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Decrease in Ambient Polycyclic Aromatic Hydrocarbon Concentrations in California's San Joaquin Valley 2000–2019

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Abstract

As part of our ongoing research to understand the impact of polycyclic aromatic hydrocarbon (PAH) exposures on health in the San Joaquin Valley, we evaluated airborne PAH concentration data collected over 19 years (2000–2019) at the central air monitoring site in Fresno, California. We found a dramatic decline in outdoor airborne PAH concentrations between 2000 and 2004 that has been maintained through 2019. This decline was present in both the continuous particle-bound PAHs and the filter-based individual PAHs. The decline was more extreme when restricted to winter concentrations. Annual mean PAHs concentrations in 2017– 2018 of particle-bound PAHs were 6.8 ng/m^3 or 62% lower than 2000 – 2001. The decline for winter concentrations of continuous particle-bound PAHs between winter 2019 and winter 2001 was 17.2 ng/m3, a drop of 70%. The 2001 to 2018 decline in average wintertime concentrations for filter-based individual PAHs was 82%. We examined industrial emissions, on-road vehicle emissions, residential wood burning, and agricultural and biomass waste burning as possible explanations. The major decline in PAHs from 2000–2004 was coincident with and most likely due to a similar decline in the amount of agricultural and biomass waste burned in Fresno and Madera Counties. On-road vehicle emissions and residential wood burning did not decline until after 2005. Industrial emissions were too low (2% of total) to explain such large decreases in PAH concentrations.

Graphical Abstract

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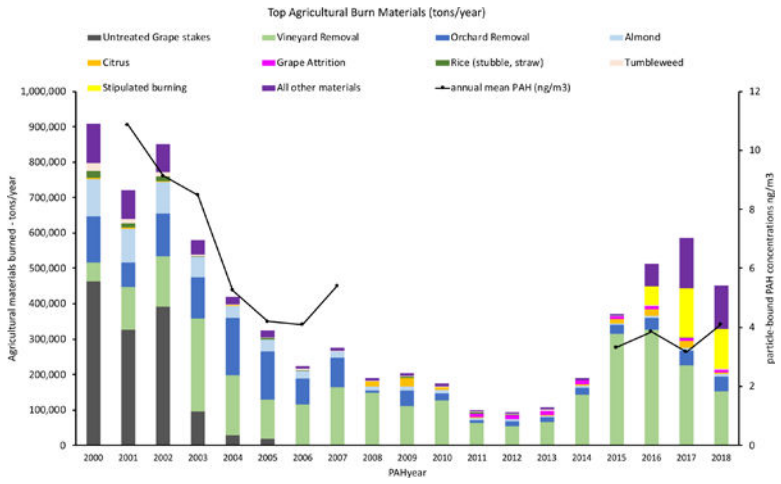
CRediT author statement

Elizabeth M. Noth: Conceptualization, Methodology, Software, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualization, Funding acquisition. **Fred Lurmann:** Conceptualization, Methodology, Software, Writing - Review & Editing, Project administration, Funding acquisition. **Charles Perrino:** Methodology, Investigation, Resources, Validation. **David Vaughn:** Methodology, Investigation, Resources, Validation, Data Curation. **Hilary A. Minor:** Methodology, Software, Investigation, Validation, Data Curation. **S. Katharine Hammond:** Conceptualization, Methodology, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Keywords

air pollution; polycyclic aromatic hydrocarbons; California; agricultural burning; residential wood burning; biomass burning; traffic-related air pollution

1. Introduction

Human exposure to polycyclic aromatic hydrocarbons (PAH) is associated with significant adverse health outcomes, but the extent and trends in environmental concentrations are poorly understood. PAHs are identified as Hazardous Air Pollutants by the US Environmental Protection Agency, as Toxic Air Contaminants by the California Air Resources Board (CARB), and as human carcinogens individually and in groups by International Agency for Research on Cancer (International Agency for Research on Cancer, 1987, 1989, 2010). None of these designations require routine monitoring of PAHs, thus information on time trends in outdoor PAH concentrations is extremely limited (Sun et al., 2006; Noth et al., 2011; Noth et al., 2016).

Our previous work in the San Joaquin Valley (SJV) of California shows that PAH exposure is associated with significant poor health in young children and pregnant women: decreased FEV1, increased asthma severity, and suppression of regulatory T-cell function (Nadeau et al., 2010); impaired systemic immunity and epigenetic modifications in FOXP3, a key locus involved in atopy (Hew et al., 2014); adverse respiratory health (Gale et al., 2012; Padula et al., 2015); and, a greater risk of pre-term birth (Padula et al., 2014). Other studies have reported similar associations of adverse health outcomes with prenatal or early life PAH exposures in other regions (Jerrett et al., 2003; Miller et al., 2004; Choi et al., 2006; Jedrychowski et al., 2007; Choi et al., 2008; Perera et al., 2009; Jedrychowski et al., 2010).

PAHs are co-emitted with regulated gaseous and particulate combustion products (VOC, PM, NOx, CO) from common sources, such as motor vehicles and biomass burning (Jenkins et al., 1996; Marr et al., 1999; Fujita et al., 2007; Navarro et al., 2017). Criteria pollutant concentrations in many parts of California have decreased over the last 20 years (McDonald et al., 2012; Lurmann et al., 2015), likely because of stationary and mobile source emission

reduction policies implemented by the California Air Resources Board (CARB) and local air districts (Propper et al., 2015), which undoubtedly also contributed to decreased ambient concentrations of PAHs (Bahadur et al., 2011). The effectiveness of programs to accelerate light-duty vehicle emission reductions starting in the early 1990s and heavy-duty vehicle emission reductions in 2004–2010 are widely recognized. Programs to reduce biomass burning emissions by local air pollution agencies are less well known. For example, the SJV Air Pollution Control District (SJVAPCD) adopted policies limiting the types of agricultural waste that can be legally burned beginning in 1992 (see Supplementary Table S1) (San Joaquin Valley Air Pollution Control District, 1992) and requiring pre-burning inspections (in January 2003). Rule 4901 (enforced beginning November 2003) aimed to reduce emissions of particulate matter from wood burning in fireplaces, heaters, and outdoor devices (San Joaquin Valley Air Pollution Control District, 2003). These biomass burning control measures likely contributed to decreased PAH ambient concentrations.

As part of our ongoing research to understand the impact of PAH exposures on health in the SJV, we evaluated airborne PAH concentration data collected over 19 years (2000–2019) in Fresno, California. Fresno is the fifth largest city in California, the largest city in the Great Central Valley and is located in the center of the SJV Air Basin (Figure 1). Fresno is the economic center for this large agricultural region, with agriculture, health care, and retail sales as the major employers (County of Fresno, 2015). Our main objective was to investigate the nature and possible causes of temporal trends in outdoor airborne PAH concentrations during this time period.

2. Methods & Materials

Samples were collected at the Fresno First Street site (3425 N. First St, 2000–2011) and the Fresno Garland site (375 meters north at 3727 N. 1st Street, 2012-present), both operated by CARB. Because they are only 375 meters apart, we considered these the same location, “Fresno central site,” but no collocated data are available to confirm this reasonable assumption. Airborne concentrations of ambient PAHs at the Fresno central site were characterized by real-time continuous monitoring and 24-hour integrated sample collection.

2.1 Sample collection

2.1.1 Continuous real-time data collection—A real-time continuous monitor of particle-bound PAHs, the Photoelectric Aerosol Sensor model 2000 (PAS2000) (EcoChem Analytics, League City, TX) collected data from October 2000 through June 2019 at the Fresno central site. The PAS2000 uses a photoelectric aerosol sensor to measure the levels of particle-bound ambient PAH with three or more rings. The PAS2000 was fitted with a $PM_{2.5}$ sharp cut cyclone inlet (MesaLabs SCC1.191). Data collected at 1-minute intervals were integrated into 24-hour average concentrations to match the sampling period of the filter samples. Monitor flow rates and baseline response to zero-particle air were checked monthly throughout the study. Collocated data were periodically collected from a secondary PAS2000 monitor, which was used to pre- and post-calibrate the primary monitor when it was refurbished by the manufacturer. Calibration was done according to the user manual, using data from the secondary PAS2000.

