RESEARCH ARTICLE

ATMOSPHERIC CHEMISTRY

Volatile chemical products emerging as largest petrochemical source of urban organic emissions

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A gap in emission inventories of urban volatile organic compound (VOC) sources, which contribute to regional ozone and aerosol burdens, has increased as transportation emissions in the United States and Europe have declined rapidly. A detailed mass balance demonstrates that the use of volatile chemical products (VCPs)—including pesticides, coatings, printing inks, adhesives, cleaning agents, and personal care products—now constitutes half of fossil fuel VOC emissions in industrialized cities. The high fraction of VCP emissions is consistent with observed urban outdoor and indoor air measurements. We show that human exposure to carbonaceous aerosols of fossil origin is transitioning away from transportation-related sources and toward VCPs. Existing U.S. regulations on VCPs emphasize mitigating ozone and air toxics, but they currently exempt many chemicals that lead to secondary organic aerosols.

Exposure to air pollution is the fifth ranking human health risk factor globally, following malnutrition, dietary risks, high blood pressure, and tobacco ([1]). Secondary organic aerosols (SOA), a major component of fine particulate matter ($PM_{2.5}$) in cities around the world ([2]), form through oxidation of volatile organic compound (VOC) precursors. Oxidation of VOCs in the presence of nitrogen oxides ($NO_x = NO + NO_2$) also contributes to tropospheric ozone (O_3), which increases risks of mortality from respiratory diseases ([3]). A recent epidemiological study suggests that adverse human health effects occur below current U.S. standards for $PM_{2.5}$ and O_3 ([4]). It is thus critical to identify and quantify the most important human-produced sources of VOC emissions to effectively mitigate air pollution and improve human health.

Automotive emissions of VOCs have decreased steadily from efforts to control tailpipe emissions in the United States ([5]) and Europe ([6]). As a result, other sources of VOC emissions are likely growing in relative importance ([7]). Transportation emissions of NO_x and VOCs have long been considered major contributors to formation of O_3 ([8]) and SOA ([9–11]) in urban areas, although recent studies have suggested the importance of nonvehicular sources as major contributors ([12–14]). Emissions from the use of chemical products have been difficult to constrain in models ([15]) or from ambient measurements ([16]). One challenge has been the lack of available atmospheric measurements of oxygenated volatile organic compounds (OVOCs) common in everyday household products ([16]). Here, we focus on volatile chemical products (VCPs), including pesticides, coatings, printing inks, adhesives, cleaning agents, and personal care products. These products contain organic solvents, which lead to substantial emissions of VOCs to the atmosphere.

We show that success in controlling air pollution has changed the proportions of sources of anthropogenic VOC emissions in the United States, decreasing the relative contribution from transportation fuels and increasing the contribution from VCPs. We consider four key pieces of evidence to support this finding: (i) energy and chemical production statistics; (ii) near-roadway measurements of transportation emissions, together with laboratory testing of chemical products; (iii) ambient air measurements away from roads; and (iv) indoor air measurements.

Mass balance of hydrocarbons in the petrochemical industry

We used energy and chemical production statistics, together with near-roadway and laboratory measurements, to construct the mass balance shown in Fig. 1 ([17]). In 2012, the amount of oil and natural gas used as fuel in the United States was ~15 times the amount used as chemical feedstocks (Fig. 1A). Chemical feedstocks are almost entirely derived from fossil hydrocarbons ([18]) and are transformed to chemicals found in everyday household products (tables S1 to S3). We focus on emissions from organic solvents, which consist mostly of intermediate-volatility organic compounds (IVOCs) and higher-volatility VOCs (fig. S1). The evaporation time scales of higher-volatility VOCs range from milliseconds to hours, and for IVOCs from hours to months ([19]). The fraction that can be emitted to the atmosphere depends strongly on product type and use (table S4). For example, a high fraction of organic compounds evaporate from architectural coatings. Most organic compounds in soaps and detergents dissolve in water and end up in sewer systems ([20]), with negligible amounts emitted from wastewater treatment plants ([21]).

