

# California Air Resources Board

## Proposed Short-Lived Climate Pollutant Reduction Strategy

Comments Submitted by the Urban Air Initiative  
May 26, 2016

The Urban Air Initiative commends CARB for its groundbreaking work in the area of low carbon transportation fuels, and appreciates this opportunity to comment on CARB's proposed Short-Lived Climate Pollutant (SLCP) reduction strategy. With this rulemaking, CARB can significantly reduce the carbon footprint of the California transportation sector, and at the same time take steps to reduce emissions of harmful air pollutants that have direct and indirect impacts on human health.

### About the Urban Air Initiative

The Urban Air Initiative is a non-profit entity dedicated to research and education in the area of fuel quality and its relationship to mobile source emissions, especially in urban areas. The climate and public health impacts of mobile source (traffic) pollution—in the U.S. and globally—are of great importance to policymakers, industries, and the billions of people that are regularly exposed to harmful pollutants in their homes, schools, and vehicles.<sup>1</sup> Among the most vulnerable are infants and children. The Urban Air Initiative believes that protecting our children's health and well-being is the most important investment society can make to build a better future.

### Context of the SLCP Reduction Strategy: Comments Will Focus on Black/Brown Carbon

For many years, California has been a global trend-setter in transportation fuels regulatory policy. The state is one of the world's largest consumers of gasoline, and it has more gasoline-powered light duty vehicles (LDVs) than most nations. Consequently, CARB has led the way in addressing the serious health and climate threats from gasoline combustion by-products. In the past, CARB experts have recognized that fuel composition is just as important as vehicle control technologies in reducing emissions of carbon and other harmful pollutants.

In the materials explaining its strategy, CARB notes that black carbon (BC) was not originally included in international climate frameworks, and it is not included in California's AB 32 inventory. However, "recent studies have shown that black carbon plays a far greater role in global warming than previously recognized". BC's climate forcing effects are second only to those of CO<sub>2</sub>, stronger even than methane. In addition to climate benefits, BC emissions reductions would provide significant health-related co-benefits. CARB notes that "the

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<sup>1</sup>See "India unlikely to boast about airy statistics", *Los Angeles Times*, May 14, 2016. "Ambient air pollution, made of high concentrations of small and fine particulate matter, is the greatest environmental risk to health, causing more than 3 million premature deaths worldwide every year", WHO said.

scientific community has concluded that diesel and black carbon particulate matter likely have similar adverse effects as PM<sub>2.5</sub>".

However, UAI respectfully disagrees with CARB's assertion that particulate and black carbon emissions from "anthropogenic sources", e.g., vehicles, are largely under control. CARB states at p. 122: "The result is that black carbon emissions are about 90 percent lower than they were in the 1960s and approximately 5,000 premature deaths are avoided in the State each year." Unfortunately, CARB seems to focus only on diesel fuels, even though gasoline-powered vehicles dominate the California and U.S. transportation fuels sector. In fact, best available science shows that the predominant urban source of particulate and black carbon emissions is gasoline exhaust, specifically, the 25 – 30% fraction of gasoline that is comprised of petroleum-derived octane boosting compounds known as gasoline aromatic hydrocarbons, hereinafter referred to as BTEX (benzene, toluene, ethyl-benzene, and xylene).

CARB asserts that "...the health-related impacts associated with diesel PM<sub>2.5</sub> are expected to continue to decrease through 2030". (Emphasis added) Unfortunately, however, unless CARB [and EPA] take appropriate and commercially feasible steps to improve gasoline quality, particulate and black carbon emissions from gasoline-powered LDVs will increase dramatically, as automakers introduce direct injection, turbocharged, and higher compression engine advances that the public has been told will make things better, not worse.

CARB defines BC as something that is "emitted from burning fuels such as coal, diesel, and biomass" (p. 36). Excluding gasoline—which fuels more than 90% of the U.S. light duty fleet—from this list is a serious oversight that hides from view one of the most important BC sources, especially for the vast majority of Americans that live near congested roadways.

Importantly, CARB notes that "new studies have suggested that certain fractions of organic carbon known as 'brown carbon' could be a stronger absorber of solar radiation than previously understood". In addition to black carbon, gasoline BTEX is a predominant source of "brown carbon". Scientists define total carbon (TC) as the combination of OC and BC/EC, but then say "...however, BC and EC measurements also include variable amount of colored and refractory organic compounds ("brown carbon") which can lead to substantially different results of mass balances and physicochemical properties of air particulate matter...The term "brown carbon" reflects the fact that a significant fraction of the light-absorbing carbon in aerosols is made of organic compounds ... with a steep increase of absorption towards lower wavelengths, including the UV range...".<sup>2</sup>

**Summary of Comments.** The comments and attachments will show that:

1. A recent study by University of California-Riverside experts warns that as gasoline direct injection (GDI) engines come to dominate the U.S. light duty fleet, failure to

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<sup>2</sup><http://aerosols.ucsd.edu/papers/Fuzzi.pdf>

reduce gasoline BTEX levels by transitioning to high octane low carbon (HOLC) mid-level ethanol blends (e.g., E30) could dramatically increase black and brown carbon (BC) emissions, by as much as 350% or more.<sup>3</sup>

Excerpt: *“Increasing aromatic content increases BC [emissions factors]. Increased octane rating in fuel reduces the BC [emissions factors] for the GDI vehicles. . . .*

*Our results show that reduced aromatic concentrations are associated with reduced PM mass and (more importantly) reduced BC from GDI vehicles. Thus, increasing the ethanol fraction in gasoline could help to reduce climate and human health impacts attributed to particle emissions from GDI vehicles. . . . As ethanol concentrations are increased in the U.S., the higher octane fuel could effectively decrease BC emissions from the high PM emitting GDI vehicles thus helping to minimize BC. . . .*