2.1.2 Integrated data collection and laboratory analysis—We collected integrated 24-hour samples for PAHs with two methods: Harvard-type impactors with two 37mm filters; Chemcomb Model 3500 Speciation Sampling Cartridges (Thermo Scientific) with three glass honeycomb denuders in sequence (to collect gas phase PAHs) and three 47mm filters; collocated sampling indicated the two methods were comparable. Filters in both collection methods were pre-baked quartz fiber filters (PallFlex Tissue Quartz) impregnated with ground XAD-4 resin (Gundel et al., 1995; Lee et al., 2004). Diagrams of the sampling methods are provided in the supplemental materials (Figure S1). The glass honeycomb denuders were also coated in XAD-4 resin, which was replaced after 5 iterations of sampling and extraction. Both samplers had PM_{10} inlets and airflow of 10 lpm (2000–2012) or 16.7 lpm (2013–2018), respectively (Noth et al., 2011; Noth et al., 2016). The sum of the filters and denuders was used herein for the Chemcomb samples (N=28).

Filter and denuder samples were extracted in dichloromethane followed by vacuum filtration, then concentrated under nitrogen. Analyses were performed by gas chromatography/mass spectrometry (HP 6890/5972 or Agilent 7820/5977E) in the selected ion-monitoring mode with a 30m (5%-Phenyl)-methylpolysiloxane column (Agilent HP-5MS).

The filters and denuders were analyzed for 16 PAHs – acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), anthracene (ANT), phenanthrene (PHE), fluoranthene (FLT), benz[a]anthracene (BAA), chrysene (CHR), pyrene PYR), retene (RET), benzo[a]pyrene (BAP), benzo[b]fluoranthene (BBF), benzo[k]fluoranthene (BKF), benzo[ghi]perylene (BGP), indeno[1,2,3-cd]pyrene (ICP), and dibenz[a,h]anthracene (DBA). Standard curves were run with the samples and sample results were blank corrected. The limit of quantitation (LQ) was calculated for individual PAH, media and day of laboratory analysis. The average LQ per filter sample was 1.5 ng or 0.05 ng/m^3 (range 1 – 2.5 ng or 0.03 – 0.09 ng/m^3) for a 24-hour sample collected at 10 lpm. The average LQ per denuder sample was 0.2 ng or 0.01 ng/m^3 (range 0 – 0.59 ng or 0 – 0.04 ng/m^3) for a 24-hour sample collected at 10 lpm. Overall, 2% of the individual PAH concentrations were less than quantifiable and were assigned half the LQ for calculations; half of these were either indeno[1,2,3-cd]pyrene or dibenz[a,h]anthracene. The average mass collected on the third denuder (in sequence) of the Chemcomb samples (N=28) was 16% of the sum of all three denuders. The average mass collected on the third filter (in sequence) of the Chemcomb samples (N=28) was 9% of the sum of the three filters. Using 2 filters had an average collection efficiency of 85%, when compared to using 3 filters. The mass on the first filter in the cartridge was typically 2–3 times greater than the mass on the second filter (median 2.5 times).

All values were blank corrected. Filter sample (37 & 47mm) duplicates before 2010 (N=26) [after 2010 (N=29)] showed a mean absolute difference of 0.57 [0.33] ng/m^3 for the 3-ring PAHs, 0.19 [0.10] ng/m^3 for 4-ring, and 0.13[0.10] ng/m^3 5- and 6-ring PAHs. Denuders were evaluated in triplicate (N=3 sets) for the 9 PAHs present in vapor-phase and showed a range of coefficients of variation (i.e. the standard deviation / mean) from 0.14 – 0.24, with a mean of 0.17.

2.2 Annual and seasonal trends in particle-bound and individual PAHs

Annual average trends were examined throughout the period. In order to keep each high particulate matter pollution season (November through February) within the same annual metric, we defined a temporal period called “PAHyear” as November thru October, named for the year in which January falls. For example, PAHyear 2008 is November 1, 2007 thru October 31, 2008. We examined the trends in average *seasonal* concentrations to learn if the relationships between seasonal and annual mean concentrations remained constant as the absolute year-to-year concentrations changed: winter (November-February), spring (March-June), and summer/fall (July-October).

2.3 Comparison to CARB Air Toxics Data

To provide context for the observed data, we compared annual and seasonal average concentrations of six individual particle phase PAHs (BAP, BBF, IDP, BKF, DBA, and BGP) with historical filter-based PAH samples collected as part of the CARB’s Air Toxics program 1990–2005. We excluded 2005 from the annual average because the CARB sampling ended in February 2005. These 24-hr PM_{10} samples were collected once every 12^{th} day November-January (i.e. 6 to 8 days per year) and had a limit of detection of 0.05 ng/m^3, similar to the mean LQ in our samples.

Hourly data for NO_2, $PM_{2.5}$ and PM_{10} collected at the Fresno central site from 2000 through 2017 were obtained through the Air Quality System and averaged to seasonal and annual concentrations for comparison to the trends in PAH concentrations.

2.4 Comparison to Criteria Pollutants

We collected the routine criteria pollutant data from EPA’s Air Quality System (AQS) for NO_2, $PM_{2.5}$, and PM_{10}. All data were subjected to quality checks and compiled as daily average concentrations.

2.5 Comparison to Potential Source Activity and Emissions

We utilized two emissions models and two sets of source-related activity to evaluate potential causes of the change in PAH concentrations. First, we used emissions estimates from the California Almanac of Emissions and Air Quality during this time period were available for years 2000, 2005, 2010, 2012, and 2015 (https://www.arb.ca.gov/aqd/almanac/almanac.htm, accessed September 23, 2019). We used the SJV Air Basin and Fresno County emissions estimates from industrial and energy production sectors, on-road motor vehicles, residential wood combustion, and agricultural burning to examine the potential influences on PAH concentrations in Fresno. No emission estimates for PAHs are available, so we used the PM_{10} emissions estimates as the closest match to our samplers, which had PM_{10} inlets.

Second, we compared the daily measured particle-bound PAH concentrations to a global emissions model of PAHs (Shen et al., 2013). This emissions model uses country- and year-specific emission factors for each of the 16 individual PAHs. We extracted years 2000–2006 and 2010–2013 (http://inventory.pku.edu.cn/home.html, last accessed June 17, 2019 when access was cut off, last failed attempt to access data was November 20, 2019). Because of the loss of access to the global emissions model website, we were able to obtain overlapping

data only for PAHyears 2001–2005. We compared the annual and seasonal modeled PAH emissions. We compared the annual and seasonal modeled PAH emissions for each of the sectors the model provides – agriculture, deforestation, energy production, industry, residential, transportation and total.

For residential wood combustion, emissions estimates from the California Almanac of Emissions and Air Quality are only available for November through February. To look at source activity we also used a dataset of historic daily decisions on allowable burning. Starting in November 2003, residential wood combustion during the winter (November – February) was restricted by Rule 4901 to days on which the AQI was forecast to be under 150 (65mg/m^3 $PM_{2.5}$).

We quantified agricultural burning in Fresno and Madera Counties from agricultural burn permit data available from SJVAPCD from 2000–2019. Each record contains: date of burn; acres or tons of material burned; type of material burned; address or cross streets of burn; and latitude and longitude of burn. Most permits reported the tons of material burned. For permits that reported acreage burned, we converted that to tons of material burned using crop-specific fuel loading (FL) factors provided by SJVAPCD.