Total gas-phase VOC emission factors of mobile source fuels and VCPs are based on field (e.g., near-roadway) and laboratory experiments reported in the literature (Fig. 2). A key finding is that VOC emission factors (emission amount per unit product use) resulting from the use of many chemical products are one to two orders of magnitude higher than from automobile exhaust. The relatively low VOC emission factor for on-road gasoline engines today (Fig. 2) results from (i) combustion oxidizing most hydrocarbons in fuel to carbon dioxide, and (ii) the increasing effectiveness of modern three-way catalytic converters in reducing tailpipe VOC emissions over multiple decades ([5–7]). Consequently, the relative importance of VCP emissions has grown. For example, mixing ratios of acetone, a marker of coating-related VCPs in this study and in the past ([16]), increased in ambient air in Los Angeles from 1990 to 2010 ([22]). This is in sharp contrast to VOCs present in gasoline exhaust, which decreased markedly during the same period ([22]), except for ethanol ([23]).

Although U.S. sales of VCPs are substantially smaller than for gasoline and diesel fuel, VOC emissions from VCPs (7.6 ± 1.5 Tg) are twice as large as from mobile sources (3.5 ± 1.1 Tg) (Fig. 1E, light green, dark green, and blue bars) because of differences in emission factors. Emissions from mobile sources and VCPs should scale with driving and population, respectively, and be concentrated in cities. Other fossil sources that occur upstream of end users (i.e., oil and natural gas extraction, oil refineries, and chemical manufacturing facilities)

