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The Air Quality Index (AQI) in historical and analytical perspective a tutorial review

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ABSTRACT

The Air Quality Index (AQI), developed by the United States Environmental Protection Agency (USEPA), has been providing the public with crucial information regarding the status of contamination of the atmosphere for the past 45 years. Prior to introduction of the AQI, only a handful of metropolitan areas reported on air quality, and each region decided on its own metric. The inception of a single AQI helped homogenize the air quality metrics across the nation and indeed served as an important future template for other governmental and regulatory agencies across the world. The formulators had the foresight to recognize that our understanding of air pollution and its effects may change over time, which are likely to change regulatory limits. They used a dynamic framework to define the AQI, such that the broad definition or principle does not need to change with every change in regulatory limits or policy, and the fundamental goal of alerting the public to deleterious air quality is not affected. The establishment of the AQI increased public awareness of the importance of clean air and has helped muster support for air quality and emission regulations. The National Ambient Air Quality Standards (NAAQS) set forth by the USEPA provides acceptable levels of criteria pollutants – namely carbon monoxide, lead, nitrogen dioxide, ozone, particulate matter, and sulfur dioxide. A comparison of the actual levels, as compared to the regulatory limits (since the cessation of leaded gasoline, lead is no longer included in the index), are used as the basis for the AQI. As the regulatory limits change, so does the exact evaluation of the AQI, making it a living index. In this paper, we provide a historical overview of the Air Quality Index, the Federal Reference Methods (FRMs) vs. Federal Equivalent Methods (FEMs) for measuring them, and as an illustrative example, we discuss the air quality for Dallas-Ft. Worth, currently the fourth most populous metropolitan region in the United States, vis-a-vis the reported AQI.

1. Introduction

A healthy life requires clean air to breathe. While breathing rates vary significantly, an average person takes 12–16 breaths per minute at rest or when performing normal activity, with a tidal volume of 0.5–1 L per breath. The total amount of air breathed by an individual depends both on lung capacity and level of activity but estimates as high as 23 m^3/day of air are not unusual [1,2]. At 20 °C at mean sea level, the mass of this amount of air will be >25 kg, far more than the daily combined amount of food and liquids. Considering that the respiratory system is not nearly as resilient as the digestive system, poor air quality may elicit both acute and long-term effects, ranging from respiratory and cardiovascular diseases to premature death [3].

Aside from highly variable water vapor content, the concentrations of the major constituents of the earth's atmosphere are more or less homogeneous throughout the world. Air is 78.1% nitrogen, 20.9% oxygen and 0.9% argon by volume, these making up 99.9% of the composition of the atmosphere [4]. The remaining 0.1% is comprised of a myriad of gases collectively referred to as "trace gases". Many of the trace gases, such as those constituting the criteria pollutants to be discussed, are *not* homogeneously distributed, either spatially or temporally. Trace pollutant gas concentration can vary wildly between geographic regions, elevations, and times. Typically, gases that show high spatial variation, also show high temporal variation. Ambient air also hosts non-gaseous species of consequence, both liquid and solid aerosols, of disparate composition and origin. Of the trace gases, those that pose an immediate risk to human and environmental health are of particular interest. In the US, the Environmental Protection Agency (EPA) tracks air pollutants across the country, publishing summaries annually for all metropolitan statistical areas (MSAs) in the United

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States [5] (An MSA is defined by the US Census Bureau as a city with >50,000 residents, or an urbanized area and total metropolitan population of >100,000; a list of active MSAs are available at https://www3.epa.gov/ttnairs1/airsaqsORIG/manuals/temp/MSAs_3_D.html). The average concentration of any of the criteria pollutants for any specific period in any MSA can be easily looked up. For example, in 2021, in the Dallas-Fort Worth (DFW) area, the average ozone concentration was 0.085 parts per million (ppm, by volume) and the average atmospheric concentrations of particulate matter with aerodynamic diameters of ≤10 μm (PM_{10}) and ≤2.5 μm ($PM_{2.5}$) were 56 and 9.6 μg/m^3, respectively.

However, communicating the risks associated with these or other pollutants is not accomplished by just posting the concentrations. While the mass concentration of PM_{10} is significantly higher than $PM_{2.5}$, it is the $PM_{2.5}$ value that is closer to breaching the NAAQS level. Even though the Ozone concentration may seem numerically small, this is actually *above* the NAAQS standard; indeed, this poses an issue for DFW, discussed later. This illustrates the problem: Unless one has prior knowledge of what concentrations of various pollutants are acceptable, the numbers by themselves are not meaningful. The health risks that the current status of air contamination holistically poses need to be communicated in a succinct, easily digestible format. This is where the Air Quality Index is of value. It acts as a bridge between the quantitative data that determines the value of a single numerical index and the qualitative spectral color scheme that the public is comfortable and familiar with. Similar systems are in place in many other countries.

In this overview, we first examine the origins and intricacies of the AQI. There is a wealth of information that gets collapsed into a single number or color that is described or discussed in a news program or displayed on a highway banner. Then we discuss the reference methods used for the measurement of these criteria pollutants. Finally, as a case study, we present a survey of the air quality over DFW, presently the 4th largest MSA in the US by population (over 7.75 million as of 2021) [6], and home to the authors.

2. Retrospective

Concern over air quality has grown in lockstep with the industrial revolution. However, human influence of the atmosphere far predates this era. Concern of cave dwellers over cooking/warming fires may have been very localized, but long-distance transport of anthropogenic pollution has been taking place for a long time: Ice cores from Greenland bear metal signatures traceable to metallurgy in Greek and Roman times [7]. However, records of air quality deterioration appeared only after the industrial revolution. Many point to the 1952 smog event in London as the catalyst for public concern for air quality [8]. In the US, the most salient event to influence environmental policy happened 4 years prior in Donora, Pennsylvania.

Donora, a small town (1948 population 14,000) 45 miles southeast of Pittsburgh, located in a steeply walled valley along the Monongahela River with the village of Webster just across the river, was home to a steel mill and a zinc smelter that emitted large quantities of SO_2, NO_x, and CO into the atmosphere [9]. The terrain made it difficult for the pollutants to be dispersed easily, albeit the concentrations decreased some with daybreak with the help of thermally induced convection. Beginning in the early 1920s, local landowners, tenants, and farmers unsuccessfully sued the local mills for damages attributed to smelter effluents [10]. On the fateful day of October 26th, 1948, the smog only thickened as the day wore on. By the 28th, panic spread through the choking town as patients in respiratory distress crowded the hospitals. The prevailing weather trapped the smog over the small town for days, until the pollutants were finally rained out. In all, 20 died and 600 fell acutely ill; a subsequent federal investigation reported that more than 5000 of the 14,000 locals had experienced moderate to severe symptoms, not to speak of long-term effects [9,11]. The media uproar was swift, gaining national coverage. The New York Times quoted the US Public Health Service as opining that it represented “a problem that transcends Donora and is nationwide in scope” [12]. Many reports followed the event, with the focus shifting from blaming the local mills towards a legislative response that addressed the effects of air pollution on public health. These seeds eventually germinated as the Clean Air Act of 1963.

The Clean Air Act has been amended many times since its inception, with amendments addressing the ever-changing needs, notably the establishment of an Air Quality Index through the Air Pollution Prevention and Control Act of 1977. This has allowed the government to respond to changes in understanding of atmospheric chemistry and the effect of atmospheric pollution on public health and the environment. In particular, the 1970 amendment provided directions in developing air quality standards for each of the criteria pollutants; this would become the National Ambient Air Quality Standards (hereafter, NAAQS). These pollutants were O_3, particulate matter (PM), CO, SO_2, Pb and NO_2. All of these are still measured and regulated to this day, although, some are of less concern today than when these standards were first established. In the US, sulfur dioxide concentrations have dramatically declined as energy production has moved away from coal, and more stringent measures have been adopted to remove SO_2 from fugitive emissions. Sadly, the same is not true about global SO_2 emissions. Leaving aside the broad aspects of acid precipitation, the immediate health effects of SO_2 tend to be more local [13].