*GDI vehicles can emit 5–6 times higher BC compared to the PFI and hybrid vehicles. In addition, the higher aromatic fuels increased the amounts of BC EFs. The 35% aromatic fuel increased the BC EF by as much as 350% from the 15% aromatic fuel. However, BC was reduced with the higher octane rating fuel. If the aromatic content in fuels continues to decrease and higher octane rating fuels become more common (due to higher ethanol blends) then reductions in BC from the higher PM emitting GDI vehicles may occur....” (Emphasis added)*

2. Numerous studies have linked particulate matter emissions, and BC in particular, to the use of BTEX compounds in gasoline. Many scientists trace substantially all BC emissions from LDVs to incomplete combustion of BTEX compounds.<sup>4</sup>
3. A recent CARB study confirmed that BC accounts for approximately 70% of all PM mass emissions from gasoline-powered LDVs.<sup>5</sup> In its Appendix P to the LEV III rulemaking<sup>6</sup>, p. 88, CARB states: “Although diesel engines are known major contributors to PM emissions, recent studies show that gasoline engines also play a key role...”, citing a 2010 Iizuka, et al. study. This study cites aromatics content as even more important factor in PM formation than distillation, and recommends replacement of aromatics with ethanol (slide 32).<sup>7</sup> Yet, having cited the study, CARB appears to have done the opposite of what the study recommends. One example occurs on p. 88, where CARB described the E10 blend's higher emissions of PN without noting that the E10 test fuel had a T90 that was thirty degrees higher than the cert fuel to which it was compared (328 vs. 297), and had a higher content of naphthalenes than the other test fuels—despite CARB’s

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<sup>3</sup> See Short et al., *Components of Particle Emissions from Light-Duty Spark-Ignition Vehicles with Varying Aromatic Content and Octane Rating in Gasoline*, Environmental Science & Technology, August 5, 2015.

<sup>4</sup> See BC discussion in Request for Correction EPA’s LCA Models, Urban Air/Boyden Gray & Associates, April 2016, pp. 27 – 32. <https://www.epa.gov/quality/epa-information-quality-guidelines-requests-correction-and-requests-reconsideration#16004>.

<sup>5</sup> California Air Resources Board, LEV III PM Technical Support Document: Development of Particulate Matter Mass Standards for Future Light-Duty Vehicles 123 (Dec. 7, 2011).

<sup>6</sup> <http://www.arb.ca.gov/regact/2012/leviiiighg2012/levapp.pdf>

<sup>7</sup> [http://www.peci.or.jp/japanese/overseas/asian/asia\\_symp\\_5th/pdf\\_5th/15-Masashilizuka.pdf](http://www.peci.or.jp/japanese/overseas/asian/asia_symp_5th/pdf_5th/15-Masashilizuka.pdf)

finding that “naphthalenes, which are high in carbon content and [double-bond equivalent values] contributed the most” to the Particle Mass Index (PMI) of the fuels.” In other words, the ethanol blend was literally adulterated with the high boiling, high double bond equivalent, PN-producing aromatics. This blending scheme was counter-intuitive and illogical, because ethanol’s superior octane-boosting properties and lower boiling point should lead to the opposite result, namely a reduction in T90 and PN producing aromatic content.

4. Another example of CARB’s questionable use of ethanol-related test data occurred in its presentation of the 2010 CARB Haagen - Smits study results.<sup>8</sup> On p. 103, CARB talks about the importance of the study, both in terms of BC, and its link to SPN and PM mass. On p. 110, CARB talks about the tests themselves, but describes only three fuel batches: an E6, E10, and Phase 2 cert fuel with MTBE blend. CARB’s own testing actually showed dramatic (e.g., as much as 90%) reductions in PM/PN for the E35, E65, and E85 blends: As ethanol content increased, PM/PN levels decreased.
5. California university researchers and others have established the close inter-relationships between gasoline BTEX and a toxic “soup” of combustion by-products, including polycyclic aromatic hydrocarbons (PAHs), ultrafine particulates (UFPs), secondary organic aerosols (SOAs)-bound toxics, and BC/PM<sub>2.5</sub>. This dangerous mixture of nano-sized particles, aerosols, and gases defies capture by even the most sophisticated vehicle emissions control technologies. Vehicle technology controls are simply not sufficient: to protect the environment and public health and welfare, regulators must improve gasoline quality.<sup>9</sup> The USC poster board notes that “soot nucleates from polycyclic aromatic hydrocarbons”, and that “current models cannot predict soot-mass growth in post-flame regions”. The authors also state that “only larger PAHs are capable of dimerizing within the hot temperature environment inherent to flames”, and that larger PAHs can “stack” and increase in soot volume fraction. Thus, the heavier weight PAHs found in gasoline exhaust nucleate to produce substantial volumes of BC which are largely overlooked by conventional models. Unfortunately, this causes CARB and other regulators to overlook the predominant role of gasoline BTEX in black and brown carbon emissions.

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<sup>8</sup><http://www.calevc.org/carbzhang.pdf>. The vehicles in this study were port fuel injection (PFI), not direct injection.

<sup>9</sup><https://www.princeton.edu/cefr/Files/2011%20EFRC%20Summit%20Talk%20and%20Posters/Dames-and-Wang-2011-EFRC-Summit-Poster.pdf>. Also, see Hofmann, *Near Highway Pollutants in Motor Vehicle Exhaust*, University of Utah, Department of Pediatrics, slides 5 and 15, <http://www.slideshare.net/StateofUtah/near-highway-pollutants>.