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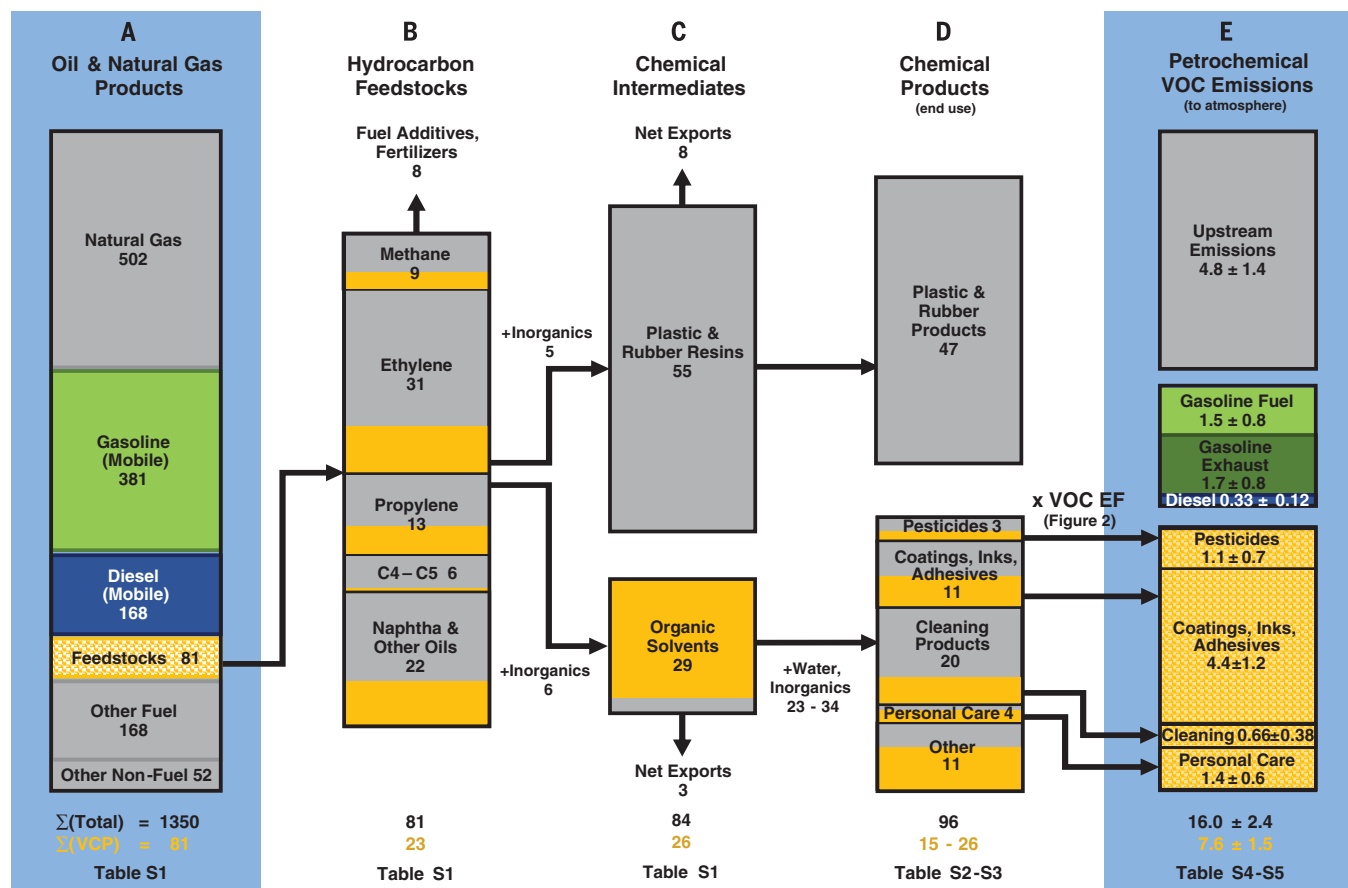
Fig. 1. Mass balance of organic compounds through the U.S. petrochemical industry in 2012, from crude oil and natural gas production to resulting VOC emissions. (**A** to **E**) Within the chemical manufacturing sector, orange sections of boxes track hydrocarbon feedstocks (A), the fraction used for production of organic solvents [(B) and (C)], organic solvents consumed domestically for chemical products (D), and resulting emissions from use of volatile chemical products (E). Emissions from plastic, rubber, and other chemical products are not considered here. All units are in Tg; boxes are sized proportionally among (B), (C), and (D) (17).
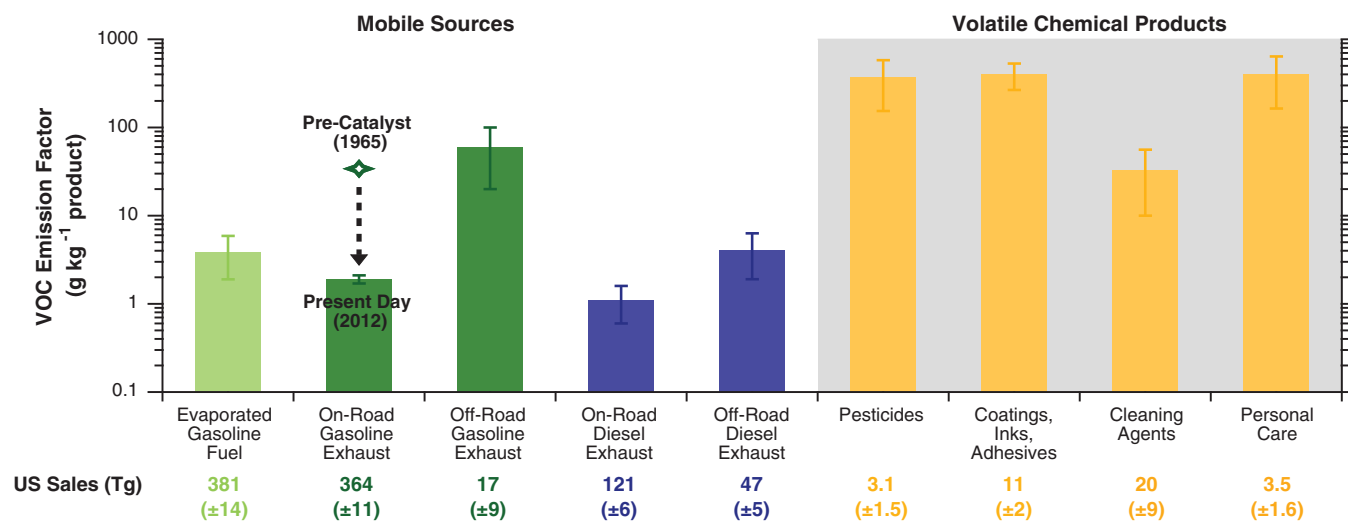

Fig. 2. Total VOC emission factors for end uses of petrochemical sources considered in this study, including from mobile sources and volatile chemical products. Shown in the bottom row are sales data of fuels for mobile sources (from Fig. 1A) and sales data of volatile chemical products (from Fig. 1D). The green symbol and dashed arrow illustrate the large reductions in tailpipe VOC emission factors as precatalyst on-road gasoline vehicles were replaced by present-day vehicle fleets. Error bars reflect the 95% confidence interval of the mean or expert judgment (17).