The choice of the particular set of criteria pollutants among the countless present in anthropogenic emissions had two distinct reasons. First, those chosen were ubiquitously found across the continental United States. The other reason involves public health and the environment. Decades of research had already shown strong correlations between excess deaths and asthma with pollutants such as SO_2, O_3, NO_x and particulate matter [14,15]. The lack of the inclusion of lead in the formulation of the AQI was because the ubiquity of airborne lead and its detrimental effects on public health, especially on child neurodevelopment were not widely appreciated [16,17]. There was also significant vested interest to keep tetraethyl lead as a gasoline additive and considering its regulation was an uphill struggle [18]. Patterson [19] first reported the ubiquitous environmental contamination by anthropogenic lead; much of the political will eventually generated to ban lead from gasoline is also attributed to him. However, it took more than a decade from the publication of Patterson’s initial work before lead was included in the NAAQS criteria pollutant list, and yet another decade before the phaseout of lead from gasoline began and yet another decade before this was completed in 1995. Ironically, Patterson died from an attack of acute asthma in the same year.

The AQI itself resulted from a 1977 amendment to the Clean Air Act that detailed instructions for air quality monitoring [20]. It included directions to establish an air quality system to be utilized across the country. The system was to be standardized; uniform criteria and methodology were to be used. Two key requirements that have shaped the AQI are the need for daily measurements and reporting, as well as establishing monitoring stations for “major urban areas”. To compile and assess the various air pollution indices used in the US and Canada, the Council for Environmental quality and the US Environmental Protection Agency sponsored a joint study in 1975. While this was eventually published as a monograph, multiple publications, noting many extant local indices with varied criteria throughout the country, documented the progress of their ruminations [21–23]. They noted the importance of communication, that concentrations expressed traditionally in scientific units should preferably be replaced with unitless numbers serving as a score. These ideas led to the eventual proposal for a standardized index, named the Pollutant Standards Index (PSI or Ψ).

The Pollutant Standards Index (Table 1) used 6 pollutants from what was then the NAAQS list. The product of SO_2 and TSP (TSP connotes Total Suspended Particulate Matter) was deemed to be of interest in that while the effects of SO_2 may be ameliorated by removal of this highly water-soluble gas by the moist walls of the upper respiratory tract such

Table 1
Criteria for the pollutant standards Index.[22].

	CO (ppm)	SO_2 (ppm)	TSP (μg/ m^3)	SO_2 x TSP (μg/ $m^3)^2$	NO_2 (ppm)	O_3 (ppm)
Averaging Time (hrs.) rowhead	8	24	24	N/A	1	1
Primary NAAQS rowhead	9	0.14	260	N/A	N/A	0.08

Table 3
Reporting instructions for specific sensitive groups per pollutant. When multiple pollutants are above 100, the reporting is condensed so that each group is only mentioned once.

Pollutant with a value greater than 100:	Sensitive Group of concern
Ozone	People with lung disease, children, older adults, persons engaging in outdoor activities, people with certain genetic variants, and people with dietary limitations
PM2.5	People with heart/lung disease, older adults, children, and people of low socioeconomic status.
PM10	People with heart/lung disease, older adults, children, and people of low socioeconomic status.
CO	People with heart disease.
NO_2	People with asthma, older adults, and children.
SO_2	People with asthma, older adults, and children.

that it does not significantly penetrate to the deep lung, there is no such barrier to SO_2 adsorbed on fine particles; indeed, aerosolized sodium sulfite exhibits inhalation toxicity at quite low levels [24]. The unitless or numbers used in the original PSI were based on the then NAAQS values. For any particular pollutant, a value equal to the primary NAAQS concentration was rated 100; half that value equaled 50 (unless a secondary NAAQS existed, which was then taken as 50). However, the protocol did not involve reporting PSI values for each of the 6 pollutants, which would be confusing. Rather, the public was to be informed of whichever the highest PSI was and the pollutant it is based on.

The design of the currently utilized Air Quality Index is very similar to the PSI. It aims to communicate pertinent health advisories to the public without technical jargon. A workbook is available to help MSAs calculate the AQI value, ensuring that the practice is uniform across the country [25]. At a minimum MSAs must report the:

- Reporting area
- Reporting period
- Critical pollutant (pollutant bearing the highest AQI value, on which the AQI is based)
- The AQI value for the critical pollutant – this is the reported AQI that dictates the category
- Color descriptor (see below)
- Which groups with particular health concerns (e.g. children, the elderly, people with preexisting health conditions, asthmatics, etc., see Ref. [26]) are sensitive to any pollutants that have a score over 100 (NAAQS value for the specific pollutant(s))

These are only the minimum reporting requirements. Many MSAs choose to report additional information, including specific reasons for the excursions, etc. The AQI must also be published daily. The color descriptors are listed in Table 2. In addition to the reported color, there are specific sensitive groups that must be reported when a given pollutant is above the NAAQS level (i.e., AQI >100, regardless of whether it is the critical pollutant), as listed in Table 3.

Breakpoints in the concentration of each pollutant that determine the subclassification in the hazard/color category are given in Table 4.

The different averaging times for the different pollutants in Table 4 have been arrived at from decades of research on the acute and long-term effects of exposure to these pollutants: many reviews cover this in great detail [27–30]. The maximum concentration measured for any given pollutant with different averaging times within a 1-month time frame can generally be approximated as (the maximum concentration observed for the shortest averaging time)^n where $n < 1$ [31]. Qualitatively, it is intuitive that at longer averaging times, the maximum observed concentration will be less than that at a shorter averaging time. Similarly, the difference will continue to decrease as the averaging windows increase [32].

In addition, the health effects associated with air pollutants may not strictly be cumulative and are often nonlinear. For example, the reviews cited above discuss the myriad ways that ozone can cause health issues, e.g., increased incidence of asthma from long term exposure at high ambient levels [33]. On the other hand, at higher concentrations ozone can induce immediate multiple pro-inflammatory responses [34,35]; acute effects, such as choking and severe fatigue, can result from higher ozone concentrations (0.6 ppm–1.0 ppm). Briefly, if significant excursions from the mean value, even for short durations, have important health consequences, then shorter averaging times are warranted, whereas if the effects are more cumulative, then longer averaging times should suffice.

Special conditions are warranted if scores for pollutants are exceptionally high or low. If a given pollutant attains a score above 500, it is considered “beyond the AQI” and retains the “hazardous” descriptor. Conversely, if *all* pollutants have a score of ≤50 *for a year*, then next year the AQI need not be reported. Additionally, if a given pollutant stays below 50 for a year, then it can be omitted from AQI considerations the next year. However, measurements must continue to be made. There is considerable flexibility in *how* the AQI gets reported, to best suit the nature of the media, promoting wide and diverse dissemination, to further the goal of public awareness. With the advent of smartphones, the local AQI (or that of a major city anywhere in the world) can be checked anywhere and anytime.

The one pollutant that often becomes the basis for the AQI is ozone; this is especially true in the summer months. It is therefore worth mentioning the existence of two separate averaging times (1 h and 8 h) for measuring Ozone. The 8-h NAAQS standard for ozone was

Table 2
Descriptors and corresponding colors for each AQI value range.

AQI Value	Descriptor	Color
0 – 50	Good	Green
51—100	Moderate	Yellow
101—150	Unhealthy for Sensitive Groups	Orange
151—200	Unhealthy	Red

Table 4

Table of AQI Breakpoints for each pollutant into color coded categories. Bold PM2.5 values refer to the absence of a standard set for the significant harm level (SHL) for PM2.5. Italicized sulfur dioxide levels are calculated using 24-h concentrations.

Breakpoints							AQI	Category
O_3 (ppm) 8-hour	O_3 (ppm) 1-hour	PM2.5 (µg/m^3) 24-hour	PM10 (µg/m^3) 24-hour	CO (ppm) 8-hour	SO_2 (ppb) 1-hour	NO_2 (ppb) 1-hour		
0.000-0.054	N/A	0.0-12.0	0-54	0.0-4.4	0-35	0-53	0-50	Good
0.055-0.070	N/A	12.1-35.4	55-154	4.5-9.4	36-75	54-100	51-100	Moderate
0.071-0.085	0.125-0.164	35.5-55.4	155-254	9.5-12.4	76-185	101-360	101-150	Unhealthy for selected groups
0.086-0.105	0.165-0.204	**55.5-150.4**	255-354	12.5-15.4	*186-304*	361-649	151-200	Unhealthy
0.106-200	0.205-0.404	**150.5-250.4**	355-424	15.5-30.4	*305-604*	650-1249	201-300	Very unhealthy
N/A	0.405-0.504	**250.5-350.4**	425-504	30.5-40.4	*605-804*	1250-1649	301-400	Hazardous
N/A	0.505-0.604	**350.5-500.4**	505-604	40.5-50.4	*805-1004*	1650-2049	401-500	Hazardous

introduced in 1997, to replace the 1-h standard. The standard for 8-h averaging time for ozone concentration was originally set at 0.080 ppm but has since been revised down to 0.070 ppm in 2015 [36]. This change effectively made the regulation of ozone more stringent, as the new regulatory limit was more easily exceeded. Though it is no longer a requirement to compute and report the 1-h average, many MSAs do still report this value.