6. In its SLCP reduction strategy proposal, CARB has singled out brown carbon as an issue of increasing concern. As noted above, the scientific community is beginning to connect the dots between BTEX, PAHs, UFPs, SOAs, and black and brown carbon.
7. Real-time measurement studies also confirm the relationships pictured above. Bahreini et al. performed real-time measurements of California urban pollution plumes which identified a surprisingly substantial contribution to SOA/BC inventories from gasoline exhaust SOAs on a global basis: *"We estimate that within a day of processing, SOA from gasoline exhaust emissions may reach 4Tg/yr., which is approx. 16% of recent global emissions of biogenic SOA. Our observations suggest that a decrease in the emission of organic species from gasoline engines may significantly reduce SOA concentrations on local and global scales."* The strong synergies between SOAs, PAHs, and BC, the fact that SOAs and carbonaceous aerosols can constitute "brown carbon", and the potentially important role that "brown carbon" can also play in global climate change, suggests that CARB should prioritize mitigation efforts to reduce the black and brown carbon emissions from today's high aromatics content gasoline.
8. Light-duty vehicle three-way catalysts (TWC) do not effectively capture the toxic mixture of nano-particles, aerosols, and gases comprised BC, SOA precursors, BTEX, and particle-borne PAHs. A 2013 study by Robinson – Maricq et al.<sup>10</sup> noted that light duty vehicle (LDV) *"Catalysts are optimized to reduce emissions of regulated pollutants (NOx, NMOG, and CO), not SOA precursors."*
9. In addition, Harvard, Robinson, Nordin, and others have reported that secondary organic aerosols (SOAs) make up a primary fraction of urban PM<sub>2.5</sub> (2013 Harvard, Robinson, Nordin, etc.).<sup>11</sup> SOAs are measured in terms of mass, not number. However, EPA officially recognizes only POAs (primary aerosols), and thus says that gasoline exhaust accounts for less than 5% of POA/PM<sub>2.5</sub> emissions. As Zelenyuk et al. have confirmed, SOAs and PAHs have a symbiotic relationship, in which the SOAs insulate

<sup>10</sup> "Secondary organic aerosol formation exceeds primary particulate matter emissions for light-duty gasoline vehicles" <http://www.atmos-chem-phys-discuss.net/13/23173/2013/acpd-13-23173-2013-print.pdf>

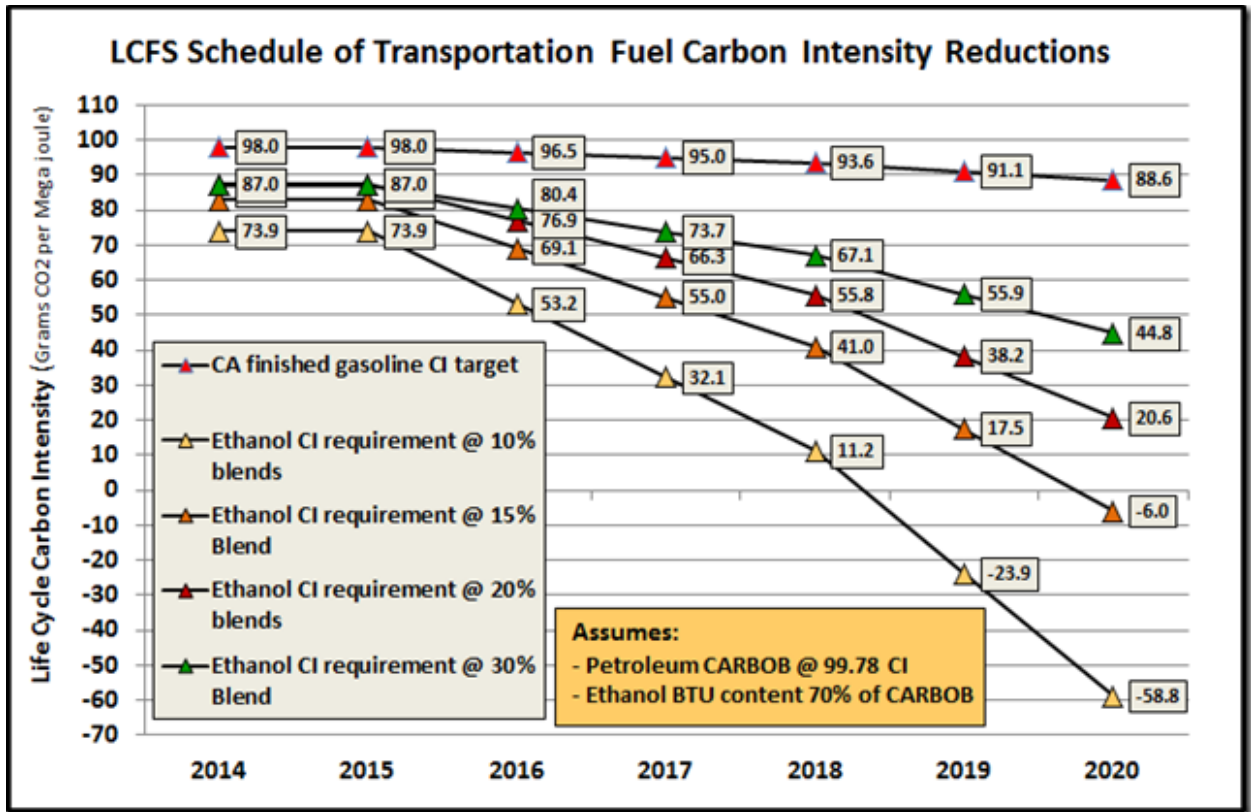
<sup>11</sup>K. von Stackelberg et al., "Public health impacts of secondary particulate formation from aromatic hydrocarbons in gasoline," Environmental Health 2013, 12:19, <http://bit.ly/25dZmzG>; E.Z. Nordin et al., Secondary Organic Aerosol Formation from Gasoline Passenger Vehicle Emissions Investigated in a Smog Chamber, Atmospheric Chemistry and Physics, June 28, 2013, <http://www.atmos-chem-phys.net/13/6101/2013/acp-13-6101-2013.pdf>.