3. Results

3.1 Trends in continuous real-time particle-bound PAHs

3.1.1 Annual trends in particle-bound PAHs—Our longest and most continuous dataset was particle-bound PAH daily concentrations derived from the PAS2000 continuous analyzer. These observations run for the majority of the period from October 2000 to June 2019. Daily data are available for 75% of the days in this period (N=5054 days), and eleven years have sufficient measurement data for valid annual means (i.e. have over 70% coverage). Despite having over 70% data in PAH year 2008, we have excluded the annual metric for PAH year 2008 because the missing months were sequential, creating a biased annual mean concentration. We did not collect continuous daily data for most of the period from 2009–2014.

There was a clear decrease in the annual mean concentration of particle-bound PAHs from 10.9 ng/m^3 in PAH year 2001 to 4.1 ng/m^3 in PAH year 2018 (Nov 2017-Oct 2018), a decrease of 62% (Table 1, Figure 2). The decline was most dramatic from 2001 to 2005 (50%), with a 4.3 ng/m^3 difference in average PAH concentration before 2005 compared to measurements collected in 2005 and later (Table 2).

3.1.2 Seasonal trends in particle-bound PAHs—Mean wintertime concentrations for each year are much higher and show a decrease similar to the annual concentrations. The mean winter PAH concentrations declined from 24.7 ng/m^3 in the winter of 2000–2001 to 7.50 ng/m^3 in the winter of 2018–2019, a decrease of 17.2 ng/m^3 or 70% (Figure 2, Table 1). As with the annual mean, the majority of the decline occurs from the winter of 2000–2001 through the end of 2004. From the winter of 2004–2005 the mean concentrations are similar and under half those of winter 2001. An average decline of 11.3 ng/m^3 (58%) was observed

in winter concentrations in measurements before 2005 to those collected in 2005 and later (Table 2).

The spring measurements show the lowest concentrations and year-to-year variability of any season, and we have the least information available for that season (Figure 2). Overall, there is a 43% decrease from the period from 2001–2004 to 2005–2019, which is the smallest relative change of all the seasons (Table 2).

The mean of the summer/fall PAH concentrations show a trend similar to the trend in the annual means (Figure 2, Table 2). The levels in 2005–2018 are 46% lower on average than the levels in 2001–2004. The average PAH concentrations in the late summer/fall are approximate half of the annual average concentrations, presumably due to the warmer temperatures and more favorable meteorological conditions for dispersion.

3.2 Trends in integrated individual PAHs

3.2.1 Annual trends in individual PAHs—We collected and analyzed 727 integrated 24-hour samples at the Fresno central site from 2002 thru 2018, approximately half in the PAH winter season (November-February) and a quarter each in the spring and the summer/fall seasons (Table 3). Of the 16 PAHs, phenanthrene and fluorene were generally the most abundant individual PAHs in Fresno and the concentration of 3-ring PAHs was consistently greater than that for 4-, 5-, and 6-ring PAHs combined. We observed a decline in the annual average for most of the individual PAHs from 2003 to 2007, and then a plateau from 2007 until 2018 (Table 3(a)). However, the sampling dates are not evenly distributed by year, and are particularly uneven from 2002 (late summer and fall only) to 2003 (winter only). Because of this and the seasonality of airborne PAH concentrations, we focus on seasonal changes in individual PAH concentrations over the two decades, rather than annual concentrations.

3.2.2 Seasonal trends in individual PAHs—The winter concentrations of all individual PAHs declined from PAHyear 2003 through 2018 (Table 3(b)). The individual PAH concentrations decreased an average of 85%, and all but two by more than 75% (the decrease for pyrene was 65% and that for chrysene 58%). The concentration of the sum of the individual 4-, 5-, and 6-ring PAHs in PAHyear 2003 compared to winter in PAHyears 2006–2018 showed a decline of 59%; this is similar to the mean decline of 58% for wintertime particle-bound PAHs during the same two time periods (Table 2; Figure 2).

The spring concentrations for individual PAHs have no consistent pattern of change from 2003–2018 (Table 3(c)). The concentrations during this season are also considerably lower than those in the winter or the late summer/fall seasons with all compounds exhibiting less than 1 ng/m^3 of change between the time periods.

The concentrations of individual PAHs are the most variable during the summer/fall season in Fresno. This season overlaps almost completely with the “fire season” in California. The wildland fires that burned during the summer/fall season account for 80% of the total acres burned. This period is highly variable year to year because wild fire emissions can play a major role in PAH concentrations (Navarro et al., 2017). Likely for this reason, we do not

see a clear trend in individual PAH concentrations or in compounds grouped by volatility (Table 3(d)).

During the 2008 multiple major wildfires burned in central California, relatively near Fresno, and the PAH concentrations during this time differ from other summers.(California Air Resources Board, 2009) The summer/fall season in 2008 was an unusually high period for acenaphthylene, fluoranthene, phenanthrene (Table S2). The mean concentration for acenaphthylene in 2008 was 21 times higher (6.4 vs 0.3 ng/m^3) than the same period during all the other years. Similarly, fluorene was increased 11-fold (24.4 vs 2.2 ng/m^3), and phenanthrene was increased 9-fold (35.5 vs 3.9 ng/m^3). We did not observe this increase in concentrations during 2008 for most 4-, 5-, or 6-ring individual PAHs. We will report more in-depth evaluation of these data in a subsequent paper focused on PAH concentrations associated with wild fires.

3.3 Comparison to CARB Air Toxics Data

The CARB PAH data declined in winter and annually from 1990–2005 at the First Street Fresno station (Figure S2). We focused on the change from 2000 to 2004, to roughly match the beginning of our measurement period (Table S3). The annual average concentrations in 2004 were 25%−46% lower than in 2000, and the winter average concentrations in 2005 were 41%−55% lower than in winter 2000. These reductions are similar to the decreases we observed concurrently in the particle-bound PAH.

3.4 Comparison to criteria pollutants

The annual mean concentrations of NO_2, $PM_{2.5}$, and PM_{10} decreased 30–40% [or, about 7%/year] from 2001 to 2005 (Figure 3a), much smaller than the contemporaneous 70% decline in particle-bound PAH. The winter concentrations declined rapidly in the first four years (Figure 3b), after which concentrations were highly variable. The decline for all three criteria pollutants from 2008–2011 is likely due to the effects of vehicle emission regulations (e.g. CARB Low-Emission Vehicle II program and Pavley regulation) and the economic downturn. The increased NO_2 and PM during 2006 to 2007, 2012, and 2014 most likely reflect adverse meteorological conditions in those years (Tai et al., 2010; Wang et al., 2017). However, annual mean PM_{10} concentrations from 2016–2018 was the same as during 2001–2003.

3.5 Comparison to Potential Source Activity and Emissions

3.5.1. Industrial and Energy Production—The California Almanac of Emissions and Air Quality PM_{10} emissions from the industrial and energy production sectors did not have a clear increasing or decreasing trend from 2000 to 2015. The average emissions doubled from 0.21 to 0.40 tons/day from 2000–2005, but then peaked in 2010 at 1.68 tons/day, and then dropped back to 0.44 by 2015. At their highest annual average in 2010, these emissions accounted for only 2.5% of the total PM_{10} emissions.

Estimated global PAH emissions (Shen et al., 2013) shows emissions from the industrial and energy production sector nearly doubling between 2000 and 2005. There was a positive correlation between our measured particle-bound PAH data and the modeled global

emissions data for the sum of the PAHs with 4, 5, and 6 rings for the industrial and energy production sectors. However, the industrial and energy production emissions make up only 2% of the total modeled emissions for the air basin.

3.5.2 On-road motor vehicles—The California Almanac of Emissions and Air Quality PM_{10} emissions from on-road vehicles decreased from 2000 to 2015. However, on-road motor vehicle PM_{10} emissions did not decline between 2000 and 2005, but remain steady at approximately 4.4 tons/day. Starting in 2005, emissions decline smoothly to 2.0 tons/day in 2015. The shape and magnitude of this decline is similar to the decline in NO_2 concentrations but different from that in PAH concentrations (Figure 5).