To calculate the AQI value, the index I_P for each pollutant p is computed as:

$$I_P = \frac{I_{Hi} - I_{Lo}}{BP_{Hi} - BP_{Lo}} \left(C_p - BP_{Lo}\right) + I_{Lo} \tag{1}$$

where C_p is the concentration of pollutant, BP_{Hi} is the concentration breakpoint greater than C_P, BP_{Lo} is the concentration breakpoint less than C_P, I_{Hi} is the index value corresponding to the upper breakpoint and I_{Lo} is the index value corresponding to the lower breakpoint. Once the index for each pollutant is calculated, the one with the highest value is the “critical pollutant”, and its score is the AQI for that day in that region.

The use of the AQI, or some index that is computed in a very similar fashion, extends beyond the United States. Many other countries have based similar air quality indices along the same principles that comprise the AQI [37]. The European Union (EU) implements the Common Air Quality Index, which uses the same linear model to derive an index value (with each pollutant being scaled individually although they have breakpoints different from those used in the U.S. AQI); one important difference being the exclusion of CO from the list of pollutants considered. However, as in the U.S., the reported value is simply the highest indexed value among the pollutants [38]. The choice to use a single pollutant to define the AQI value has certainly been amply criticized over the years, because such simplification may delete important information and correlations present in the holistic data [39–41]. Thus, many indices have been proposed that simultaneously take multiple pollutants into account [42–44]. The Multisite-Multipollutant Air Quality Index advocated by Plaia and Ruggieri [43] for example, factors both the combination of pollutants and their spatial concentration distribution in an area. They formulate a three-dimensional array with the form $X_{[T \times S \times K]}$ where there are K pollutants in S sites across T time. The index relies on scaling each pollutant based on their respective effect on health (not unlike the different breakpoints of the current AQI). The data is preprocessed and reported on a daily basis, so different averaging times for different pollutants are eliminated (the premise being that the averaging times used are too long and much of the temporally meaningful information is lost). Principal component analysis is then performed on the dataset to account for the individual contributions of each pollutant. Such an analysis can also show the importance of spatial data - that certain areas contribute more to the overall index score than others. While their illustrative data set did show larger contributions from measuring stations near busy roadways, not all their measurement stations were equipped to measure all pollutants, and thus the dataset was not strictly complete. Realistically, without significant capital investment it will be difficult to generate data sets both spatially and temporally comprehensive enough to provide such index information on a routine basis, not to speak of the ability of laypeople to interpret the results.

There are many other proposed indices that factor in health effects, meteorological conditions and so on. Still, regardless of any real or perceived shortcomings of the present practice, the AQI is a powerful tool to alert the public to potential health hazards. History suggests that the continual progress in science and technology and in our understanding of the effects of air pollutants will themselves dictate the implementation of new indices as needed.

3. Reference methods for criteria pollutants

In the US, regulatory measurement of pollutants can be made only by two classes of methods: Federal Reference Methods (FRMs) and Federal Equivalent Methods (FEMs), a list describes all USEPA methods as of 2022 [45]. To support monitoring efforts, EPA scientists develop and evaluate methods for accurately and reliably measuring the criteria pollutants in outdoor air. These methods — called FRMs — are used by states and other monitoring organizations to assess implementation actions needed to attain compliance to the NAAQS. The FRMs are the gold standards/benchmarks of air pollution monitoring systems that ensure air quality data collected at different sites are gathered in the same manner and are accurate.

However, to foster innovation and advance new technologies, the EPA also has a mandate to review, test, and approve other methods, based on sampling/analyzing technologies different from FRMs, which nevertheless must provide results of at least equal quality and reliability to make decisions on NAAQS attainment questions. FEMs often utilize new technology that make them advantageous over FRMs, e.g., less expensive to own or operate, provides or is able to perform beyond FRM requirements, e.g., generate real time data. The equivalent methods must excel in accuracy, precision, limits of quantitation, provide pollutant specificity without interferences from other pollutants/contaminants, and exhibit minimal drift. Additionally, they may be automated, which reduces the need for specialized personnel. However, all the present FRMs have now remained in existence over long periods of time; the same cannot be said for all the FEMs. Still the vast majority of the devices being used across the country are based on FEMs, largely because of lower capital or operating costs; for example, UV absorption-based ozone measurement, an FEM, is the most widely used method today for measuring ozone.

3.1. Instrument calibration

Calibration is an important aspect of the design and implementation of FRMs/FEMs. The USEPA Quality Assurance Handbook [46] outlines aspects to be considered so that the measurement remains accurate, and any necessary correction is appropriately made. Note that aside from zero-point corrections, post-processing of data to correct for failed quality control checks is not considered acceptable. The calibration span is the pollutant concentration range over which an instrument is calibrated – and while it must of course be within the performance range of the instrument, a monitoring organization is free to choose a span that is relevant to their location and season. The calibration should rely on more data at lower concentrations within the typical range the instrument is expected to encounter, as the majority of the data will be in this domain and adherence to linear response can be verified. To correct for baseline drift, a blank (zero air) measurement is suggested twice a week. When the arrangement permits for automated zero air measurement, then this process should be programmed to take place daily. For gas measurement instrumentation, the upper span measurement point should be at a concentration that is the highest among the following: (a) at 80–90% of the intended measurement range, (b) 120% of the NAAQS value point, and (c) concentration at 99th percentile of values found at this locale and season. In addition to a biweekly zero-point calibration, a one-point QC is also to be performed biweekly (between 5 and 80 ppb for O_3, SO_2 and NO_2 and 0.5–5 ppm for CO). Annual performance evaluations are also performed to test an instrument with at least 3 of 10 audit levels [47] of gaseous pollutants. One of these points must be within 2-3x the method detection limit. The second point should be less than or equal to the 99th percentile of data for that area. The third point is at either the NAAQS or the highest 3-year concentration measured in the area. Ozone, SO_2 and NO_2 measurements should be within ±1.5 ppb or ±15% (whichever is greater) of the concentration of the audit gas. For CO, the measurement should be within ±0.03 ppm or ±15% (whichever is greater).

3.2. Sulfur dioxide

There are unique, and occasionally multiple, federal reference methods for measuring each of the criteria pollutants. For SO_2, the older FRM is based on bubbler collection of air into an absorber, to which specific color development chemicals are then added. A magenta coloration develops, the intensity of which is dependent on the level of SO_2 present and is measured by visible light spectrophotometry [48]. Although this classic approach has relatively low capital cost, it is rarely practiced any more, at least in the US, both because this entirely manual process is highly labor intensive (an autoanalyzer based equivalent method was introduced later to automate reagent addition, color development and absorbance measurement [49]), and also because the gas absorber used in the method contains a complex mercury salt, a toxic compound.

The more recent FRM for SO_2 is the UV fluorescence method [50]. This fluorescence can be excited with light in wavelengths ranging from 190 to 230 nm; in practice, the 214 nm emission line from a zinc lamp, filtered by an interference filter, is used. The emission from SO_2, centered at 320 nm, is detected by a UV-sensitive photomultiplier tube at right angles to the excitation beam (see Fig. 1). However, aromatic hydrocarbons, e.g., xylene, naphthalene, etc. also fluoresce under the same conditions and can interfere severely with the measurement. These must be first removed, which is accomplished by passage of the air sample through a selective permeation membrane (often of proprietary composition) based scrubber that allows the unwanted hydrocarbons to permeate out but does not let acid gases like SO_2 to pass through [51,52].

For calibration, the FRM describes an apparatus that can dilute SO_2 gas with clean air by way of a mixing chamber to achieve desired concentrations. It is important that the flow rate is regulated to within 1–2% and that the mixing chamber is composed of an inert substance. While available commercial instruments already provide for sampling at a constant flow rate, the effects of deviations from the reference temperature and pressure are not automatically accounted for; the correction procedure is provided in the FRM.

3.3. Carbon monoxide

The FRM for the detection of airborne carbon monoxide utilizes Non-Dispersive Infrared Spectrophotometry [53]. Infrared energy from a source is passed through a cell containing the air sample to be analyzed, and the quantitative absorption of energy by CO in the sample cell is measured by a suitable detector (see Fig. 2). The photometer is made specific to CO by employing CO gas in a filter cell in the optical path, which, when compared to an optical path without a CO filter cell in a differential arrangement, essentially renders the measured absorption to be due only to CO. However, to meet measurement performance requirements, manufacturers may introduce various refinements, e.g., the use of optical filters, moisture traps, etc. to improve performance parameters and to decrease interference from high and variable concentrations of particular gases, most notably water vapor [54]. Calibration of the system is done in a similar way as for SO_2, where a calibration curve is created from measuring specific concentrations of a CO standard and any deviations from the reference temperature and pressure are corrected for.