Fig. 3. Box modeling of petrochemical VOC emissions in outdoor Los Angeles air and in buildings.
(**A** and **B**) Evaluations of our two-compartment box model with ambient observations of individual VOCs measured at Pasadena, CA, in 2010. In (A), we input only emissions from fossil fuels (mobile + upstream sources) into the model and evaluate against outdoor data under "no chemistry" conditions; (B) is the same as (A) but with the addition of VCP emissions. (**C** and **D**) Comparison of our box model against indoor observations of residential/commercial buildings. In (C) we allow outdoor VOCs to age by 3 hours at [OH] = 1.5×10^6 molecules cm^{-3} in the model, typical of ambient conditions at the ground site; (D) is the same as (C) but with the addition of VCP emissions indoors. For all panels, points below the 1:1 line indicate that the box model underpredicts ambient or indoor concentrations relative to observations. Shown at the lower right of each panel is the mean relative bias and R^2 of the model calculated in log space. Model statistics exclude aldehydes, which appear to be from other emission sources.
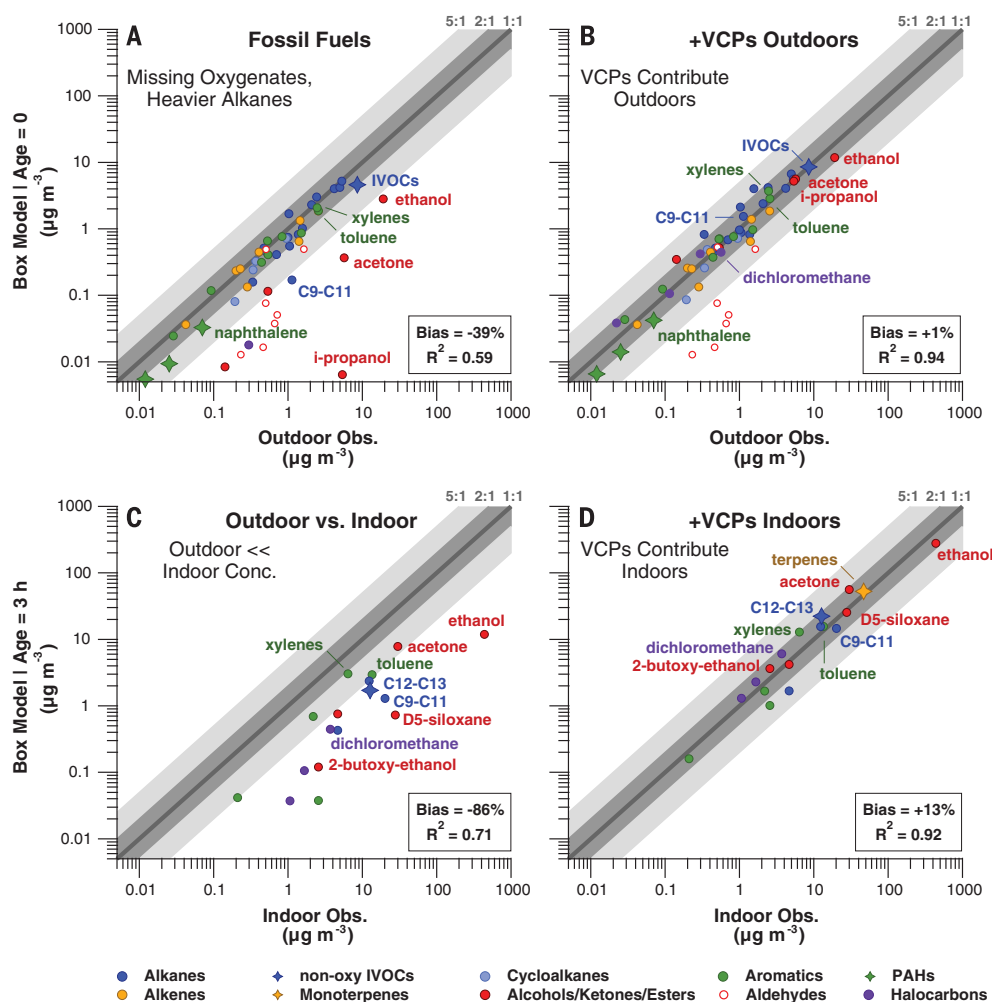
represent substantial VOC emissions (Fig. 1E, gray bar). Note that methane emissions are not shown in these estimates. Upstream processes are uncertain, and more research is needed to better constrain their emissions of VOCs (24–27).