Estimated global PAH emissions (Shen et al., 2013) shows emissions from the transportation sector nearly doubling between 2000 and 2005. As a result, there was a strong negative correlation between our measured particle-bound PAH data and the modeled global emissions data for the sum of the PAHs with 4, 5, and 6 rings for emissions from the transportation sector.

3.5.3 Residential wood combustion—Estimated California PM_{10} emissions from residential wood combustion decreased from 2.3 tons/day in 2000 to 0.7 tons/day in 2015. Similar to on-road motor vehicle emissions, residential wood combustion emissions did not show substantial decreases until after 2005.

Estimated global PAH emissions (Shen et al., 2013), again showed a strong negative correlation between our measured particle-bound PAH data and the modeled global emissions data for the sum of the PAHs with 4, 5, and 6 rings for emissions from the residential sector.

During the first year of restrictions on residential wood burning based on AQI forecasting, PAHyear 2004, only two “no burn” days were declared of the 120 possible winter days. The same was true for the following winter in PAHyear 2005 – only two “no burn” days. It was not until the winter of 2008–2009, when Rule 4901 lowered the mandatory curtailment level to a forecasted $PM_{2.5}$ concentration of $30 mg/m^3$, that the number of “no burn” days increased. During the winters from PAHyear 2004–2008, there were an average of 6.8 “no burn” days per winter. After the amendment effective in winter of PAHyear 2009 and through 2014, the average “no burn” days per winter increased to 48.5 days. This increase of “no burn” days tracks well with the estimated PM10 emissions from residential wood combustion, but not with our measured particle-bound PAH observations.

3.5.4 Agricultural burning—Over 6 million tons of agricultural materials were burned in Fresno and Madera Counties from January 2000 - May 2019, 54% during the winter season, 30% during the spring, and 15% during the summer/fall season. During 2000–2005, the amount (total tons) of agricultural materials burned dropped precipitously, similar to the decline in PAH concentrations (Figure 4). The annual mean tonnage burned for the years 2001–2004 vs 2005–2018 decreased by 61% (392,814 tons). Likewise, the winter mean tonnage burned decreased by 54% (165,248 tons). These percentage changes compare closely with the decreases in PAS2000 measurements over the same periods, i.e., decreases

of 50% in the annual mean and 58% in the winter mean PAH concentrations, in contrast to the 25% decrease in annual the 40% decrease in winter PM2.5 concentrations. In 2015–2018 agricultural material burned increased to an annual mean of 56% of the annual 2001 tonnage; winter tonnage burned rose to an average of 63% of the 2001 winter tonnage. However, we did not observe a corresponding increase in PAH concentrations, which may be explained by multiple factors.

Estimated California PM_{10} emissions from agricultural waste burning decreased from 8.6 tons/day in 2000 to 1.3 tons/day in 2015. The relative changes in agricultural burning emissions are very similar to those reported for agricultural waste (tons) burned, as expected, and drop dramatically from 2000 to 2005, and then more slowly over the next ten years, similar to the declines in PAH concentrations (Figure 5).

Estimated global PAH emissions (Shen et al., 2013) exhibited a strong negative correlation with the total tons of agricultural waste burned per year.

4. Discussion

There was a dramatic decrease in outdoor airborne PAH concentrations in Fresno from 2001 to 2004 that has been maintained through 2019. The CARB Air Toxics data for six individual PAHs at the same site in 2000–2005 corroborate the trends demonstrated by our continuous and integrated filter data. We are not aware of other multi-year ambient PAH data for California.

In an effort to uncover the cause of decline in PAH concentrations, we reviewed changes to potential sources. One possibility was to attribute the decreased concentrations to traffic-related emission reductions, but the timing did not align. The major programs put in place by CARB (Propper et al., 2015) were either too gradual (e.g., Low Emissions Vehicle Programs I and II) or too late (2005 and later) to be credited as the main reasons for the decline. A second possibility was agricultural burning where the percentage reductions in amount burned and emissions are similar to those for ambient PAH concentrations from 2000 to 2004, with continuing decline until a small rise in 2014 and later. A third possibility was residential wood burning where emissions in Fresno were restricted by Rule 4901 starting in November 2003, but was not very effective until November 2008 when the mandatory curtailment level was lowered from a forecasted $PM_{2.5}$ concentration of 65mg/m3 to $30mg/m^3$. While reduction in wood burning emissions may have contributed, the timing is not well aligned. The decline in PAH concentrations preceded Rule 4901. Winter PAH concentrations had dropped each year after winter 2000 – 2001, indicating a major contribution from another source that occurred earlier than the reduction in residential wood burning. Furthermore, compliance is challenging in the early years of restricted residential wood burning programs and the CARB's emissions estimates show the first reduction from enforcement of Rule 4901 in 2005 which is too late to explain the trends in the observed PAH. A final possibility was change in industrial emissions, but the total emissions for industrial activities in the region was too low to explain any change in observed air quality in this region. Thus, we found that PAH concentrations were more closely correlated to reported emissions for agricultural burning than to residential wood burning or on-road

vehicle emissions. The combined evidence of timing and the shape of the decline, plus the emissions data lead us to conclude that the decrease in agricultural burning in the SJV was the most probable major contributor to the decline in PAH concentrations in Fresno.

In addition to reductions in the tonnage allowed in agricultural waste burning, the SJVAPCD's Smoke Management System has steadily improved their methods of forecasting safe burning days. The Smoke Management System has incorporated advanced meteorological model results into its model for selection of allowable agricultural waste burning days. In 2001, CARB began declaring agricultural waste burn/no-burn days by 3 large regions within the SJV Air Basin. In 2002, the SJVAPCD assumed responsibility for declaring agricultural waste burn/no-burn days in the SJV Air Basin. SJVAPCD implemented multiple improvements to weather predictive capabilities, e.g., using the National Center for Environmental Predictions models, and tightened the rules on how much total emissions are allowed within each of 100 specified agricultural burn allocation zones. These improvements appear to have made a big difference in the ability of the air district to minimize the impact of agricultural waste burning, even as absolute tonnage of burned waste increased in years 2014–2018. Second, the types of materials that are burned has changed since the early 2000s, and that may also influence PAH concentrations. Last, other sources have declined during the middle of the time period (2005–2013) which may have contributed to decreased PAH concentrations even as agricultural burning increased.

We did not find that the global PAH emissions model provided additional insight; it is likely that the country-level spatial resolution does not allow for fine enough detail at the air basin spatial scale. A recently published study comparing PAH emissions inventories to PAH measurements found a similar limitation (Yu et al., 2019).

Individual PAHs with lower molecular weights had larger declines from the early period (2001–2003) to the later period (2006–2016). Fujita et al. (2007) reported measurements of vehicle exhaust composition that indicate 3- and 4-ring PAHs primarily come from compression ignition (diesel) vehicles rather than spark ignition (gas) vehicles. The major change in compression ignition vehicle PM emissions occurred with the requirement of particulate filters on new vehicles starting in 2007. It is likely that reduction in diesel vehicle emissions contributed to reduction in lower molecular weight PAHs especially after 2009, but this doesn't explain the decline in earlier years. It is likely that change in agricultural burning activity contributed to this reduction. PAH emissions from agricultural burning may contain a disproportionate amount of lower molecular weight PAHs compared to other sources. Jenkins et al. (1996) reported that cereal crops and agricultural wood waste emit two orders of magnitude greater amounts of acenaphthalene and phenanthrene than 5- and 6-ring PAHs.