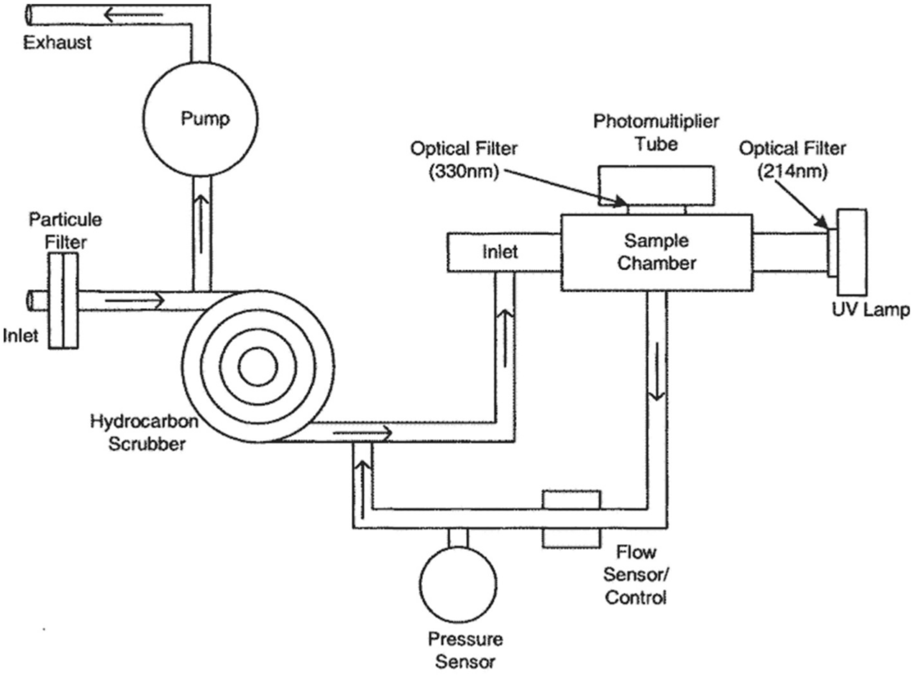


Fig. 1. Schematic for the FRM for SO_2 analysis as defined in 40 U.S.C. app 50. A-I.

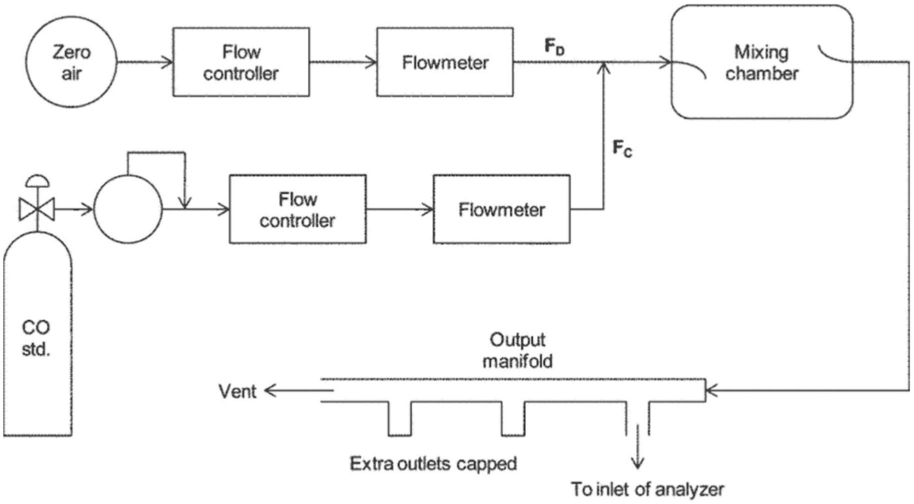


Fig. 2. Schematic of NDIR calibration system for carbon monoxide as defined in 40 U.S.C. app 50.C.

3.4. Ozone

The FRM for ozone measurement in the atmosphere relies on the measurement of light (chemiluminescence (CL)) produced when ozone reacts with either ethylene or nitric oxide [55]. Ozone produces CL with a number of compounds, both in solution and the gas phase. With ethylene and NO, the products are formaldehyde and nitrogen dioxide respectively [56]. The product of the ozone-ethylene reaction (an unstable primary ozonide intermediate of 1,2,3-trioxolane structure) is formed in an excited electronic state and relaxes by radiative emission centered at 440 nm. The NO–O_3 reaction results in an excited NO_2^* molecule that emits over a broad range of 590–1085 nm, with a maximum in the near-infrared [57]. The light emission in this case is relatively weak, so it needs to be measured by a near-infrared sensitive photomultiplier tube that typically needs to be thermoelectrically cooled to get a sufficient signal to noise ratio. The advantage of using the NO reaction over that with C_2H_4 is that it is less sensitive to variations in relative humidity. Whenever light detection is involved, particulate matter must first be removed; the problem with ozone is that it is rather easily taken up or decomposed by contact with particles deposited anywhere in the system and in particular, the inlet particle filter. For this reason, the system must be subjected to regular and frequent cleaning and inlet filter replacement (see Fig. 3).

Ozone is an unstable compound that cannot be bottled in a known concentration as a cylinder gas. The calibration approaches used for most other stable gases, including the other gases in the NAAQS, cannot be used for ozone. Fortunately, the absorption cross section for ozone at 254 nm is very well known and the concentration of ozone generated by an ozone generator (which typically illuminates a flowing airstream with low-wavelength UV radiation or subjects it to dielectric barrier discharge) can therefore be accurately computed by measuring the absorption of 254 nm light in a cell of fixed path length at a known temperature and pressure.

There are specific protocols for computing and reporting the 8-h

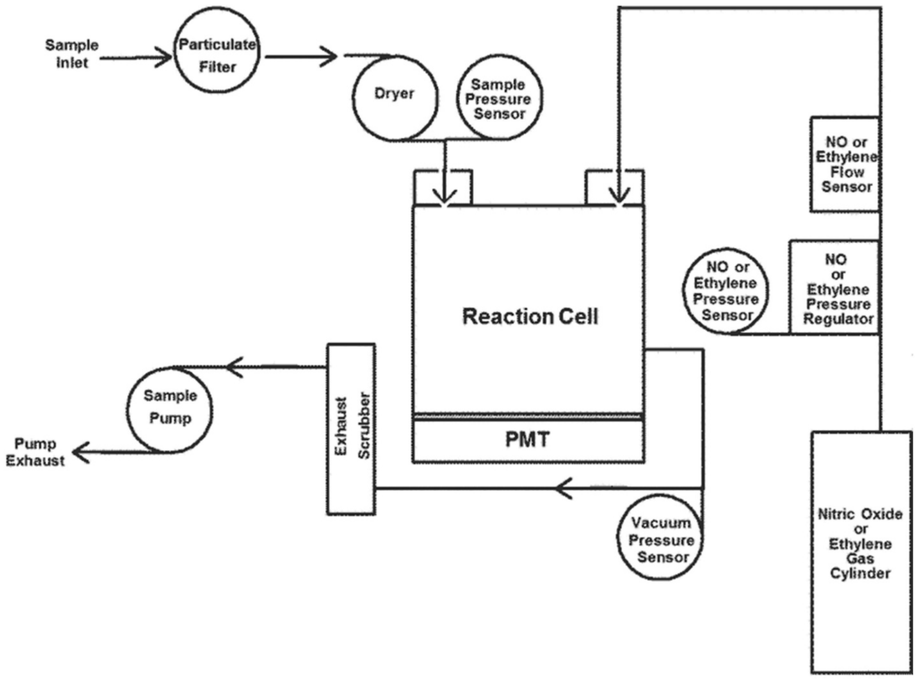


Fig. 3. Schematic of the chemiluminescence detection system of ozone as defined in U.S.C. app 50 D.

averaging of ozone levels [58]. To ensure accurate and consistently uniform reporting, the hourly ozone concentration data is averaged for each 8-h period, with the stipulation that at least 75% of the possible 8-h averages (in a 24-h day, there are 24 possible 8-h averages) provides valid data. The daily maximum 8-h concentration for a given calendar day to be reported is the highest of the 24 possible 8-h average concentrations computed for that day. Such specific instructions assure uniformity of the reported data.