PAHs from oxidation, and preserve them for long-range transport, allowing them to persist for weeks and even months.<sup>12</sup> Unspeciated NMOG (or interchangeably VOC) emissions are not recognized by conventional models and traditional gas chromatograph (GC) detection methods. The bulk of those unspeciated emissions emanate from C<sub>12</sub> and higher compounds, most of which in turn are combustion byproducts of aromatic hydrocarbons. The unspeciated organic emissions produce more SOA per unit mass than the speciated NMOG (VOCs), which means today's chemical transport models are in great need of repair, due to their under-prediction of gasoline aromatics' contribution to SOA/PM<sub>2.5</sub>/BC levels. Bahreini et al. real-time measurement studies of California pollution plumes attributed 80% or more to gasoline exhaust components, which presumably would have captured both number- and mass-based gasoline exhaust emissions.

10. SOAs are important not only as a carrier of black and brown carbon, along with highly toxic PAHs, but also as contributors to the formation of ground level ozone. Again, because they do not recognize aromatics' full contributions to SOA formation, regulators fail to acknowledge aromatics' important (if not predominant) role in the formation of ground level ozone. Instead, EPA and CARB have mistakenly targeted ethanol's evaporative emissions as a larger contributor to ozone. In addition to their predominant role in SOA formation, aromatic hydrocarbons also play an important role in gasoline permeation emissions, which are a primary contributor to gasoline evaporative emissions in urban areas.
11. Numerous automaker and U.S. Department of Energy studies have confirmed EXX/E30 HOLC fuels can reduce BC and BTEX toxics precursors by 60% or more (see elaboration in notes following this section). An orderly transition to mid-level ethanol blends such as E30 HOLC fuels in California would facilitate cost-effective compliance with CARB's Low Carbon Fuels Standard (LCFS) as shown in the chart below.

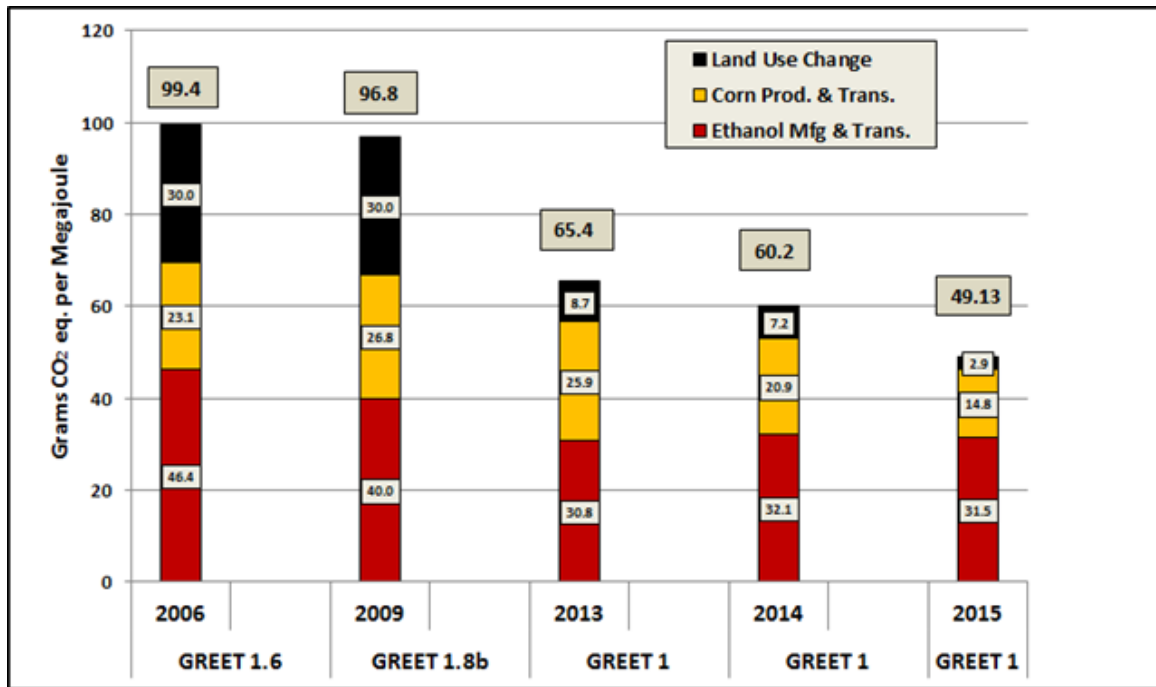
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<sup>12</sup>A. Zelenyuk et al., "Synergy between secondary organic aerosols and long-range transport of polycyclic aromatic hydrocarbons," *Environ Sci Technol.* 2012 Nov 20;46(22):12459-66, <http://pubs.acs.org/doi/abs/10.1021/es302743z>.



New science confirms that high-yield corn acres are substantial carbon sinks. Best available science evaluating upstream and downstream lifecycle carbon emissions of corn ethanol feed-stocks and production facilities confirm that U.S. corn ethanol is a high octane gasoline component with a carbon footprint at least 50% smaller than that of CARB’s baseline gasoline, see Argonne GREET chart below. Importantly, corn ethanol’s carbon footprint is shrinking rapidly as agricultural practices and technologies continue to improve, while the fossil fuel carbon footprint is expanding rapidly as tar sands and tight oil supplies expand their market share. That same Argonne research gives no credit for corn’s ability to fix carbon in soil permanently. However, recent research confirms that modern, high-yield continuous corn grown using conservation or no-till practices is in fact sequestering and rebuilding the carbon content of soil in the Midwest. Argonne is beginning a new study of soil carbon fixation, as well as NOx emissions related to fertilizer use, with regard to its GHG estimates for corn ethanol. Current EPA and CARB life-cycle analysis models similarly underestimate corn’s superior ability as a highly efficient C4 plant in sequestering carbon, and should be updated accordingly. Proper attribution of corn’s ability to sequester carbon and modern nitrogen management practices would reduce corn ethanol’s carbon footprint to only 15 grams of CO<sub>2</sub> per Mj, or nearly 80% less than CARB’s gasoline baseline (see graph below).