While other researchers have not examined or reported a correlation between reductions in agricultural burning emissions and pollution reduction, they provide supporting evidence for the importance of biomass burning in Fresno. Gorin et al. (2006) present findings on $PM_{2.5}$ sources during the winter in Fresno Using levoglucosan as a wood smoke tracer, they concluded that wood smoke from biomass burning was a major contributor. The concentrations of levoglucosan were similar across the 5 sites in Fresno, suggesting wood

smoke is ubiquitous and somewhat regional, rather than strongly dependent on proximity to nearby sources. Levoglucosan is an indicator of all biomass burning, including agricultural waste (Schauer and Cass, 2000). Similarly, Chen et al. (2007) concluded that residential wood combustion was a major contributor to $PM_{2.5}$ concentrations in the SJV during 2000 and 2001. Despite excluding agricultural burning as a source, the model fitting components (K^+, OC3, OC4, EC1, EC, CL^-, and Fe) are common to all biomass burning sources considered in their analyses. As we presented above, agricultural burning during November 2000 to February 2001 was very high, with the agricultural emissions estimated at over twice those of residential wood burning. This previous work on biomass burning in Fresno supports our suggestion that agricultural burning has had a large impact on air pollution in this area.

In our previous work in California's SJV, we found that fuel emissions from vehicles (cars, trucks, and rail), residential heating fuel, and industrial activities were the most important contributors to the spatial and short-term temporal differences in PAH exposures within the communities of Fresno and Bakersfield (Noth et al., 2011; Noth et al., 2013; Noth et al., 2016). Agricultural burning was a potential explanatory variable in our analyses, but it did not contribute enough explanatory value to include it in any models. However, if agricultural burning is more of a regional pollutant rather than a neighborhood-scale pollutant, it is less likely to provide explanatory power in these types of models.

Our conclusions are limited by the lack of complete time series for either sampling method (continuous, particle bound PAH and filter-based PAH speciation). PAH filter samples for individual PAHs had good temporal coverage during the middle and later years of the time period, but less coverage in the early years. However, the CARB Air Toxics data provide good supporting evidence during those years. Our continuous real-time data have some gaps in the time series, primarily from 2009–2013, reflecting gaps in study funding.

5. Conclusion

We have presented unique air pollution data on PAH concentrations over 18 years in one of California's largest, most polluted cities. Additionally, we have shown that policies implemented to decrease biomass burning were successful in decreasing the mass of agricultural waste burned which in turn played a large role in decreasing PAH emissions and concentrations in the San Joaquin Valley. This rich dataset may be relevant for evaluating the role that agricultural and other managed burning plays in regional air pollution. Many cities both domestic and international are similar to Fresno, with waste burning as a major method for waste removal. Continued monitoring of air concentrations is important both to avoid unhealthy conditions for SJV residents and to understand both the pollutant sources and the efficacy of regulations.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Particle-bound polycyclic aromatic hydrocarbons (PAHs) in the San Joaquin Valley of California have decreased by over 60% from 2000–2019.
- Winter-time concentrations of individual PAHs have decreased by over 80%.
- We examined industrial emissions, on-road vehicle emissions, residential wood burning, and agricultural and biomass waste burning as possible explanations for the declines.
- The major decline in PAHs from 2000–2004 was coincident with and most likely due to a similar decline in the amount of agricultural waste burned in the region.

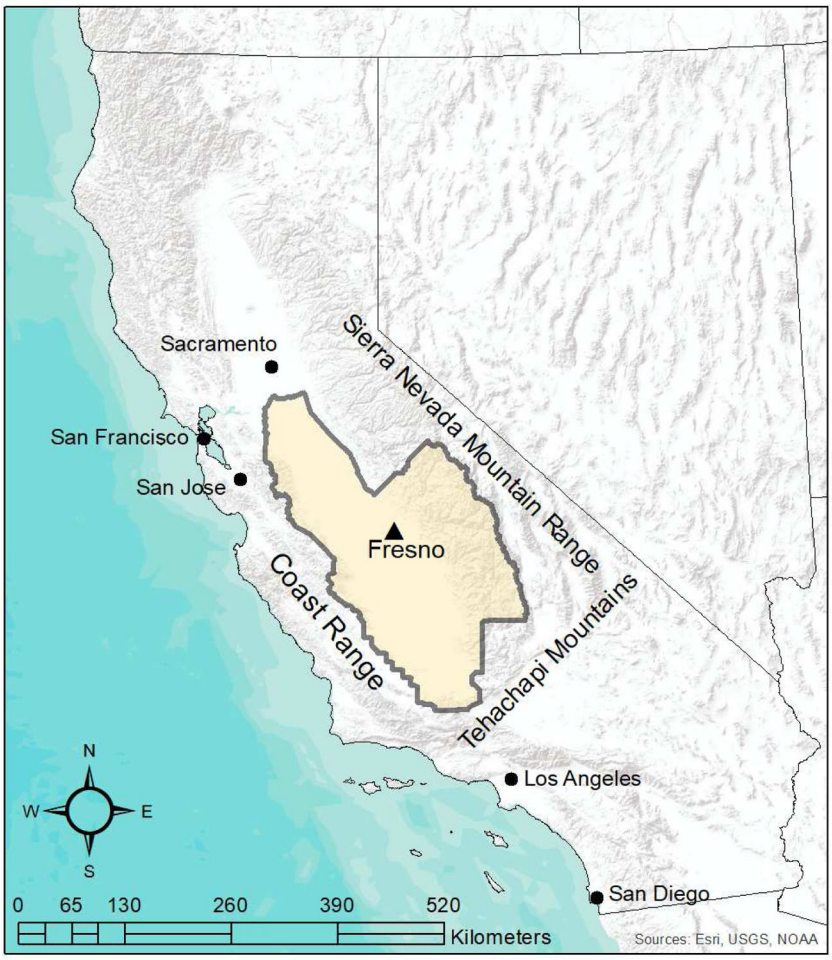

Figure 1.

The San Joaquin Valley Air Basin (outlined in grey) is confined by the Southern Sierra Nevada Mountains in the East, the Tehachapi Mountains on the south, and the Coast Range mountains in the West. Pollution flowing into the San Joaquin Valley Air Basin from the San Francisco Bay Area and Sacramento, as well as emitted by stationary and mobile sources within the valley, is often trapped by these mountain ranges. Fresno is at the center of the San Joaquin Valley.

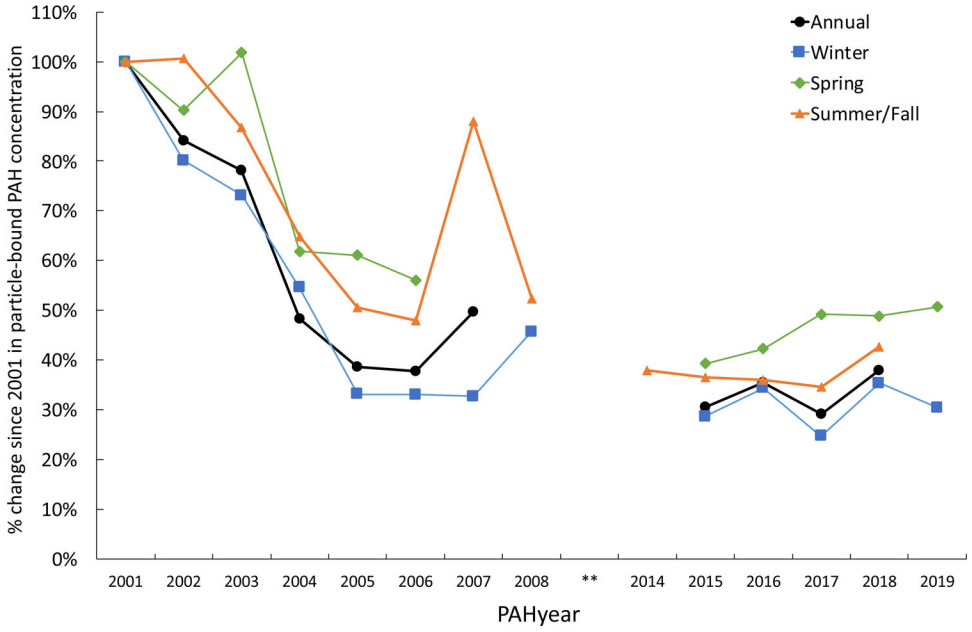

Figure 2.