3.5. *Nitrogen dioxide*

The FRM for the measurement of nitrogen dioxide also uses the CL reaction between ozone and nitric oxide but in an indirect manner [59]. This concept of (a) first measuring NO in air by its CL reaction with ozone, and then (b) reducing NO_2 present in the air by passing over a thermal converter and subjecting the effluent to CL reaction with ozone, thereby measuring NO_x (as NO + NO_2 is often called) and then (c) thus measuring the NO_2 concentration as NO_x – NO was first proposed by Breitenbach and Shelef [60].

Nitrogen dioxide may be made to decompose as $NO_2 \rightleftharpoons NO + \frac{1}{2}O_2$, but to get this endothermic reaction to be near-quantitative by thermal means alone requires temperatures impractical for an analytical instrument, especially one to be used in the field. As Le Chatelier's principle will indicate, the reaction is favored at lower pressures. Certain heated metals (copper, and especially molybdenum) and glassy carbon will reduce NO_2 to NO. Although they are often referred to as "catalysts", their role is not catalytic. One major manufacturer states, for example, that the life of their "Moly" converter is about 20,000 ppm-hours [61]. Thermal converters also convert virtually all non-ammonia/amine nitrogenous atmospheric species that can be produced from the oxidation of NO_x (these include nitric acid, nitrous acid, dinitrogen pentoxide, peroxyacetyl nitrate, alkyl nitrates, peroxyalkyl nitrates, the nitrate radical, and peroxynitric acid, sometimes cumulatively referred to as NO_z) to NO [62,63]. The sum of NO_x and these NO_z compounds are often referred to as NO_y. It is generally assumed that when NO_2 concentrations are high enough to be of concern, the NO_z concentrations are too small in comparison to cause statistically significant errors in NO_2 measurements. If this is not the case in a particular location, the EPA recommends using a FEM that either uses near UV-irradiation to convert NO_2 to NO or utilizes sensitive absorbance measurement methods that directly and selectively measures NO_2 via its light absorption.

The current listing of approved NO_2 methods contain some 31 FRMs and 10 FEMs. Nearly all of the FRMs are based on the NO–O_3 reaction using a thermal converter. The individual FRMs vary in operational details; these may differ in converter details or operational conditions, presence, or absence of a particulate filter, etc. If a particulate filter is used, it must be changed frequently to reduce on-filter reactions. In ambient air, both NO and O_3 are present. Atmospheric samples are not in chemical equilibrium in either space or time. For this reason, the residence time between the sampling inlet and the analyzer must be minimum to avoid significant conversion of ambient NO to NO_2 by reaction with ambient ozone.

3.6. *Lead*

Though atmospheric lead levels have been declining since tetraethyl lead was removed as a fuel additive, the EPA still lists it as a criteria pollutant, and in fact has made the regulations more stringent as our understanding of deleterious effects of lead, even at very low levels, have increased [64]. In 2008, the regulatory limit for airborne lead in the atmosphere was reduced by an order of magnitude, from 1.5 $\mu g/m^3$ to 0.15 $\mu g/m^3$. Such a stringent standard essentially requires eliminating all anthropogenic lead emissions. By and large airborne lead is becoming less of a concern with time, lead is not factored into formulating the AQI any longer.

The measurement method for lead involves first using 24-h high-volume sampling for Total Suspended Particulate matter (TSP) using glass, quartz, or PTFE filters [65]. A (portion of the) sampled filter is then extracted by one of two methods: In the first, a solution of HNO_3 and HCl is added to the filters or filter strips, in plastic digestion tubes, submerging the entire filter in the extractant. The tubes are placed in a heated ultrasonic bath for 1 h to facilitate the extraction of lead. Following ultrasonication, the samples are made up to volume (40 or 50 mL), vortex mixed or shaken vigorously, and centrifuged prior to aliquots being taken for Inductively Coupled Plasma Mass Spectrometry

(ICP-MS) analysis. In the second method, a solution of dilute HNO_3 is added to the filter strips in plastic digestion tubes and the tubes placed in a hot block digester and covered with polypropylene watch glasses; the solution is allowed to reflux and afterwards made up to volume.

Lead concentration in the extract solution is measured, after filtration, by ICP-MS. The quantitation of total Pb is based on the summation of signal intensities for the isotopic masses 206, 207, and 208, while ^{115}In, ^{165}Ho or ^{209}Bi are used as internal standards [66].

3.7. Particulate matter

Measurement of particulate matter measurement is separated into two categories, PM_{10}, and $PM_{2.5}$. The EPA defines the FRM for the measurement of PM_{10} to be the measurement of the mass concentration of particulate matter bearing an aerodynamic diameter less than or equal to a nominal 10 μm (PM_{10}) in ambient air over a 24-h period (±1 h, elapsed time accurate to 15 min, which is equivalent to ~1% uncertainty over 24 h) [67]. Almost the same general approach is applied to $PM_{2.5}$ except for the size specification and as such, these two measurements are discussed together [68]. While the standard method does not distinguish the constituents of the collected matter, it stipulates that the collection and subsequent measurement protocol must be nondestructive so that analyses of the collected material can be implemented if desired.

The FRM for PM_{10} describes a system in which the air sample is drawn at a constant flow rate through a specially shaped inlet which inertially separates the sampled particulate matter into one or more size fractions within the PM_{10} size range. Each size fraction in the PM_{10} size range is then collected on a separate filter for 24 h. The FRM does not prescribe an inlet of specific geometry but the particle size discrimination characteristics (sampling effectiveness and 50% cut point) of the sampler inlet are part of the performance specifications. The filters are weighed prior to sampling after 24 h equilibration at 20–45% RH (controlled @ ± 5% RH) at 15–30 °C (controlled @ ± 3 °C) and the same equilibration protocol is followed post sampling prior to weighing. For PM_{10} concentrations $\leq$80 μg/m^3, the sampler is expected to show a precision of $\leq$5 μg/m^3 and at higher concentrations a relative precision of $\leq$7%.

The volume of air passed through the system is then corrected to EPA reference conditions, which is 25 °C at 1 atm (101.3 kPa). Knowing the nominal flow rate and the collection period, calculating the air volume is trivial. Then it is only a matter of weighing the collected particulate matter and dividing by the volume of air to express the results in units of μg/m^3 [69].

The FRM for PM10 does not specify the nature of the filter material to be used, except the stipulation that the alkalinity of the filter must be $\leq$ 25 μeq/g. (Excess alkalinity promotes acid gas adsorption and leads to positive artifacts). $PM_{2.5}$ is measured in a similar fashion as PM_{10} except that a different size fraction is collected and in this case the filter material is specified to be PTFE.

There can be multiple error sources in PM measurement. Volatile particles collected on filters are often lost during shipment and/or storage of the filters prior to the post-sampling weighing. Although shipment or storage of loaded filters is sometimes unavoidable, filters should be reweighed as soon as practical to minimize these losses. Alkaline filters will cause acidic gases like SO_2 and HNO_3 to adsorb to the surface and cause a positive interference, this occurs especially on glass or quartz fiber filters and cellulose ester filters. Lastly, errors in the variation of sample flow rate and subsequent air volume determination will affect the results. This is minimized by the use of a flow control device and an elapsed time meter or a flow totalizer.

The volatility error is particularly problematic in $PM_{2.5}$ measurement, so much so that the FRM recognizes that the absolute accuracy may be difficult to define. The size and volatility of ambient particulate matter vary over a wide range and the mass concentration of particles varies with particle size. Accordingly, the FRM for $PM_{2.5}$ defines accuracy as the degree of agreement between a subject field $PM_{2.5}$ sampler and a collocated $PM_{2.5}$ reference method audit sampler operating simultaneously at the monitoring site location of the subject sampler and includes both random (precision) and systematic (bias) errors.