In the United States, current inventories consistently underestimate total VOC emissions from VCPs by factors of 2 to 3 nationally (table S5) and regionally (table S6). Nationally, mobile-source emissions are overestimated by ~40%. The main effect of our analysis is to shift the relative contribution of VOC emissions from petrochemical sources, away from mobile sources and toward VCPs (fig. S2). At national and urban scales, we attribute 15 to 42% of petrochemical VOCs to mobile sources and 39 to 62% of petrochemical VOCs to VCPs. The rest is from upstream sources associated with oil and natural gas production and distribution.

European inventories also show half of VOC emissions from VCPs (15, 28). This is in contrast to source apportionment studies of ambient measurements in Europe, which suggest that emissions from traffic are the largest source, with chemical product emissions substantially overestimated (28). However, we expect VCPs to be an important source of urban VOC emissions in both European and U.S. cities, because (i) transportation-related

VOCs are similar across industrialized countries (29), (ii) VOCs emitted from use of VCPs (e.g., acetone) are found in ambient air on both continents (30, 31), and (iii) indoor levels of VOCs from chemical products are similar (32, 33). As discussed below, our emissions inventory is well constrained by a comprehensive set of ambient and indoor measurements, and is more extensive in terms of chemical speciation than measurements used in prior source apportionment studies. Previous studies typically relied on ambient VOC measurements mainly of compounds found in fossil fuels, while not including many species found in chemical products (16). This may explain why prior source apportionment studies have underestimated the influence of VCP emissions as sources of urban VOCs.

Chemical fingerprint of VCPs found in ambient and indoor air

If chemical products are an important source of urban air pollution, then their chemical fingerprint (fig. S3) should be consistent with ambient and indoor air quality measurements. To test our hypothesis, we used Los Angeles as a case study and modeled emissions from petrochemical sources in a two-compartment box model, where one box represents ambient air and a second box rep-

resents indoor air of buildings located within the basin (fig. S4).

California has an extensive regulatory reporting program for consumer products (34), including residential and commercial uses, which we used to speciate emissions. These speciation profiles provided us with target compounds to characterize in both outdoor and indoor environments. We also accounted for industrial emissions from VCPs (e.g., degreasing, adhesives, and coatings). The reporting data are in agreement with a U.S. database of chemicals (35) used as key constituents in chemical products (table S7). The VOC speciation profiles of VCPs (table S8) are distinguishable from those of fossil fuels (table S9), although there is some overlap in species present.

