matter emissions have underpinned the start of a decisive shift towards gasoline in some cities and countries. Examples include the diesel 'bans' and taxes in Paris and London, among others in Germany and Spain[6] (Fig. 1).

Grange et al.[3] present valuable field data that add to this discussion on the ratio of NO_2 to NO_x over six generations of European emissions standards. Specifically, they leverage an impressive distributed dataset of roadside measurements from 61 cities over the period 1995–2015. These data clearly show that for the majority of sites in Europe, NO_2/NO_x ratios were consistently increasing from 1995 to 2008. They then levelled off on average, with decreases in most cities from 2010 to 2015.

Diesel vehicles emit substantially greater amounts of NO_x and particulate matter per mass of fuel burned than gasoline-powered vehicles, owing to the inherent engine conditions necessary for diesel combustion. As a result of the introduction of post-combustion controls for particulate matter — such as diesel oxidation catalysts and diesel particulate filters — NO_2/NO_x emission ratios increased. Diesel oxidation catalysts were first introduced in Euro 3 for light-duty vehicles (Euro 4 for heavy-duty vehicles), with partial NO oxidation to NO_2 being a by-product. Diesel particulate filters were then required in Euro 5 (Euro 6 for heavy-duty) and needed the conversion of NO to NO_2 for regeneration[1,2]. The NO_x emissions scandal compounded the problem of increased NO_2 concentrations by producing high, non-compliant total NO_x emissions at a time when NO_2/NO_x emission ratios were already high due to evolving exhaust after-treatment technologies. In dense, NO_x-rich cities like London this exacerbated the problem of ambient NO_2 concentrations by preventing the intended reductions in total NO_x emissions.

Grange et al. attribute the declining NO_2/NO_x ratios since 2010 to a lower conversion rate of NO to NO_2 as existing diesel oxidation catalysts aged and the platinum content was reduced in newer catalysts. In addition, low-NO_x traps or selective catalytic-reduction systems in the newest vehicles have dramatically decreased NO_2 and total NO_x emissions[1–3,7]. Given the large market share of diesel vehicles and greater urban NO_x concentrations in Europe, these findings are important for European emissions control policy since current emission inventories over-predict NO_2/NO_x ratios.

Fig. 1 | London congestion. The diesel-heavy fleet of motor vehicles in Europe plays a key role in detrimental urban NO_x pollution. Grange et al.[3] present roadside measurements from 61 European cities that suggest a recent stabilization and decrease in the fraction of NO_x emitted as NO_2 by the fleet, which suggests that air quality standards for NO_2 could be reached earlier than expected. Credit: David Burton / Alamy Stock Photo.

The problem is less extensive in the US, where there is a smaller fleet of diesel vehicles. Still, similar increases in NO_2/NO_x ratios were observed in heavy-duty vehicles with the implementation of diesel oxidation catalysts and diesel particulate filters, and NO_2 emission factors peaked in 2007–2009 models and retrofitted vehicles[8,9]. Going forward, the findings are important for informing air-quality policies in diesel-vehicle-heavy developing regions, which typically inherit used vehicles and have emissions standards that lag slightly behind the US and Europe[1,2].

There is a central truth in the field of air quality: accurate data on emissions are essential to the formulation, execution and monitoring of air pollution mitigation plans. Anthropogenic emissions present the largest controllable factor in the air pollution system. We have control over the magnitude and composition of anthropogenic emissions; we have much less control over biogenic emissions, chemical–physical processes in the atmosphere or the mechanisms and rates of pollutant removal from the atmosphere. Significant advances in air quality in the US and Europe have come from the strategic and sometimes selective control of anthropogenic emissions of primary pollutants and reactive precursors to secondary pollution, such as in Los Angeles. Field measurements play a critical role in this mitigation process: they allow validation of emission inventories, provide inputs for air quality models and facilitate air quality management policies derived from these inventories and models.

Grange et al. present a great example of the importance of evaluating real-world, in-use motor-vehicle fleets outside of unrealistic test conditions. Even without emissions cheating, motor-vehicle fleets are very diverse in their design, use, maintenance and age. Single-vehicle studies on a limited sample set are not representative of in-use vehicle fleets, whose emissions over their lifetimes are key to determining the dynamic mixture of emissions that drive many aspects of urban primary and secondary pollution[3,10]. Emissions studies that collect data from motor-vehicle tunnels or via remote sensing have provided robust approaches to constraining emissions and monitoring real-world compliance[7–9]. The use of well-outfitted measurement sites in urban areas to track near-road concentrations[3] presents a complementary approach to traditional techniques, but all are limited in their ability to capture spatial heterogeneity with only one or a few sites in each city.