4. Dallas – Fort Worth MSA: AQI and an investigation of air quality

The Dallas – Fort Worth (DFW) metropolitan area (metroplex) is the 4th largest metroplex by population in the country, consisting of the larger city of Dallas at 1.3 million, Fort Worth at 936 thousand, and surrounding cities with a combined population 7.8 million as of the 2021 census. However, at 345 people/km^2, the population density is substantially lower than many other MSAs in the country, much less the world [70]. The low density of a relatively high population, coupled with a lack of significant investment into public transit, has led to a large population essentially completely dependent upon cars for any transportation [71]. (Arlington, TX, the home of the authors, a part of the DFW MSA, is 50th in population (~400,000) in the US, has the dubious distinction of being the largest city in the country, without *any* mass transit system.) The DFW MSA has seen an order of magnitude growth in population since 1950; A population of well below 1 million in 1950 has increased to 7.8 million as of 2021 [72]. Poor air quality and high traffic density are of course correlated: the incomplete combustion of fuel leads to a direct increase of CO, NO_2, and particulate matter, and photochemical reactions between emitted NO_2 and volatile organic compounds (VOCs) then becomes a source for ozone. Considering the amount of driving that the people of the DFW MSA must do (average one-way commuting time 28.5 ± 0.2 min), it is no surprise that the region has struggled with air quality issues for decades [73]. Compared to other MSAs in Texas, DFW is unique in that the majority of its ambient NO_2 and O_3 does not originate from industrial emissions but rather emissions from on-road vehicles, construction equipment and airports (the two major public airports in the MSA rank 3rd and 33rd in the nation in the number of flights they handle) [74–76].

In the past twenty years, the MSA has been in nonattainment for both ozone, and surprisingly, lead [77–79]. As stated before, the EPA lowered the NAAQS value for ambient lead levels to 0.15 μg/m^3 in 2008. Collin County, in the northeastern part of the MSA, was found then to be in nonattainment, with one monitoring station reporting a 3-month average lead concentration of 0.23 μg/m^3 in the 2006–2008 period. An area is designated in nonattainment if within a 3-year period, the measured value at any monitoring location, averaged over 3-months, exceeds the NAAQS level. The monitoring station that made the measurement was located less than a mile from a lead-acid battery recycling plant [80]. The nonattainment designation was accompanied by compliance requirements to be attained before 2016. The link between lead-acid battery recycling and lead pollution is rather obvious, and it did not take long to make the connection to the particular plant [81]. In 2012, the Texas Commission on Environmental Quality (TCEQ), the State's equivalent to the Environmental Protection Agency, published the State Implementation Plan (SIP) to attain compliance, including an agreement with the plant owners. Later in the year, the owners notified TCEQ that the plant will be permanently shut down before 2013. Between 2013 and 2015, no exceedance was noted, and compliance attainment was recognized in 2017. Since then, no monitoring location of the MSA has reported any exceedance of the lead standard.

This actually highlights the dilemma in locating air monitoring stations. It was serendipitous that there was a monitoring station close to the lead battery processing plant. Had it been located at the other end of the county, far away from the plant, the excursion in lead levels may never have been detected. While a callous view may be that such a location would have saved the MSA significant amounts of time and money, the area near the plant has significant residential population, which would have continued to be exposed to unhealthy levels of lead.

Ideally, monitoring stations should represent the spectrum from the least likely to most likely locations to encounter adverse air quality to give the best representation possible, but given that there would never be enough available resources, perhaps priority should indeed be given to protect the most susceptible residentially populated region.

Unfortunately, the story behind this MSA's compliance with the ozone NAAQS has been much more complicated and no such simple remedy such as that fixed the lead problem, has been possible. In 2008, DFW was found to be in severe nonattainment with the NAAQS ozone standard of 0.075 ppm [82]. Airborne pollutants are easily transported and in fact, *all* 10 counties in and around the DFW MSA have struggled with ozone levels. As the regulations for ozone have changed frequently, we only address here the standards set in 2008. In 2012, all 10 counties were designated as in nonattainment, with the requirement that attainment be reached within 2018. The first SIP was published in 2015. Part of an SIP is to develop an "emissions inventory", in which models are used to estimate the origin of the precursors of ozone – specifically in this case NO_x and VOCs. Such a study determined that the majority of the NO_x in the MSA is of vehicular origin.

Photochemical reactions leading to ozone production are obviously promoted when the insolation intensity is higher, and the "ozone season" peaks annually in the summer. In 2014, as a result of a lawsuit brought by the Natural Resources Defense Council, a Federal Court ruled that the definition of the attainment year ozone season be changed to the season occurring *before* the due attainment date [83]. Thus, the attainment year was changed to 2017 from 2018. With this change, TCEQ petitioned the EPA regarding its inability to meet the new deadline while providing revisions to the 2015 SIP. One such revision included a report of reasonable further progress (RFP) and a motor vehicle emissions budget that claimed an 18% reduction in ozone precursors from 2011 through 2018 [84]. However, the 2015–2017 ozone value for the MSA was 0.079 ppm, still above the 2008 standard of 0.075 ppm. By late 2019, the EPA reclassified the MSA from being in "moderate" nonattainment to "serious" nonattainment [85].

The EPA did approve a new SIP submitted by TCEQ in 2020 [86]; the target level of emissions for NO_x and VOCs, (303.10 and 408.95 Mtons per day respectively) based on a revised emission inventory. Measures for reducing precursor emissions were also declared, including adherence to the Federal Motor Vehicle management program, using gasoline with a low Reid Vapor Pressure (vapor pressure at 37.8 °C) among other measures with smaller contributions [87]. In mid-2021, the EPA noted to TCEQ that while work has been done by the State to reduce emissions, to reach reduction milestones and provide objective evaluations, much work was still needed to reach the 2008 NAAQS [88].

However, the ozone value published by the EPA between 2018 and 2020 for the MSA was 0.076 ppm, still above the standard. In a ruling on October 2022, the EPA redesignated the MSA from being in "serious" to "*severe*" nonattainment [89]. Under this new classification, the MSA must meet the 2008 NAAQS for ozone by the end of 2026 to meet the 2027 attainment deadline. Automobile traffic and thus the ozone levels declined during COVID. But now, given that the MSA population is growing 1.3–1.4% annually and in post-COVID years, the transient lull in vehicular traffic is gone, chances of attaining regulatory limits are not high.

Returning to the AQI, in Fig. 4, AQI values for Dallas and Tarrant, the two most populous counties in the MSA, are plotted for the 2011–2021 period [90]. It will be apparent that the peak AQI values (most often based on ozone) occur seasonally. Fig. 5 plots both the AQI values as well as sunlight hours: these data provide direct evidence of photochemical origin of the ozone.

Fig. 6 depicts the number of times in a 10-year period how often a given NAAQS pollutant has been the determinant of the AQI. For over 2000 days in the ten-year period, ozone was the pollutant that determined the AQI. It is not unusual for $PM_{2.5}$ to be the determinant of the AQI, as is observed here but this can probably be accounted for the large number of vehicle miles driven in the MSA and wildfires in neighboring areas.

Dallas County has higher incidences of exceedances of the $PM_{2.5}$ standard. But Tarrant County not only has higher number of ozone exceedances, but it also typically shows higher AQI values, despite having a significantly lower population (about 84% of Dallas County, in addition, the population of bordering counties is much higher for Dallas County compared to Tarrant County). This suggests that some of the pollution seen in Tarrant County may actually be transported *into* it from bordering regions, notably Dallas County, which lies to the East. This conjecture is supported by wind data available for the Arlington Municipal airport, located between the city centers of Dallas and Fort Worth (the seat of Tarrant County). During the ozone season, the monthly average wind direction is always east to west.

This is corroborated by wind data for July 2021 from the DFW

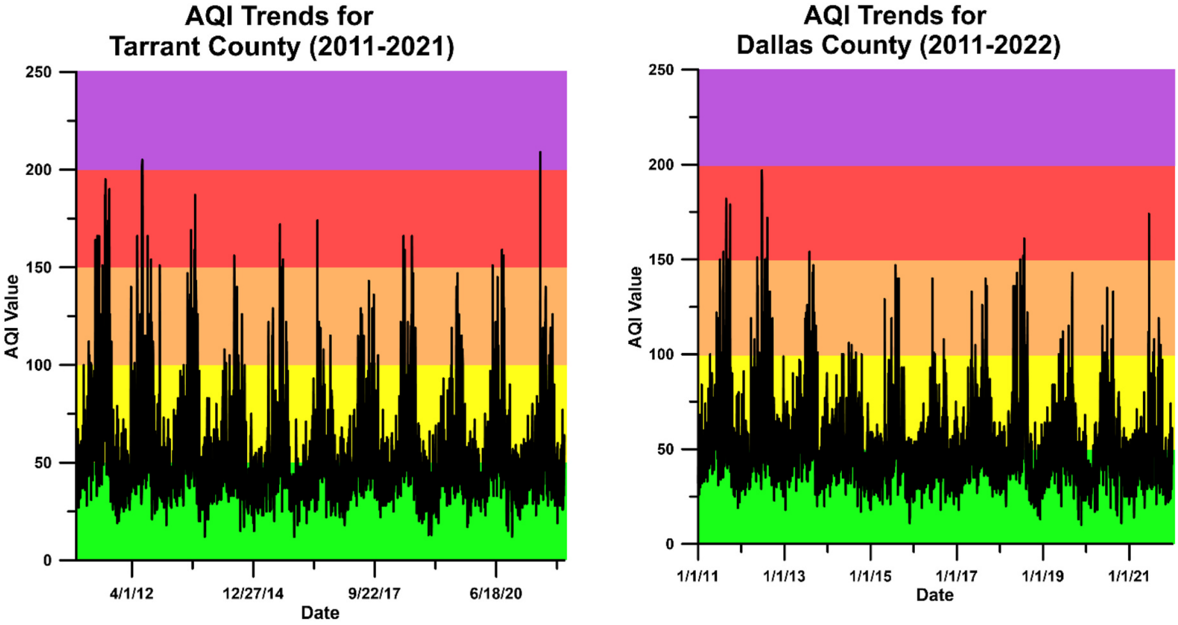


Fig. 4. AQI Values for Tarrant and Dallas counties plotted against time.