The outdoor box model predictions were evaluated against summertime ambient VOC measurements made in Pasadena during 2010 (30) (table S10). In ambient air, we found that fossil fuel VOCs [from mobile sources and from local oil and natural gas production and distribution (36)] can only account for 61% of the mass of freshly emitted VOCs measured, and 59% of their variability (Fig. 3A). The model could be underestimating emissions as a result of biases in emission inventories, chemistry, and/or transport. However, to account for the effects of
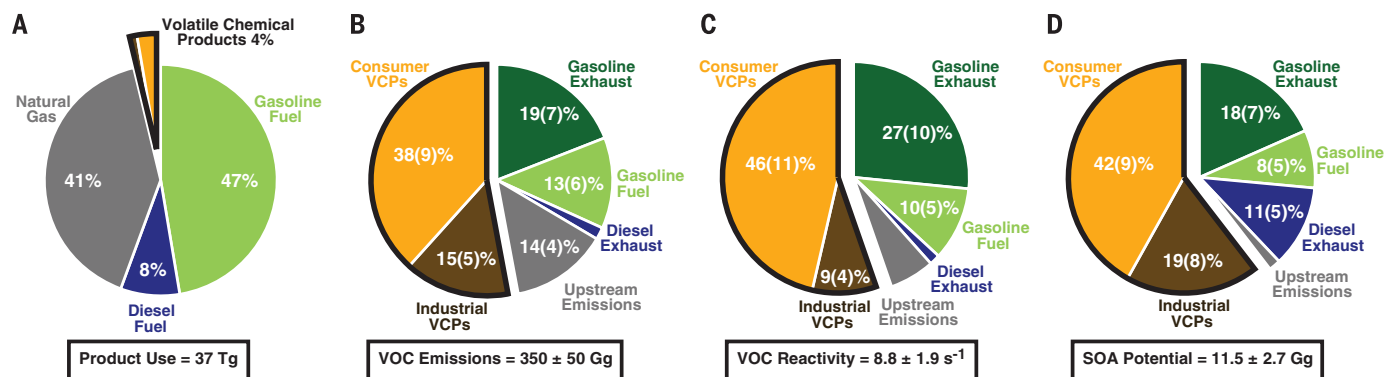
Fig. 4. Contributors to ambient air pollution in Los Angeles. (**A** to **D**) Distribution of (A) petrochemical product use, (B) VOC emissions, (C) VOC reactivity with OH, and (D) SOA formation potential across petrochemical sources only. Contributions from nonfossil sources are not shown. Uncertainties in source apportionment were determined by Monte Carlo analysis.

chemistry, we used a technique that extrapolates measured concentrations to fresh emission conditions (*30*), and the atmospheric dilution in our box model is consistent with three-dimensional chemical transport modeling of the Los Angeles basin (*37*). We therefore conclude that large underpredictions are due to missing emission sources. A surprising result is that mobile-source emissions of ethanol account for less than 20% of ambient concentrations, even though gasoline blends now routinely include at least 10% ethanol. This suggests that other sources are contributing substantially to ambient ethanol concentrations, which we attribute to VCPs.

Adding emissions from VCPs (Fig. 3B) reduces the model bias in ambient air from –39% to +1%, and the R^2 in the box model improves from 0.59 to 0.94. Emissions from key markers in VCPs are now consistent with ambient observations, including those for ethanol. Ethanol and isopropanol are in personal care products, cleaning agents, and alcoholic beverages. Acetone is a common ingredient in paint thinners (*16*) and is exempt from VOC regulations because of its low reactivity. Nonane, decane, undecane, and heavier nonoxygenated IVOCs are present in mineral spirits, a petroleum distillate common in solvent-borne coatings. Chlorinated hydrocarbons (e.g., dichloromethane) are in various VCPs, including cleaning agents and paint thinners (*38*). Except for formaldehyde, primary emissions of aldehydes do not appear to be good markers of fossil fuels (Fig. 3A) or VCPs (Fig. 3B) considered in this study, and are therefore excluded from our model bias and R^2 calculations. One possible source of aldehydes is cooking emissions (*39*).

Because a high fraction of the emissions from consumer VCPs occurs in residences and commercial buildings, their chemical fingerprint should be even stronger in indoor air. We tested our indoor model with measurements of residential (*32*) and commercial buildings (*40*) (table S11). Indoor concentrations of compounds found in VCPs were ~7 times those in ambient air (Fig. 3C). We took into account chemical removal and formation of ambient VOCs before exchange with the indoor environment (Fig. 3B versus Fig. 3C). Next, we

injected consumer VCP emissions into our indoor box model, accounting for typical air exchange rates of buildings. The correspondence between our model predictions and indoor air quality measurements is high (Fig. 3D, R^2 = 0.92). The model results are now consistent with typical indoor air concentrations for key markers (e.g., acetone, C9–C11 n-alkanes, ethanol, and dichloromethane) and important classes of SOA precursors, including terpenes (e.g., limonene) (*41*), glycols and glycol ethers (e.g., 2-butoxyethanol) (*42*), volatile methyl siloxanes (e.g., D5-siloxane) (*43*), aromatics (e.g., toluene, xylenes) (*44*), and heavier alkanes (e.g., C12–C13 n-alkanes) (*45*).