Annual and seasonal particle-bound PAH (ng/m^3) as measured by PAS2000 at the Fresno central site (FSF 2001–2011, FGS 2012–2019), represented as the % of 2001 PAH concentration for comparable year or season [PAH year 2001 (Nov 2000-Oct 2001)].

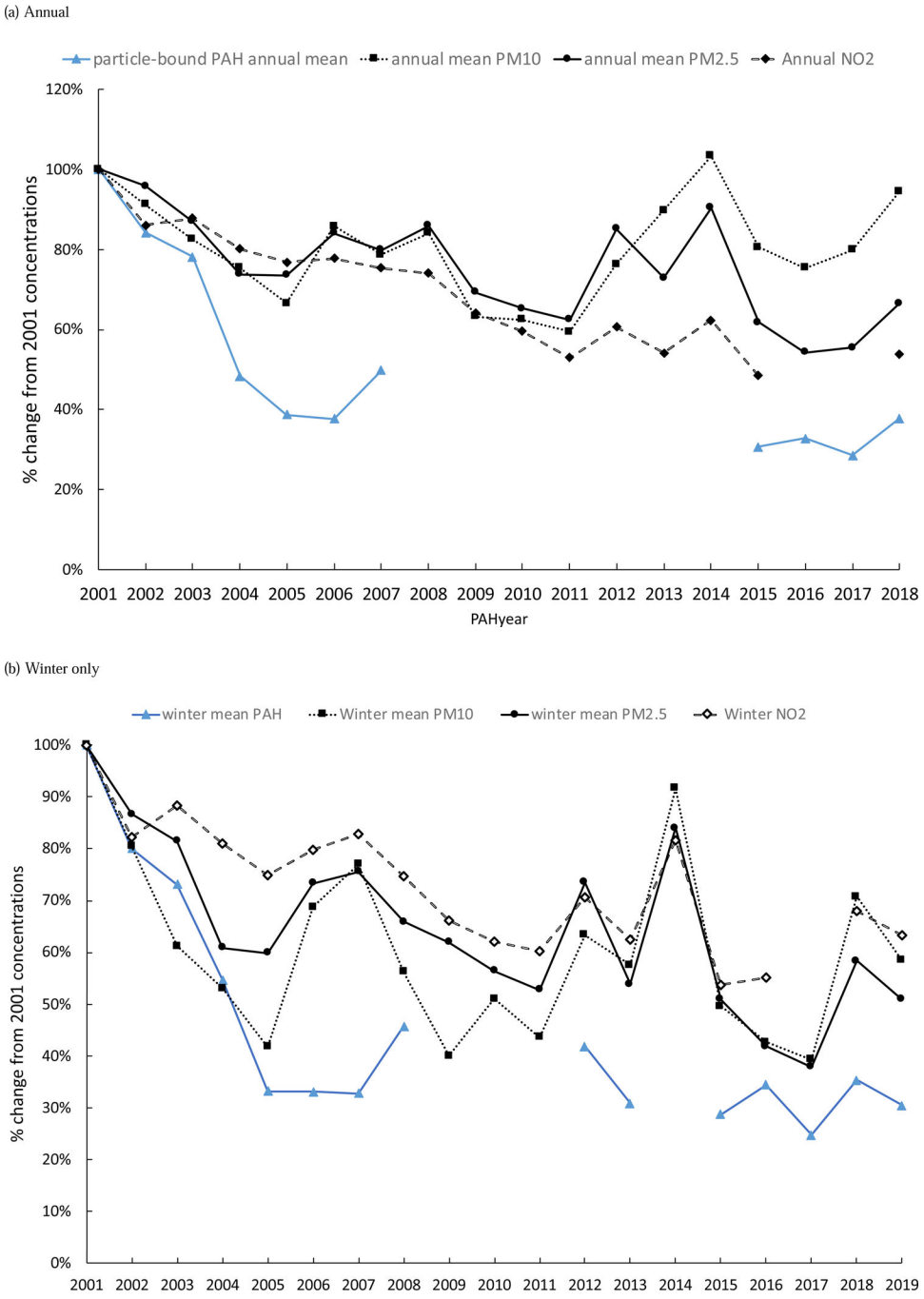

Figure 3.

NO_2, $PM_{2.5}$, and PM_{10} concentrations standardized to PAH year 2001, compared to PAH concentrations. The missing annual averages are due to insufficient measurement days in those years.

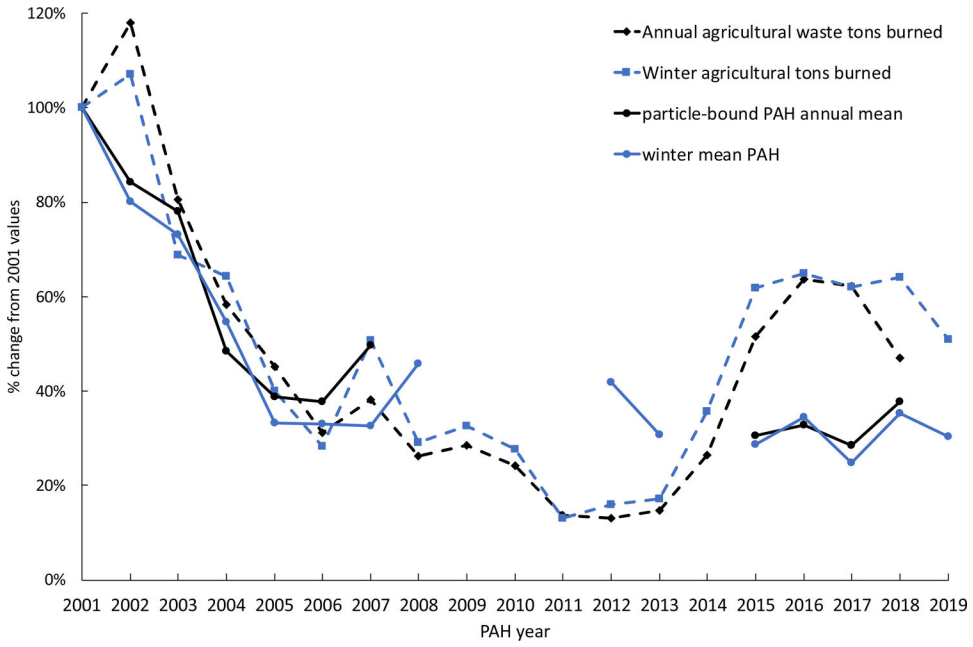

Figure 4.

Annual and winter tons of agricultural waste burned 2001–2019, presented as % change from 2001 values.

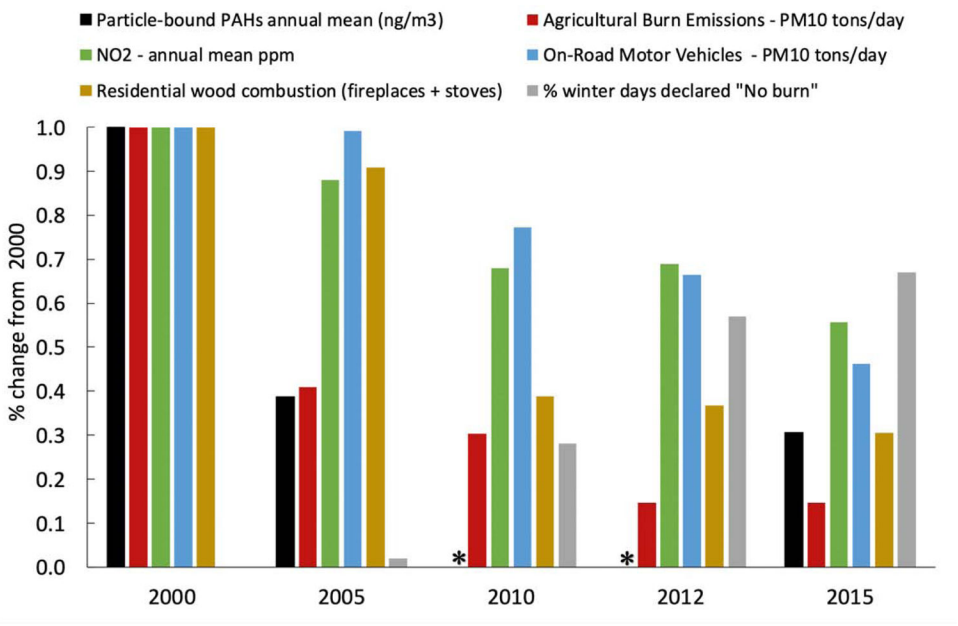

Figure 5.