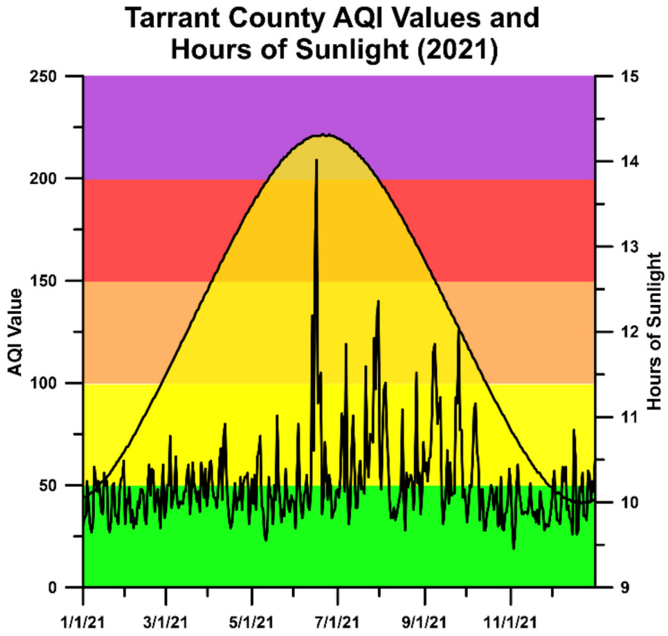


Fig. 5. Plotting AQI values along with hours of sunlight in Tarrant County for 2021.

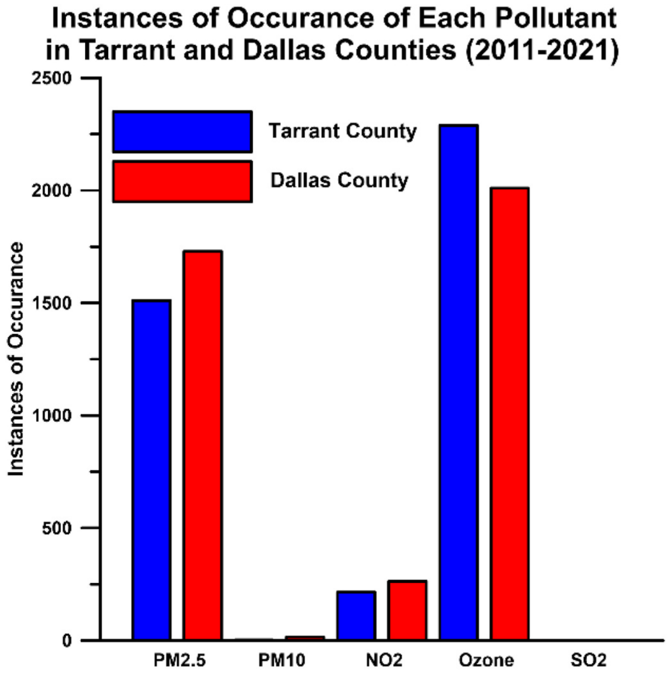


Fig. 6. Instances of occurrence of each pollutant in Tarrant and Dallas Counties for 2011–2021.

International Airport, which lies slightly north of both city centers (see Fig. 7). This shows a general westward trend of air flow (southwestern from the perspective of the airport location).

The air mass is dominantly transported to the southwest, with an average direction of 229 ± 19° with an average wind speed of 8.74 ± 4.80 miles per hour. The air mass that moves into Tarrant County therefore typically originates in Dallas County, as well as those further north: Denton and Collin Counties. As with the rest of the metroplex, these counties produce significant amounts of NO_2 from traffic, which leads to photochemically mediated formation of ozone that is formed along the way before being measured in Tarrant County. This is one potential explanation of the higher ozone values observed in Tarrant County relative to the more densely populated Dallas County (2020 data: 2440 people/square mile vs. 2995), also bearing heavier traffic. Such an explanation does not apply when particulate matter is the primary pollutant, as the transport characteristics are not the same as that of gases.

A more sophisticated analysis is possible using the publicly available HYSPLIT model from the National Oceanic and Atmospheric Administration (NOAA) that permits back trajectory calculations at different altitudes and addressing back trajectories over different periods of time [92] (See Fig. 8). Tutorials are available for using HYSPLIT [93]. For all of the dates and times analyzed by the HYSPLIT model in late afternoon hours (peak ozone period) in the ozone season, the transport was to the west, reinforcing the belief that a significant part of the ozone observed in Tarrant County is from ozone generated or its precursors transported from regions further east. The caveat is that the model only looks only at transport of the entire air mass and not individual airborne constituents, the concentrations of which will also change due to any contributions along the trajectory. The results become particularly difficult to interpret if the air mass slows down (or worse, becomes stagnant or recirculates for some period over an emission source).

This trend can be further noticed when one plots the Dallas County AQI values against the difference between the Tarrant and Dallas County AQI values. For any given day, it is three times more likely that Tarrant County will experience worse air quality than Dallas County, though the magnitude of difference can be rather small (7 AQI units on average), the trend is consistent throughout the ozone season, although there is a high degree of variation in the data. Plotting of the difference in AQI vs the wind direction is also suggestive of the excess pollution in Tarrant County being due to sources located further east and north (see Fig. 9).

Despite its value, the AQI does not communicate all the important information about air quality one might want to know. Of course, detailed data reveal much more to the cognoscenti than can be gleaned from a single number/color. Still, it is an important tool in alerting the general public. The AQI is also limited by the few criteria pollutants that it is composed of. Some of these pollutants have waning importance as industrial practices move away from their promulgation. Still, this is the heart of what makes it so versatile. As new pollutants come into focus, they may one day be incorporated into the AQI, these being hazardous air pollutants (HAPS) like benzene, perchloroethylene, methylene chloride, radioactive materials, and perfluoroalkyl substances (PFAS), etc. Many other air quality indices have been proposed; most lack simplicity and run into issues of practicality. These two are the driving principles that make the current AQI formulation ubiquitous in the United States and across the world. Indeed, Air quality indices across the world are now instantaneously available to anyone (see e.g., https://waqi.info/or multicolor maps provide broad regional information (https://www.iqair.com/world-air-quality). The extent to which awareness will prevent more instances like that in Donora in 1948, London in 1952, etc. is not clear. Looking at the worst numbers in the worldwide maps, it is clear that clean air is hardly to be taken for granted in many parts of the world and much progress still have to be made.

Declaration of competing interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome. We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

Data availability

No data was used for the research described in the article.