12. For several years now, automakers have asked for regulatory policies that would open the door to widespread use of the high octane, low carbon fuels they need to power highly efficient, high compression engines. CARB and EPA have a perfect opportunity in the pending Mid-Term Evaluation (MTE) of the GHG –CAFE rule. CARB and EPA should collaborate with automakers during the MTE negotiations to provide consumers with cost effective, lower carbon, and cleaner-burning fuels, thus benefiting consumers, automakers, and the environment.<sup>13</sup>

<sup>13</sup> A primary theme of the recent Society of Automotive Engineering meeting was automakers’ need for higher octane gasoline. Ford, Chrysler, and GM executives singled out 100 RON as the preferred fuel by 2020. “Tony Ockelford, director of product and business strategy for Ford’s power-train operations, outlined two ways to elevate the octane debate: the auto industry needs to educate drivers on the benefits of higher octane and how it enables cleaner and more powerful and efficient engines, and continue collaborating. “100 RON has been on the table for a long time,” Ockelford said. “The only way we will ever get there is to continue to push and work in a collaborative way,” he added. “Higher octane is necessary for better engine efficiency,” said GM’s Nicholson. “It is a proven low-cost enabler to lower CO2. 100 RON fuel is the right fuel for the 2020-25 timeframe.” <http://www.governorsbiofuelscoalition.org/?p=16924>



## Summary & Conclusions

**Higher Octane, Lower Carbon Gasoline is imperative if CARB wants to achieve its SLCP/LCFS targets.**

- 1. Gasoline-powered internal combustion engines will dominate the U.S. transportation sector for many years; thus, automakers must increase engine efficiency to meet LCFS standards and reduce greenhouse gas emissions.**

Meeting the California LCFS standards by 2020 and the more aggressive targets for 2030 forecast for California will require a fleet-wide transition to light-duty vehicle technologies capable of much greater efficiency. While electric vehicles are gaining traction, they are not expected to achieve substantial market penetration in that time, nor are hydrogen fuel cell vehicles likely to be commercially viable at scale. Even in 2040, according to the U.S. Energy Information Administration, cars with gas- and diesel-powered engines will still represent some 95% of the international car market. A recent DOE Energy Information Administration study projected that by 2025, 83.3% of U.S. light-duty vehicles will be turbocharged, and dominated by direct injection engines. Experts are confident that continued evolution of today's internal combustion engines can achieve the fuel economy targets at an affordable cost. Highly efficient high-compression engines offer the most cost effective and most certain path to the GHG and fuel economy standards of the future. The limiting factor is not scalable vehicle technology, but fuel—most importantly, its octane rating.

To perform adequately, high-compression engines require higher-octane fuel than today's regular-grade gasoline. Today's premium-grade gasoline—which delivers higher octane at a higher cost—is produced by the addition of a blend of toxic aromatic hydrocarbons (BTEX), implicated in a range of serious health effects. Clean-burning alcohol fuels such as ethanol, on the other hand, are inherently high in octane. These fuels – which, unlike gasoline, can be produced from a variety of feedstocks, including cellulosic biomass, municipal waste, and even natural gas – can enable greater fuel economy while providing substantial environmental benefits and dramatically reducing oil dependence in the next decade, at a price that mainstream Americans can afford.

Automakers have asked EPA for higher-octane gasoline to comply with the new fuel efficiency-carbon reduction rules.<sup>14</sup> Higher-octane gasoline would enable a compression ratio increase of approximately 2 numbers, significantly increasing fuel efficiency while reducing the most

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<sup>14</sup>See, e.g., Cynthia Williams, Ford Motor Company, Comments on Proposed Tier 3 Rule, EPA-HQ-OAR-2011-0135-4349, at 3 (July 1, 2013) (“strongly recommend[ing] that EPA pursue regulations . . . to facilitate the introduction of higher octane rating market fuels,” noting that they “offer the potential for the introduction of more efficient vehicles”).

harmful emissions. To do that, automakers need an octane pool of 94 AKI (100 RON) gasoline, as compared with today's U.S. market standard of 87 AKI.

Ethanol has superior octane enhancement properties compared to other alternatives. Technically, economically, and legally (because the Clean Air Act limits the amount of aromatics in reformulated gasoline), the best and perhaps only way to make 94 AKI gasoline available nationwide is with mid-level ethanol blends (discussed here as E30). These blends have been shown in tests by automakers and Oak Ridge National Laboratory to have superior performance and emissions characteristics – mid-level ethanol blends have been called by Oak Ridge a “renewable super premium” fuel.

Recalling that the “primary goal of the LCFS regulation is to reduce the carbon intensity of transportation fuels used in California,” ethanol has the following significant carbon-reducing effects compared to gasoline:

- Argonne National Laboratory has devoted 20 years of research and analysis to the life-cycle greenhouse gas impacts of transportation fuels. As a 2012 Argonne paper summarized, “advances in technology and the resulting improved productivity in corn and sugarcane farming and ethanol conversion ... have increased the energy and greenhouse gas (GHG) benefits of using bioethanol.” Compared to regular gasoline, it showed a “well-to-wheels” reduction in GHG emissions from corn-based ethanol of 34% and from cellulosic ethanol of 88-108%.<sup>15</sup>

To be sure, as agricultural production increases to support ethanol production, concerns about land use and indirect GHG effects must also be considered. A widely circulated and globally influential paper by Timothy Searchinger concluded that those effects are so negative as to overwhelm ethanol's GHG benefits. However, this paper has since been shown to be simplistic in its approach and wrong in its conclusion. Several peer-reviewed analyses have been published, most notably by Argonne, that show the indirect land use impacts hypothesized by Searchinger were overestimated by an order of magnitude. Argonne's most recent estimates of land-use change CO<sub>2</sub> from corn ethanol are very low (3.2g CO<sub>2</sub>e/MJ)—about thirty times lower than Searchinger's initial estimates, and three times lower than Argonne's estimate in 2012.<sup>16</sup>

- Gasoline itself is increasing in carbon intensity as oil from energy-intensive operations, such as heavy crudes from the Alberta tar sands and North Dakota fracking operations in the Bakken field, come to market.