Annual emissions, % of winter days declared “no burn” days in Fresno County, NO_2 concentrations, and particle-bound PAH concentrations. Emissions data (from the California Almanac of Emissions and Air Quality), source, and NO_2 concentrations are presented as % change from PAH year 2000 and PAHs from PAH year 2001.

* Insufficient measurement days for a valid average.

Table 1.

Annual particle-bound PAH concentrations (ng/m^3) at the Fresno Central Site for PAHyears 2001–2019.

PAHyear	Annual Number Observations	Annual Mean	Standard deviation	Annual Median	Winter Number Observations	Winter mean	Winter Standard deviation	Winter Median	Ratio of Winter to Annual means
2001	365	10.86	12.84	4.74	120	24.67	13.98	22.06	2.27
2002	365	9.14	10.02	4.48	120	19.76	10.85	18.9	2.16
2003	365	8.49	8.99	4.08	120	18.03	9.66	16.74	2.12
2004	324	5.25	6.66	2.43	79	13.48	8.83	11.13	2.57
2005	365	4.20	4.44	2.43	120	8.18	5.68	6.24	1.95
2006	365	4.09	4.07	2.29	120	8.16	4.75	7.38	1.99
2007	296	5.41	4.24	3.72	120	8.08	5.01	7.26	1.49
2008	273	*	*	*	119	11.28	6.76	9.46	*
2009	61	*	*	*	61	*	*	*	*
2010	0	*	*	*	0	*	*	*	*
2011	145	*	*	*	5	*	*	*	*
2012	178	*	*	*	116	10.33	6.25	9.90	*
2013	98	*	*	*	98	7.61	4.80	6.93	*
2014	195	*	*	*	0	*	*	*	*
2015	362	3.33	3.68	1.54	117	7.07	4.32	6.01	2.12
2016	366	3.86	4.43	1.57	121	8.48	5.04	7.70	2.20
2017	354	2.95	3.54	1.46	109	6.10	4.72	4.67	2.06
2018	365	4.11	4.66	1.82	120	8.72	5.68	7.07	2.12
2019	212	*	*	*	120	7.50	5.07	6.37	*

* Insufficient measurement days for a valid average.

Table 2.

Comparison of particle-bound PAH concentrations (ng/m3) at the Fresno central site for 2001–2004 and 2005–2019.

	PAHyear	# Obs	Mean	95th% confidence	Median
All	2001–2004	1419	8.53	(8.00, 9.05)	3.82
	2005–2019	3643	4.28	(4.13,4.43)	2.24
	Change (ng/m^3)		−4.25		
	Change (%)		−50%		
Winter					
November-February	2001–2004	439	19.50	(18.39, 20.60)	17.43
	2005–2019	1351	8.16	(7.86, 8.45)	6.83
	Change (ng/m^3)		−11.34		
	Change (%)		−58%		
Spring					
March-June	2001–2004	488	3.08	(2.85, 3.30)	2.19
	2005–2019	1133	1.75	(1.68, 1.81)	1.37
	Change (ng/m^3)		−1.33		
	Change (%)		−43%		
Summer/Fall					
July-October	2001–2004	492	4.14	(3.85, 4.43)	2.95
	2005–2018	1157	2.24	(2.14, 2.34)	1.64
	Change (ng/m^3)		−1.90		
	Change (%)		−46%		

Table 3(a).

Annual average individual PAH concentrations (ng/m^3) at the Fresno central site for PAHyears 2002–2018.

PAHyear	2002[a]	2003[b]	2007	2008	2009	2014	2015	2016	2017	2018[c]
N	*40*	*32*	*189*	*164*	*119*	*4*	*66*	*52*	*27*	*34*
ACY	0.18	6.46	0.32	1.55	1.18	0.37	0.91	1.88	1.1	0.81
ACE	0.59	2.41	0.79	1.32	0.61	1.81	1.25	1.1	0.53	0.82
FLU	1.99	6.88	1.55	6.59	7.91	4.66	3.03	2.53	1.43	1.51
PHE	4.01	17.67	4.66	12.04	10.36	6.83	4.82	5.16	4.1	2.62
ANT	0.04	1.49	0.17	0.45	0.09	0.29	0.24	0.48	0.44	0.47
FLT	0.78	3.71	1.00	2.16	1.39	1.71	1.32	1.7	1.51	0.54
PYR	0.57	3.52	0.76	1.44	1.21	1.65	1.04	1.37	1.19	0.88
RET	0.03	2.78	12.62	5.44	1.26	0.09	0.53	1.15	1.08	0.43
BAA	0.08	1.42	0.18	0.34	0.18	0.07	0.20	0.5	0.49	0.05
CHR	0.07	1.06	0.26	0.55	0.26	0.07	0.29	0.58	0.64	0.30
BBF	0.22	1.58	0.36	0.78	0.37	0.06	0.46	0.95	0.97	0.10
BKF	0.10	0.87	0.24	0.28	0.28	0.04	0.26	0.38	0.35	0.10
BAP	0.12	1.67	0.24	0.42	0.18	0.03	0.28	0.54	0.64	0.31
ICP	0.36	2.54	0.34	0.90	0.71	0.03	0.49	1.01	0.82	0.10
DBA	0.10	0.69	0.13	0.37	0.17	0.01	0.30	0.29	0.24	0.02
BGP	0.31	1.82	0.43	0.72	0.29	0.08	0.51	0.79	0.77	0.08

[a] PAH year 2002 included samples collected in only July – October 2002

[b] PAH year 2003 included samples collected in only November 2002 – February 2003

[c] PAH year 2018 included samples collected in only December 2017 – June 2018

Table 3(b)

Winter (November-February) average individual PAH concentrations (ng/m^3) at the Fresno central site for PAHyears 2003–2018.

PAHyear	2003	2007	2008	2009	2015	2016	2017	2018	Change (ng/m^3) from 2003 to 2018	Change (%) from 2003 to 2018
N	*32*	*20*	*81*	*99*	*29*	*29*	*18*	*20*	-	-
ACY	6.46	0.39	0.28	1.28	1.74	2.96	1.32	0.90	−5.56	−86%
ACE	2.41	1.68	0.66	0.63	1.67	1.26	0.57	0.60	−1.81	−75%
FLU	6.88	0.08	2.36	9.26	3.16	2.88	1.45	1.15	−5.73	−83%
PHE	17.67	11.93	8.08	11.18	5.46	6.05	4.38	2.27	−15.40	−87%
ANT	1.49	0.64	0.47	0.1	0.38	0.62	0.42	0.26	−1.23	−83%
FLT	3.71	2.26	1.77	1.42	1.54	2.01	1.73	0.47	−3.24	−87%
PYR	3.52	1.87	1.64	1.25	1.24	1.64	1.47	1.22	−2.30	−65%
RET	2.78	1.51	9.05	1.28	1.05	1.73	1.39	0.58	−2.20	−79%
BAA	1.42	0.68	0.49	0.19	0.41	0.88	0.70	0.07	−1.35	−95%
CHR	1.06	0.99	0.79	0.25	0.56	0.96	0.84	0.44	−0.62	−58%
BBF	1.58	0.48	0.96	0.38	0.92	1.62	1.26	0.12	−1.46	−92%
BKF	0.87	0.5	0.31	0.32	0.53	0.65	0.44	0.14	−0.73	−84%
BAP	1.67	0.88	0.59	0.18	0.58	0.95	0.89	0.08	−1.59	−95%
ICP	2.54	1.28	1.4	0.74	0.98	1.73	1.08	0.12	−2.42	−95%
DBA	0.69	0.23	0.44	0.18	0.64	0.49	0.31	0.03	−0.66	−96%
BGP	1.82	1.06	0.99	0.29	0.99	1.32	0.99	0.09	−1.73	−95%

Table 3(c).