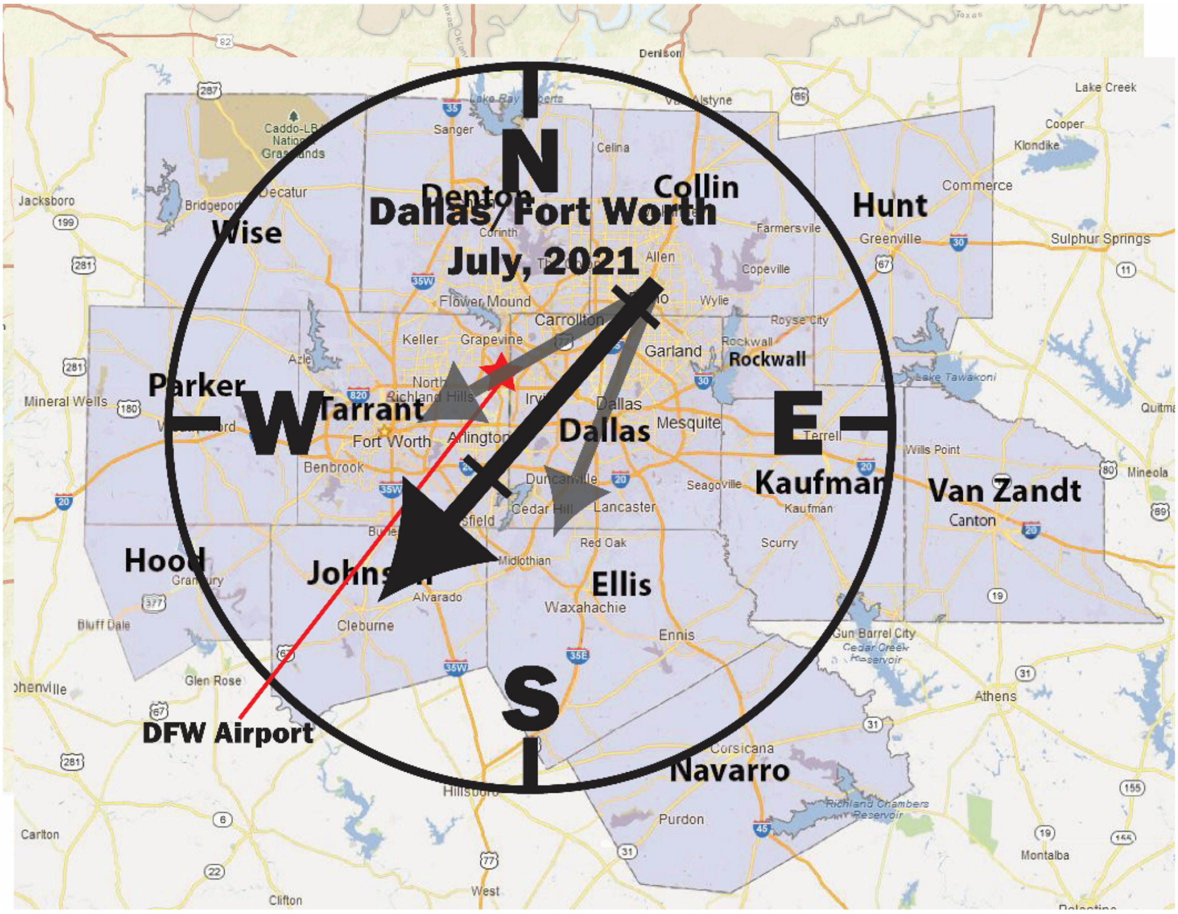
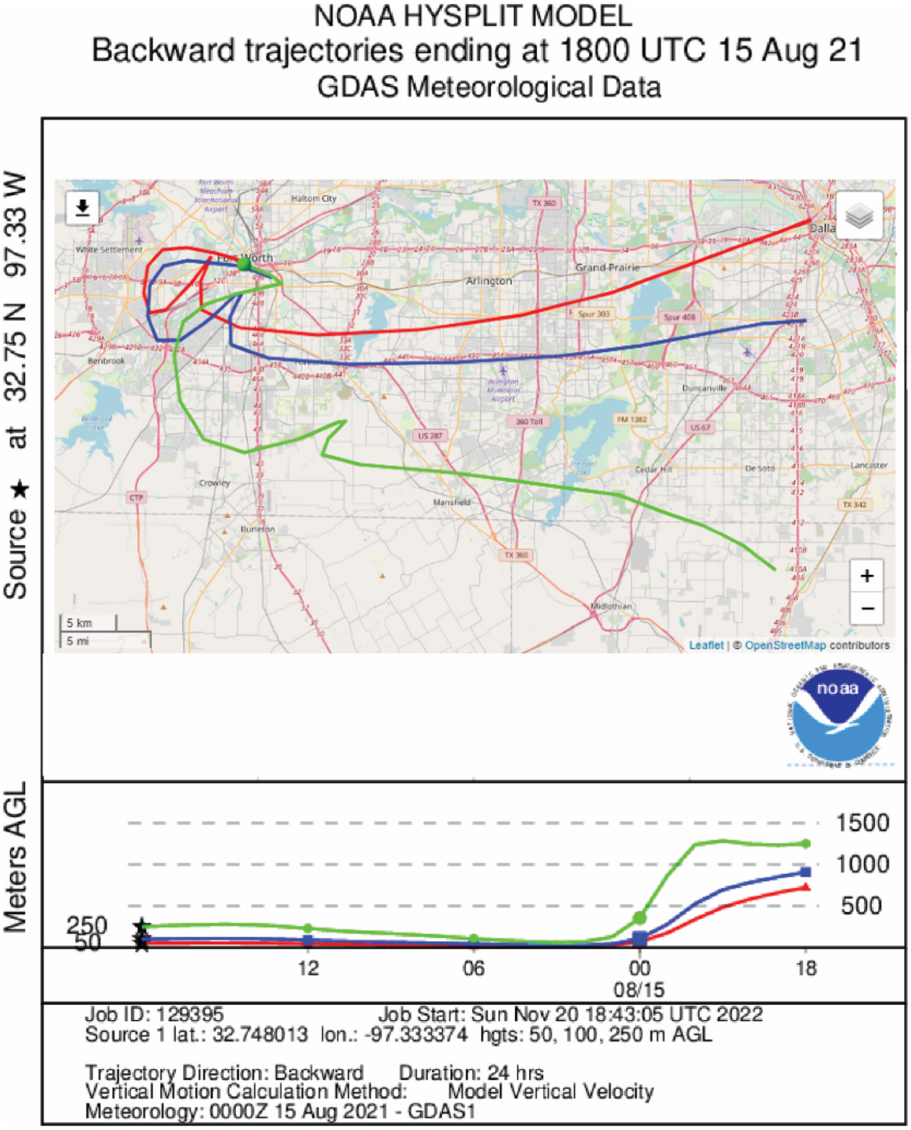


Fig. 7. Average wind direction for July 2021 in the DFW metroplex, as measured from DFW International Airport (data obtained from accessible weather records [91]. The length of the central arrow is proportional to the wind speed (the length beyond the error bars indicate ± 1 standard deviation. The cone represented by the outer arrows encompasses ±1 standard deviation.



NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 15 Aug 21
GDAS Meteorological Data

Job ID: 129395 Job Start: Sun Nov 20 18:43:05 UTC 2022
Source 1 lat.: 32.748013 lon.: -97.333374 hgts: 50, 100, 250 m AGL

Trajectory Direction: Backward Duration: 24 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 15 Aug 2021 - GDAS1

Fig. 8. Twenty-four hours back trajectory of the airmass arriving at Fort Worth, Texas at 6:00 p.m. on June 15, 2021. The green, blue, and red traces correspond to altitudes of 50, 100 and 250 m above ground level, respectively.

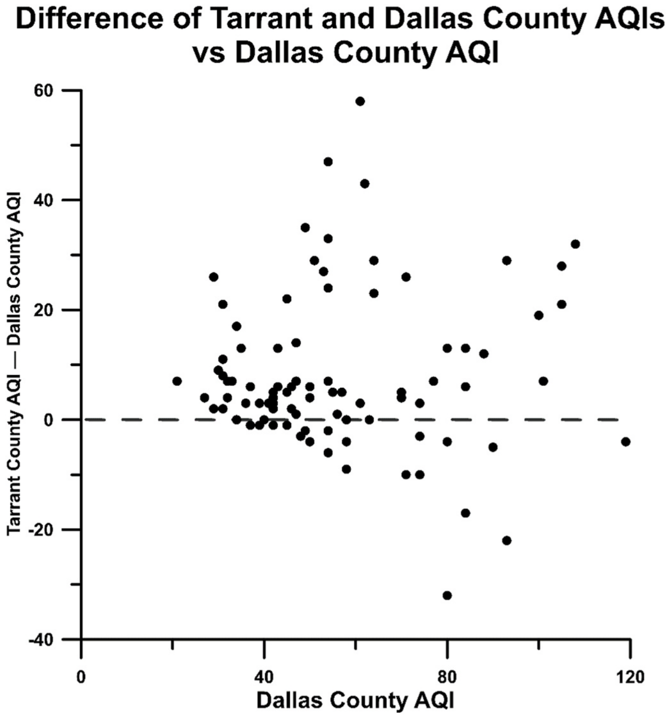


Fig. 9. Difference in AQI between Tarrant and Dallas Counties vs Dallas County AQI.

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