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<sup>15</sup> M. Wang *et al.*, “Well-to-wheels energy use and greenhouse gas emissions of ethanol from corn, sugarcane and cellulosic biomass for US use,” 2012 Environ. Res. Lett. 7 045905 (<http://iopscience.iop.org/1748-9326/7/4/045905>).

<sup>16</sup> Jennifer B. Dunn *et al.*, DOE Argonne Nat'l Lab., Carbon Calculator for Land Use Change from Biofuels Production, ANL/ESD/12-5, at 21 (2015).

- Aromatics require the most energy to produce in the already energy-intensive oil refining process. An E30 blend would reduce refinery CO<sub>2</sub> emissions by 10%.<sup>17</sup>
- Because of their chemical structure, aromatics are among the most carbon-rich components of gasoline. A recent report by a Health Effects Institute panel noted that aromatics “represent one of the heaviest fractions in gasoline” and said: “The aromatic content of gasoline has a direct effect on tailpipe carbon dioxide emissions. The EPEFE study<sup>18</sup> demonstrated a linear relationship between CO<sub>2</sub> emissions and aromatic content. A reduction of aromatics from 50 to 20% was found to decrease CO<sub>2</sub> emissions by 5%.”<sup>19</sup>

## **2. Displacing aromatics now used for octane in gasoline would produce substantial benefits for public health.**

Aromatic hydrocarbons have been known for a long time to be toxic in their own right. California has limited the amount of aromatics in diesel fuel since 1988, and the Clean Air Act Amendments of 1990 limited the permissible amount of aromatics in reformulated gasoline. Yet the BTEX group of chemicals still comprises 25-30% of typical U.S. gasoline. Benzene is a proven human carcinogen that can cause leukemia in exposed persons, and the other aromatics (mainly toluene and xylene) are neurotoxins. Combustion of these aromatics can lead to the formation of benzene in the exhaust gas. According to the HEI report just cited, “It is estimated that about 50% of the benzene produced in the exhaust is the result of decomposition of aromatic hydrocarbons in the fuel.” The same report also noted, “Lower levels of aromatics enable a reduction in catalyst light-off time for all vehicles. Research indicates that combustion chamber deposits can form from the heavier hydrocarbon molecules found in the aromatic hydrocarbon portion of the gasoline. These deposits can increase tailpipe emissions, including carbon dioxide, hydrocarbons and NO<sub>x</sub>.”

Of even greater concern, aromatics’ emission products are transformed in the atmosphere into secondary organic aerosol (SOA). An important study from the Harvard Center for Risk Analysis, which focused specifically on the public health impacts of secondary particulate formation from aromatic hydrocarbons in gasoline, reported: “Evidence is growing that aromatics in gasoline exhaust are among the most efficient secondary organic matter precursors. ... For example, a source apportionment study of SOA formation during a severe photochemical smog event in Los Angeles found that gasoline engines represented the single-

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<sup>17</sup>See the 2014 MathPro – GM/Ford/Chrysler linear program study, “Refining Economics of U.S. Gasoline: Octane Ratings and Ethanol Content” (attachment).

<sup>18</sup> The European Programme on Emissions, Fuels and Engine Technologies, 1996

<sup>19</sup> Health Effects Institute Panel on the Health Effects of Traffic-Related Air Pollution, “Appendix B. Fuel Composition Changes Related To Emission Controls” in Special Report 17, “Traffic-Related Air Pollution: A Critical Review of the Literature on Emissions, Exposure, and Health Effects,” Chapter 2. Emissions from Motor Vehicles. 2010. <http://pubs.healtheffects.org/getfile.php?u=555>

largest anthropogenic source of SOA. ... Source-specific speciation of total VOC in the 2005 National Emissions Inventory reveals that the U.S. emissions of single-ring aromatic hydrocarbons are 3.6 million tons per year, of which 69% are from gasoline-powered vehicles."<sup>20</sup> The Harvard study predicted 3,800 premature mortalities per year due to aromatics.

Among the toxic SOA emission products from partial combustion of the aromatics in gasoline are polycyclic aromatic hydrocarbons (PAHs). At an EPA Workshop on Ultrafine Particles on February 11, Michael Kleeman of the University of California presented new results from the California Teachers Study by B. Ostro et al., accepted for publication in *Environmental Health Perspectives*. Initial epidemiological results show a hazard ratio of 1.25 for ischemic heart disease from anthropogenic SOA. Research by Verma et al. has found that "photochemical transformations of primary emissions with atmospheric aging enhance the toxicological potency of primary particles in terms of generating oxidative stress and leading to subsequent damage in cells"<sup>21</sup> and that "the oxidative potential was strongly correlated with organic carbon and PAHs."<sup>22</sup>

Delfino et al. strongly linked PAHs with mobile sources: "Indoor and outdoor PAHs (low-, medium-, and high-molecular-weight PAHs), followed by hopanes (vehicle emissions tracer), were positively associated with biomarkers, but other organic components and transition metals were not. ... Vehicular emission sources estimated from chemical mass balance models were strongly correlated with PAHs ( $R = 0.71$ ). ... Traffic emission sources of organic chemicals represented by PAHs are associated with increased systemic inflammation and explain associations with quasi-ultrafine particle mass."<sup>23</sup>

How do PAHs created during combustion of aromatic hydrocarbons undergo long-range transport? Zelenyuk et al. found that they are trapped inside highly viscous semisolid SOA particles and thus prevented from evaporation and shielded from oxidation. "In contrast, surface-adsorbed PAHs rapidly evaporate leaving no trace. The data show the assumptions of instantaneous reversible gas-particle equilibrium for PAHs and SOA are fundamentally flawed,