Urban air quality implications

Here, we assess the importance of VCP emissions to ambient air pollution, again using Los Angeles as a test case (Fig. 4). Los Angeles currently violates the U.S. 8-hour O_3 standard, and O_3 formation remains sensitive to the reactivity of VOCs emitted and their secondary products with respect to the hydroxyl radical (OH) (*46*). We attribute half of VOC reactivity (Fig. 4C) from petrochemical sources to VCPs and the other half to mobile and upstream sources. Because the VOC reactivity of VCPs is similar to that of transportation fuels (table S12), the distribution looks similar to that of VOC emissions (Fig. 4B). The ambient and indoor air measurements shown in Fig. 3 constrain primary emissions from VCPs that contribute ~70% of the OH reactivity from VCPs. Consumer products contain reactive OVOCs and terpenes, which emit upon use, even after accounting for sewer losses (*20*).

Prior studies often report missing sinks of OH reactivity in urban atmospheres (*47*), which can degrade forecasting capabilities of regional models of O_3 (*27*). Specifically in the Los Angeles basin, a recent model (*48*) underestimated OH reactivity by a factor of ~2 relative to measurements. Here, we compare our inventory-based estimate of VOC reactivity with direct measurements made at Pasadena (*48*). In fig. S5, we show that half of measured OH reactivity (21 ± 7 s^{-1}) can be explained by fossil fuel VOC emissions (3.9 ± 1.8 s^{-1}) and other non-VCP sources of OH reactivity (7.3 ±

1.6 s^{-1}). The emissions from use of VCPs contribute an additional 4.8 ± 3.4 s^{-1}, bringing the summed OH reactivity to within ~25% of the observations (fig. S5). Although our inventory slightly underestimates OH reactivity, it is now within uncertainties of measurements. The inclusion of typically unmeasured or unreported oxygenated compounds from VCPs can help to resolve some of the missing OH reactivity observed over cities.

In the past, aerosol models substantially underestimated SOA in cities (*49*). Advances in model representations of semivolatile/intermediate-volatility organic compounds have helped to bring better closure between models and observations (*50–53*). However, questions remain with respect to whether the models accurately represent the mixture of emission sources and multigenerational aging schemes (*50*, *53*). In Fig. 4D, we show VCPs to be larger contributors to fossil SOA (60 ± 9%) than are mobile and upstream emission sources (40 ± 9%). This is in contrast to prior studies in the United States and Europe finding that the transportation sector is currently the leading source of SOA formation in cities (*10*, *11*). The aerosol yields used in this study (table S12) are mostly estimated from the Statistical Oxidation Model (SOM) (*54*), along with a one-dimensional volatility basis set (*51*) for OVOCs. SOM approximately accounts for multigenerational aging and can be used to estimate yields for compounds lacking laboratory measurements in the interim.

The model-observation comparison of fossil-derived SOA improves substantially when we add VCP emissions to traditionally considered transportation emissions (fig. S6). Note that nonfossil contributions to SOA, such as from wood burning, cooking, and biogenic sources, are not considered here. If we consider emissions from mobile sources and upstream emission sources alone, then the amount of fossil SOA predicted by SOM is lower than measurements at the Pasadena ground site by a factor of 3.4 ± 1.7 (*55*, *56*). The inclusion of VCP emissions is required to bring the modeled and measured SOA to agreement, within their respective uncertainties (fig. S6). Although aerosol yields are uncertain (fig. S7), the air quality measurements shown in Fig. 3 constrain primary

emissions from VCPs, which contribute ~70% of the SOA formation potential.

Straight, branched, and cyclic alkanes account for 42 ± 4% of the SOA formation potential from VCPs, followed by OVOCs (29 ± 12%), alkenes and terpenes (17 ± 5%), and aromatics (12 ± 3%). We find SOA distributed over a wide spectrum of species, and not dominated by any individual compound (table S8). The use of petroleum distillates is a major source of heavier alkanes and cycloalkanes (C_5 to C_{15}) as well as aromatics (e.g., toluene and xylenes). Fragrances are major contributors, most prominently of limonene, α-pinene, β-pinene, and 3-carene (57). Relatively few experiments to date have characterized aerosol formation from primary emissions of oxygenated IVOCs (42), especially those with six or more carbon atoms, and whose emissions are potentially important.