Spring (March-June) average individual PAH concentrations (ng/m^3) at the Fresno central site for PAHyears 2002–2018.

PAHyear	2002	2007	2008	2009	2015	2016	2017	2018	Change (ng/m^3) from 2002 to 2018	Change (%) from 2002 to 2018
N	*16*	*66*	*49*	*20*	*21*	*14*	*5*	*14*	-	-
ACY	0.11	0.26	0.25	0.65	0.3	0.66	1.04	0.68	0.57	518%
ACE	0.56	0.76	0.52	0.51	1.12	1.03	0.43	1.14	0.58	104%
FLU	1.27	1.19	1.26	1.23	3.68	2.21	1.30	2.02	0.75	59%
PHE	2.84	4.09	2.33	6.29	4.75	3.79	3.80	3.13	0.29	10%
ANT	0.05	0.15	0.69	0.06	0.15	0.24	0.24	0.77	0.72	1440%
FLT	0.71	0.78	0.58	1.27	1.17	1.27	1.41	0.66	−0.05	−7%
PYR	0.32	0.4	0.51	1.02	0.89	1.04	1.13	0.4	0.08	25%
RET	*	1.02	0.56	1.13	0.19	0.35	0.72	0.21	*	*
BAA	0.05	0.08	0.17	0.13	0.05	0.02	0.14	0.03	−0.02	−40%
CHR	0.1	0.13	0.22	0.32	0.12	0.1	0.32	0.10	0.00	0%
BBF	0.14	0.21	0.58	0.32	0.14	0.09	0.55	0.07	−0.07	−50%
BKF	0.07	0.08	0.17	0.08	0.06	0.03	0.22	0.03	−0.04	−57%
BAP	0.09	0.11	0.28	0.19	0.04	0.02	0.23	0.64	0.55	611%
ICP	0.44	0.22	0.48	0.57	0.12	0.08	0.50	0.07	−0.37	−84%
DBA	0.13	0.09	0.29	0.12	0.04	0.03	0.15	0.005	−0.13	−96%
BGP	0.22	0.18	0.47	0.27	0.15	0.11	0.59	0.07	−0.15	−68%

*Insufficient measurement days for a valid average.

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Table 3(d)

Summer/Fall (July-October) average individual PAH concentrations (ng/m^3) at the Fresno central site for PAHyears 2002–2017.

PAH year	2002	2007	2008	2014	2015	2016	2017	Change (ng/m^3) from 2002 to 2017	Change (%) from 2002 to 2017
N	*24*	*103*	*34*	*4*	*16*	*9*	4	-	-
ACY	0.22	0.34	6.43	0.37	0.21	0.30	0.18	−0.04	−18%
ACE	0.61	0.63	4.02	1.81	0.66	0.69	0.48	0.08	13%
FLU	2.47	2.07	24.35	4.66	1.92	1.91	1.48	−0.56	−23%
PHE	4.79	3.61	35.48	6.83	3.73	4.40	3.18	−0.39	−8%
ANT	0.03	0.09	0.06	0.29	0.10	0.40	0.78	0.37	1233%
FLT	0.83	0.89	5.38	1.71	1.12	1.35	0.62	0.52	63%
PYR	0.74	0.77	2.29	1.65	0.86	1.01	0.02	0.27	36%
RET	*	22.20	3.87	0.09	0.05	0.51	0.01	*	*
BAA	0.10	0.15	0.20	0.07	0.02	0.04	0.16	0.05	100%
CHR	0.05	0.20	0.44	0.07	0.04	0.10	0.23	−0.13	−48%
BBF	0.27	0.43	0.63	0.06	0.06	0.14	0.08	−0.08	−67%
BKF	0.12	0.28	0.38	0.04	0.02	0.04	0.02	−0.08	−57%
BAP	0.14	0.20	0.21	0.03	0.02	0.06	0.02	−0.05	−63%
ICP	0.31	0.23	0.33	0.03	0.06	0.10	0.08	−0.21	−68%
DBA	0.08	0.15	0.33	0.01	0.03	0.03	0.03	−0.24	−65%
BGP	0.37	0.47	0.43	0.08	0.09	0.13	0.18	−0.24	−65%

*Insufficient measurement days for a valid average.

Table 4.

The winter average concentrations (ng/m^3) for individual and groups of PAHs collected before and after PAHyear 2004 at the Fresno central site. This table excludes retene, since it was not measured in the 2003 data.

PAH year	2003			2006–2018			Change (ng/m^3)	Change (%)
	N	Mean	Std	N	Mean	Std		
ACY	32	6.46	7.08	296	1.14	1.64	−5.32	−82%
ACE	32	2.41	1.96	296	0.87	0.8	−1.54	−64%
FLU	32	6.88	3.8	296	4.5	6.89	−2.38	−35%
PHE	32	17.67	10.08	296	8.3	7.24	−9.37	−53%
ANT	32	1.49	1.27	296	0.35	0.47	−1.14	−77%
FLT	32	3.71	2.2	296	1.6	1.31	−2.11	−57%
PYR	32	3.52	2.22	296	1.45	1.18	−2.07	−59%
BAA	32	1.42	1.04	296	0.42	0.61	−1.00	−70%
CHR	32	1.06	1.33	296	0.6	0.76	−0.46	−43%
BBF	32	1.58	1.05	296	0.76	0.94	−0.82	−52%
BKF	32	0.87	0.64	296	0.38	0.61	−0.49	−56%
BAP	32	1.67	1.26	296	0.49	0.69	−1.18	−71%
ICP	32	2.54	2.23	296	1.06	1.31	−1.48	−58%
DBA	32	0.69	0.67	296	0.33	0.48	−0.36	−52%
BGP	32	1.82	1.19	296	0.73	0.92	−1.09	−60%
Sum of 3-ring[a]	32	34.91	21.65	296	15.16	13.15	−19.75	−57%
Sum of 4-ring[b]	32	9.71	5.85	296	4.06	3.55	−5.65	−58%
Sum of 5-ring[c]	32	4.80	3.26	296	1.96	2.32	−2.84	−59%
Sum of 6-ring[d]	32	4.36	3.29	296	1.79	2.17	−2.57	−59%
PAH456	32	18.87	11.37	296	7.8	7.51	−11.07	−59%
Gas-phase only[e]	32	15.76	11.34	296	6.51	7.82	−9.25	−59%
Gas/particle phase[f]	32	28.87	16.64	296	12.71	10.17	−16.16	−56%
Particle-phase only[g]	32	9.16	6.42	296	3.74	4.36	−5.42	−59%
8 carcinogenic PAHs[h]	32	11.64	8.34	296	4.76	5.54	−6.88	−59%
Total of 15 PAHs	32	53.79	30.74	296	22.96	17.26	−30.83	−57%

a) sum of ACY, ACE, FLU, PHE, and ANT

b) sum of FLT, PYR, BAA, and CHR

c) sum of BBF, BKF, BAP, and DBA

d) sum of BGP and ICP

e) sum of ACE, ACY, and FLU

f) sum of PHE, ANT, FLT, PYR, CHR, and BAA

g) sum of BBF, BKF, BAP, ICP, DBA, and BGP

h) sum of BAA, CHR, BBF, BKF, BAP, ICP, DBA, and BGP