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<sup>20</sup>K. von Stackelberg et al., "Public health impacts of secondary particulate formation from aromatic hydrocarbons in gasoline," *Environmental Health* 2013, 12:19. <http://www.ehjournal.net/content/12/1/19>

<sup>21</sup>V. Verma et al., "Redox activity of urban quasi-ultrafine particles from primary and secondary sources," *Atmospheric Environment*, 43(4), December 2009, 6360–6368. <http://www.sciencedirect.com/science/article/pii/S1352231009007857>

<sup>22</sup>V. Verma et al., "Physicochemical and oxidative characteristics of semi-volatile components of quasi-ultrafine particles in an urban atmosphere," *Atmospheric Environment*, 45(4), February 2011, 1025–1033. <http://www.sciencedirect.com/science/article/pii/S1352231010009301>

<sup>23</sup>R. Delfino et al., "Association of Biomarkers of Systemic Inflammation with Organic Components and Source Tracers in Quasi-Ultrafine Particles," *Environ Health Perspect.* 2010 Jun; 118(6): 756–762. <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2898850/>

providing an explanation for the persistent discrepancy between observed and predicted particle-bound PAHs.”<sup>24</sup>

PAHs have been summarized by one leading researcher as: “carcinogenic, immunotoxic, neurotoxic, mutagenic, and endocrine disruptors.”<sup>25</sup> Prenatal exposure to low levels of PAHs from ambient air pollution has been associated with multiple adverse effects, including developmental delay at age 3, reduced IQ at age 5 (effects similar to lead), symptoms of anxiety/depression and attention problems at ages 6–7, and ADHD behavior problems in children.<sup>26</sup> At a time when the rising incidence of autism is increasingly linked to disruption by environmental factors, and when the mutagenic effect of PAHs is well established, reducing exposure to PAHs should be a high public health priority.

### **3. Increased use of domestically produced renewable ethanol is essential to both objectives and would have additional co-benefits.**

Ethanol’s value for octane is not a new discovery. In fact, it was only the competition from tetraethyl lead that knocked ethanol out of that role a century ago. When lead was phased out, however, ethanol was not available in sufficient supply to provide a substitute. That is no longer true today. U.S. ethanol production has risen to roughly 15 billion gallons per year, and almost all gasoline sold today contains 10 percent ethanol. A phased increase to supply an E30 market, sufficient to supply the octane needed for higher-compression engines – reducing aromatics by 60%<sup>27</sup> – is entirely achievable.

The demand for farmland to produce corn for ethanol has been mitigated by continuing increases in yield and by the diversion of the protein in corn to supply animal feed. Increased use of conservation tillage has reduced soil erosion and water runoff while saving labor and fuel.

### **4. CARB’s SLCP Reduction Strategy should fully reflect the latest research on the value of mid-level ethanol blends to reduce GHGs and benefit public health and the environment through the displacement of aromatics.**

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<sup>24</sup> A. Zelenyuk et al., “Synergy between secondary organic aerosols and long-range transport of polycyclic aromatic hydrocarbons,” *Environ Sci Technol*. 2012 Nov 20;46(22):12459-66.

<http://www.ncbi.nlm.nih.gov/pubmed/23098132>

<sup>25</sup>F. Perera et al., “The Relationship Between Prenatal PAH Exposure and Child Neurocognitive and Behavioral Development,” PowerPoint presentation, Sept. 2011.

<sup>26</sup>F. Perera et al., “Early-Life Exposure to Polycyclic Aromatic Hydrocarbons and ADHD Behavior Problems,” PLOS ONE, November 5, 2014, DOI:10.1371/journal.pone.0111670.

<http://journals.plos.org/plosone/article?id=10.1371/journal.pone.0111670>

<sup>27</sup>See the 2014 MathPro – GM/Ford/Chrysler linear program study, “Refining Economics of U.S. Gasoline: Octane Ratings and Ethanol Content” (attachment).

The Urban Air Initiative respectfully urges CARB to consider the role that EXX HOLL fuels could play in delivering a nationwide low carbon, high octane transportation fuels system.

- As a renewable fuel, reflecting its production and land use, ethanol offers substantial GHG (CO<sub>2</sub> and black/brown carbon) reduction benefits relative to gasoline and particularly to aromatics. CARB should incorporate the latest values from Argonne's life-cycle analysis into its calculations.
- In the fall of 2013, the World Health Organization's International Agency for Research on Cancer (IARC) published its findings that traffic-related particulate matter emissions represented a Group 1 carcinogenicity threat to humans. WHO noted that in 2010, 223,000 worldwide deaths from lung cancer alone were attributable to air pollution, and singled out particulate matter and transportation-related pollution as a major source.
- Advanced GDI (gasoline direct injection) systems could make black and brown carbon, and SOA-bound toxics emissions worse unless fuel composition is improved by reducing aromatic content. EXX HOLL fuels have been shown to reduce particulate and black carbon emissions by 45 to 80% in direct injection and port fuel injection engines, respectively. Some have argued for the use of particulate filters on gasoline engines; however, the much smaller particles in gasoline exhaust (compared to diesel exhaust) elude capture by such filters, which also will interfere with, possibly even reverse, important fuel efficiency and carbon reduction gains.

The most important fuel quality improvement to achieve reductions in both carbon and particle-borne toxics emissions would be to substantially reduce aromatic hydrocarbons in gasoline. The need for octane can easily be supplied by cleaner-burning ethanol blends. They would:

1. Facilitate automaker compliance with tighter fuel efficiency and carbon reduction requirements.
2. Improve vehicle performance and reduce costs to the consumer.
3. Reduce harmful urban particulate matter, black and brown carbon, and toxics emissions.
4. Provide market-based demand signals to meet national biofuels targets in a cost-effective manner.
5. Provide an alternative to ineffective and costly gasoline particulate filters.
6. Generate billions of dollars annually in carbon reduction and health savings co-benefits.
7. Reduce refinery crude oil usage and diversify the transportation sector away from reliance on crude oil.
8. Stimulate the rural economy and create new jobs.
9. Provide a more stable investment climate for next-generation biofuel technologies.
10. Simplify California's path to low carbon fuels.