Expanding on the study by Grange et al.[3], the development of cost-effective, accurate monitoring networks using low-cost sensor components will provide the potential to monitor real-world emissions through dense spatiotemporal measurements of multi-pollutant concentrations. Effective use of these networks requires careful instrument design, strict quality control of system components and data streams, and calibration. Placement of monitor nodes is also essential for capturing the full range of sources and processes that affect air quality, and should include near-source sites such as roadside sites to monitor motor vehicles.

Grange et al.[3] present a powerful multisite approach to monitoring air quality using real-world data. Next-generation approaches to routinely track changes in emissions of pollutants, reactive precursors and greenhouse gases across key sources enable us to track compliance and better understand the key players in urban emissions and air quality. This is essential because an evolving spectrum of urban sources can shift the driving factors of urban air quality and potentially urban chemistry. ❐

Drew R. Gentner[1,2,3]* and Fulizi Xiong[1,2]

[1]*Department of Chemical & Environmental Engineering, Yale University, New Haven, CT, USA.* [2]*SEARCH (Solutions for Energy, Air, Climate and Health) Center, Yale University, New Haven, CT, USA.* [3]*School of Forestry and Environmental Sciences, Yale University, New Haven, CT, USA.*

**e-mail: drew.gentner@yale.edu*

https://doi.org/10.1038/s41561-017-0027-y

References

1. Sanchez, F. P., Bandivadekar, A. & German, J. *Estimated Cost of Emission Reduction Technologies for Light-Duty Vehicles* (ICCT, 2012).
2. Posada, F., Chambliss, S. & Blumberg, K. *Costs of Emission Reduction Technologies for Heavy-Duty Diesel Vehicles* (ICCT, 2016).
3. Grange, S. K., Lewis, A. C., Moller, S. J. & Carslaw, D. C. Lower vehicular primary emissions of NO_2 in Europe than assumed in policy projections. *Nat. Geosci.* https://doi.org/10.1038/s41561-017-0009-0 (2017).
4. Hoek, G. et al. Long-term air pollution exposure and cardio-respiratory mortality: a review. *Environ. Heal.* **12**, 43 (2013).
5. Anenberg, S. C. et al. Impacts and mitigation of excess diesel-related NO_x emissions in 11 major vehicle markets. *Nature* **545**, 467–471 (2017).
6. *Cities Driving Diesel Out of the European Car Market* (ICCT, 16 May 2017); http://www.theicct.org/blogs/staff/cities-driving-diesel-out-european-car-market
7. Carslaw, D. C., Murrells, T. P., Andersson, J. & Keenan, M. Have vehicle emissions of primary NO_2 peaked? *Faraday Discuss.* **189**, 439–454 (2016).
8. Dallmann, T. R., Harley, R. A. & Kirchstetter, T. W. Effects of diesel particle filter retrofits and accelerated fleet turnover on drayage truck emissions at the Port of Oakland. *Environ. Sci. Technol.* **45**, 10773–10779 (2011).
9. Dallmann, T. R. et al. On-road measurement of gas and particle phase pollutant emission factors for individual heavy-duty diesel trucks. *Environ. Sci. Technol.* **46**, 8511–8518 (2012).
10. Gentner, D. R. et al. Review of urban secondary organic aerosol formation from gasoline and diesel motor vehicle emissions. *Environ. Sci. Technol.* **51**, 1074–1093 (2017).

Competing interests

D.R.G. and F.X. have externally funded research projects on low-cost air quality monitoring networks, and Yale University has licensed out their technology.

CARBON CYCLE

Zircons reveal ancient perturbations

A link between CO_2 outgassing from carbonatite volcanoes during the Ediacaran and one of the most prominent carbon cycle perturbations in Earth's history is suggested by an analysis of the trace-element composition of detrital zircons.

N. Ryan McKenzie

Today, only a single volcano, Ol Doinyo Lengai in the East African Rift, produces markedly CO_2-enriched carbonatite lavas[1]. Due to their rarity and underlying questions regarding the efficiency of how carbon moves through the mantle[2,3], the impacts of carbonatitic magmatism on the long-term carbon cycle are not entirely realized. However, writing in *Nature Geoscience*, Paulsen et al.[4] report that they have used the age and trace-element composition of detrital zircons to identify a pulse of carbonatitic magmatism about 580 million years ago (Ma), coincident with one of the most significant carbon cycle perturbations in Earth's history — the Shuram negative carbon isotope excursion.

Carbonatites, which are comprised of greater than 50 weight percent $CaCO_3$, belong to a suite of alkaline igneous rocks derived from CO_2-enriched melts. They generally occur in intraplate settings and continental interiors, as they originate from zones of mantle upwelling rather than the subduction-related magmatism found around plate margins. If this has been the case historically, then the likelihood of finding in situ carbonatites may be low to begin with: rocks formed in continental interiors generally have low