In the United States, O_3 regulations do not address lower-volatility compounds (vapor pressure <0.1 mm Hg at 20°C) (21), yet these can evaporate on atmospherically relevant time scales (19) and contribute to SOA (13). Volatile methyl siloxanes are also exempt, and their oxidation is also known to form SOA (43). Disclosure of ingredients used to make fragrances is not required (57), but terpenes are common and known aerosol precursors (41). Chemical manufacturers have reformulated products to reduce aromatic content, such as in cleaning agents (33). However, single- and multiplering aromatics are still present in products and in indoor air (32), and they contribute to SOA outdoors (44, 58).

Human health implications

Although fossil fuels remain important sources of urban air pollution, exposure to ambient $PM_{2.5}$ is increasingly from chemical products as the transportation sector becomes cleaner. Additionally, because a large fraction of VCP emissions occurs in buildings, exposure to air toxics is of concern indoors (59). Below we summarize two implications for human health:

(1) The average fossil contribution to carbonaceous aerosols ($\sum$ = black carbon + organic aerosol) measured in ambient air at Pasadena was 3.4 ± 1.0 µg m^{-3} (55, 56), which does not include nonfossil components from cooking or biogenic sources. Of the fossil total, ~40%, or ~1.3 µg m^{-3}, is attributed to directly emitted particles (55, 56), mainly from diesel engines (7). The SOA from use of VCPs (Fig. 4D) is of similar magnitude and accounts for ~35% of the fossil total, or ~1.2 µg m^{-3}. As diesel particle filters and oxidation catalysts become more widespread, and reduce diesel contributions to $PM_{2.5}$ (60), the fraction of $PM_{2.5}$ from VCPs will grow because SOA precursor emissions from VCPs are not decreasing as quickly (7).

(2) We show that indoor emissions of aromatics and chlorinated hydrocarbons from use of VCPs are consistent with typical indoor concentrations (Fig. 3D), which are of concern because of their human toxicity (61). Indoor emissions of aromatic compounds have decreased by ~7% per year between 1981 and 2001 (33), comparable to decreases in transportation emissions of ~8% per year (7, 22). Consumer uses of VCPs likely remain key sources of human exposure to air toxics relative to fossil fuels, especially because people spend most of their time indoors (62).

Traditional approaches to mitigating air pollution emphasize transportation and industrial sources (63). However, chemical products are an emerging source of urban VOCs (22), including SOA precursors (7), because VOC emissions from VCPs are not declining as fast as those from transportation. New paradigms leveraging research tools from the indoor and outdoor air quality communities could strengthen efforts to reduce human exposure to O_3, $PM_{2.5}$, and air toxics. As the composition of chemical products has evolved to remove chlorofluorocarbons to address stratospheric O_3, shifted from solvent- to water-borne formulations to mitigate tropospheric O_3, and phased out toxic components (33), VCPs have begun to contribute significantly to SOA formation outdoors. Given that global mortality from fine particles is significantly greater than for ambient O_3 pollution (1), further study is needed on whether chemical products currently designed to mitigate O_3 are also sufficient to protect humans from exposure to fine particles.

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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/359/6377/760/suppl/DC1
Materials and Methods
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Science

Volatile chemical products emerging as largest petrochemical source of urban organic emissions

Brian C. McDonald, Joost A. de Gouw, Jessica B. Gilman, Shantanu H. Jathar, Ali Akherati, Christopher D. Cappa, Jose L. Jimenez, Julia Lee-Taylor, Patrick L. Hayes, Stuart A. McKeen, Yu Yan Cui, Si-Wan Kim, Drew R. Gentner, Gabriel Isaacman-VanWertz, Allen H. Goldstein, Robert A. Harley, Gregory J. Frost, James M. Roberts, Thomas B. Ryerson and Michael Trainer

Air pollution evolution

Transport-derived emissions of volatile organic compounds (VOCs) have decreased owing to stricter controls on air pollution. This means that the relative importance of chemicals in pesticides, coatings, printing inks, adhesives, cleaning agents, and personal care products has increased. McDonald *et al.* show that these volatile chemical products now contribute fully one-half of emitted VOCs in 33 industrialized cities (see the Perspective by Lewis). Thus, the focus of efforts to mitigate ozone formation and toxic chemical burdens need to be adjusted.

Science, this issue p. 760; see also p. 744

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