## Glossary of Terms

**Black Carbon (BC):** The elemental carbonaceous component of particulate matter that is formed through incomplete combustion of organic substances. BC is the most strongly light-absorbing component of PM<sub>2.5</sub>, and thus has important climate effects. It has a Global Warming Potential of 680 on a 100 year basis (Sierra Nevada Research Institute, 2010). It has been called the second greatest greenhouse gas pollutant, exceeding that of methane. This, along with its short lifetime of a few hours to a few days, makes fossil fuel BC control one of the quickest and most effective ways of slowing global warming. Fossil fuel BC has low OC to elemental carbon ratio, producing an overall warming effect, whereas biomass BC has high OC to EC ratio, with the potential of neutralizing the warming effect of the EC. In addition to its adverse climate impacts, due to the porosity of BC particles and their large surface area, BC can adsorb a variety of chemicals that are present in combustion exhaust, including polycyclic aromatic hydrocarbons (PAHs), which are carcinogenic or mutagenic.

**Elemental Carbon (EC):** Often used interchangeably with BC. However, whereas BC is the result of incomplete combustion in anoxic environments, EC is carbon fractions measured after oxidative combustion in the presence of oxygen above a certain temperature threshold. EC accounts for approximately 70% of the PM mass emissions from gasoline-powered LDVs (CARB, P-123).

**Endocrine Disruptor Compounds:** Chemicals that interfere with endocrine (or hormone system) in animals, including humans. These disruptions can cause cancerous tumors, birth defects, and other developmental disorders. Specifically, they are known to cause learning disabilities, severe attention deficit disorder, cognitive and brain development problems, deformations of the body (including limbs); sexual development problems, feminizing of males or masculine effects on females, etc. Any system in the body controlled by hormones can be derailed by hormone disruptors. The critical period of development for most organisms is during the transition from a fertilized egg into a fully formed infant. Experts have identified PAHs and BPAs as the “two classic endocrine disruptors.”

**HOLC Fuels:** High Octane Low Carbon Fuels, e.g., E30 blends.

**PM<sub>2.5</sub>:** Particles with a nominal mean aerodynamic diameter of less than or equal to 2.5 micrometers (µm). While this definition technically covers the most pathogenic sub-group of PM (UFPs, defined as .1µm = 100 nanometers or less), EPA has not established a separate regulatory category for UFPs, as has Europe. Since gasoline exhaust particles are typically smaller than diesel, frequently in the 20 - 100 nanometers range, EPA's regulatory approach fails to account for the considerable health and climate costs that are imposed by UFPs and the highly toxic PAHQs which coat them (see **Ultrafine Particles** definition below).

**Polycyclic Aromatic Hydrocarbons (PAHs):** Semi-volatile organic compounds (SVOCs) that exist in both gas and particle phases. PAHs are a group of over 100 different compounds that



have two or more fused aromatic rings, and are a byproduct of incomplete combustion of gasoline and diesel fuels. Some PAHs, such as benzo[a]pyrene, found in gasoline exhaust and cigarette smoke, are carcinogenic, mutagenic, and genotoxic. PAHs are also endocrine disruptor compounds (EDCs), which mimic the body's natural hormones, and have been linked to a variety of adverse medical conditions. Contrary to conventional wisdom that PAHs originate mainly from diesel exhaust, light-duty vehicles are the main source of high molecular weight (HMW) PAHs in many urban areas, where gasoline-powered engines predominate. High molecular weight (HMW) PAHs have high affinity to BC.

**Secondary Inorganic Aerosols (SIAs):** Sulfates, nitrate, and ammonium, generally from stationary sources, the formation of which are widely understood compared to the SOAs. SIAs are formed by the oxidation of gas-phase precursors such as sulfur dioxide, nitric oxide, and nitrogen oxides.

**Secondary Organic Aerosols (SOAs):** Formed by photo oxidation of gas phase volatile organic compounds (VOCs) in the atmosphere. Approximately 50% of anthropogenic VOCs are emitted by combustion sources. Generally, SOA-forming VOCs have more than six carbon atoms, since the oxidation products of organic compounds with lower carbon numbers are too volatile to condense under ambient temperature conditions. Conventional models significantly understate the amount of SOAs in the atmosphere. Generally, SOA are formed by the oxidation of high molecular weight volatile organic compounds to produce low-volatility products, which subsequently condense onto the existing aerosols.

**Semi-Volatile Organic Compounds (SVOCs):** Organic compounds that volatilize slowly at standard temperature (20° C and 1 atmosphere). PAHs are SVOCs that exist in both gas and particle phases. A large fraction of primary aerosols generated by combustion includes SVOCs. The semi-volatile fraction of the PM can account for 10 – 30% of the PM mass, and 70 – 90% of PN (CARB, P-70).

**Ultrafine Particles (UFPs):** Largely organic primary combustion products, including particles with a mobility diameter of less than or equal to 0.1µm, emitted directly to the atmosphere or formed by nucleation of gaseous constituents in the atmosphere. Compared to PM<sub>2.5</sub>, UFPs are more lethal and pathogenic, due to their smaller size and larger particle numbers; their greater bioavailability and lung retention; and their greater content of redox active compounds (inducing oxidative stress). UFPs contain much higher mass fractions of PAHQs than other particles. CARB reports that  $2.5 \times 10^{12}$  SPN (solid particle numbers) are equivalent to 1 mg/m<sup>3</sup> (milligram per cubic meter) of EC/BC, and that a total SPN limit of  $7.5 \times 10^{12}$  particles per mile corresponds to a PM mass limit of 3 mg/mile. UFP/SPN emissions vary linearly with EC emissions (CARB, P-128).