

Ethylene Glycol Emissions from On-road Vehicles

Ezra C. Wood,^{*,†} W. Berk Knighton,[‡] Ed C. Fortner,[§] Scott C. Herndon,[§] Timothy B. Onasch,[§] Jonathan P. Franklin,^{§,▲} Douglas R. Worsnop,[§] Timothy R. Dallmann,^{||,▽} Drew R. Gentner,^{||,■} Allen H. Goldstein,^{||,⊥} and Robert A. Harley^{||}

[†]Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, United States

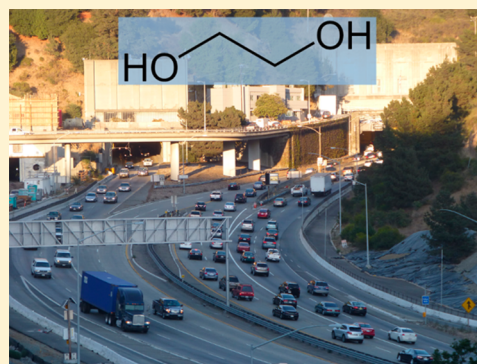
[‡]Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59717, United States

[§]Aerodyne Research, Inc., Billerica, Massachusetts 01821, United States

^{||}Department of Civil and Environmental Engineering and [⊥]Department of Environmental Science, Policy and Management, University of California, Berkeley California 94720, United States

Supporting Information

ABSTRACT: Ethylene glycol (HOCH₂CH₂OH), used as engine coolant for most on-road vehicles, is an intermediate volatility organic compound (IVOC) with a high Henry's law coefficient. We present measurements of ethylene glycol (EG) vapor in the Caldecott Tunnel near San Francisco, using a proton transfer reaction mass spectrometer (PTR-MS). Ethylene glycol was detected at mass-to-charge ratio 45, usually interpreted as solely coming from acetaldehyde. EG concentrations in bore 1 of the Caldecott Tunnel, which has a 4% uphill grade, were characterized by infrequent (approximately once per day) events with concentrations exceeding 10 times the average concentration, likely from vehicles with malfunctioning engine coolant systems. Limited measurements in tunnels near Houston and Boston are not conclusive regarding the presence of EG in sampled air. Previous PTR-MS measurements in urban areas may have overestimated acetaldehyde concentrations at times due to this interference by ethylene glycol. Estimates of EG emission rates from the Caldecott Tunnel data are unrealistically high, suggesting that the Caldecott data are not representative of emissions on a national or global scale. EG emissions are potentially important because they can lead to the formation of secondary organic aerosol following oxidation in the atmospheric aqueous phase.



INTRODUCTION

Vehicular emissions of organic compounds contribute greatly to ambient concentrations of primary pollutants (e.g., volatile organic compounds, particulate matter) and to the formation of secondary pollutants such as ozone and secondary organic aerosol (SOA).^{1–3} Both primary and secondary pollutants affect climate and have adverse effects on public health.^{4,5} There is considerable uncertainty regarding the sources and atmospheric transformations of organic aerosol: models underpredict SOA concentrations and oxygen-to-carbon (O/C) ratios and overpredict aerosol volatility.^{1,6}

Although most vehicular organic compound emissions are from evaporation and incomplete combustion of hydrocarbon fuels and lubrication oil,^{2,7} engine coolant is another potential vehicular source of organic compound emissions. The most common type of engine coolant used is a 50% by volume solution of ethylene glycol (EG, 1,2-ethanediol, HOCH₂CH₂OH) in water. In light-duty vehicles, approximately 5–15 L of engine coolant is pumped at high pressure (2 bar) and temperature (up to 130 °C) past the engine cylinders and through the vehicle's radiator. Leaks of coolant can develop in numerous places within a vehicle, for example, the water

pump's shaft seals, engine head gaskets, radiator cap, rubber transport hoses, and the radiator itself. Liquid EG can leak from a vehicle onto the road and subsequently evaporate or can evaporate directly from a malfunctioning cooling system (e.g., as part of the visible mist emitted by an overheating vehicle).

Besides its use as an engine coolant, EG is also used for numerous industrial purposes such as production of polyethylene terephthalate (PET) bottles (~45% of global use)⁸ and for aircraft deicing. The U.S. Environmental Protection Agency (EPA) 2011 Toxic Release Inventory lists airborne EG emissions of 0.8 Gg/year from point sources in the United States,⁹ but this is a lower limit given that not all EG-emitting facilities are required to report emissions. To our knowledge, vehicular emissions of EG have not been quantified in any emission inventory.

In the atmosphere, ethylene glycol can be oxidized either in the gas phase or in the aqueous phase following uptake to a

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cloud, fog, or wet aerosol particle. Atmospheric oxidation of gaseous EG by OH is rapid (rate constant $1.5 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$),¹⁰ corresponding to an atmospheric lifetime, due to reaction with 10^6 molecules of $\text{OH} \cdot \text{cm}^{-3}$, of 19 h. Glycolaldehyde (HOCH_2CHO), glycolic acid (HOCH_2COOH), and formaldehyde are presumably the main reaction products by analogy with larger diols.¹¹ The major products from photolysis of glycolaldehyde are formaldehyde and carbon monoxide, and the main products of reaction of glycolaldehyde with OH in the gas phase are glyoxal and formaldehyde.¹² Gas-phase chemistry and gas-particle partitioning of EG and its oxidation products do not lead to SOA formation.¹³ The high Henry's law coefficients of EG, glycolaldehyde, glyoxal, and glycolic acid ($k_{\text{H}} = 10^3$ to $5 \times 10^5 \text{ M} \cdot \text{atm}^{-1}$),^{14,15} however, lead to facile uptake into the atmospheric aqueous phase, wherein oxidation leads to highly oxidized products such as glyoxylic acid, oxalic acid,¹⁶ and oligomers.¹⁷ Following liquid water evaporation, these highly oxidized products can form SOA with high oxygen/carbon ratios.¹⁸ Due to current estimates of industrial and vehicular emissions, EG is not currently considered a significant SOA precursor.

In this paper we present observations of unexpectedly high concentrations of EG in a California highway tunnel and discuss possible emission mechanisms and atmospheric implications.

EXPERIMENTAL METHODS

Tunnel Sampling. Pollutant concentrations in bore 1 of the Caldecott Tunnel near Oakland, CA, were measured from July 22 to July 28, 2010, by a combination of real-time (1-s time resolution) and integrated measurement devices housed in the east fan room or the Aerodyne Mobile Laboratory (AML).¹⁹ The sampling point for all measurements was through an access grate at the roof of the tunnel. Bore 1 of the Caldecott Tunnel (1 km long) has a 4% uphill grade and the preceding 4 km of road (Route 24) has grades of 4–6.5%. Diesel-fueled vehicles accounted for 1–4% of total traffic, with the rest being gasoline-powered.²⁰ Ambient temperatures in nearby Oakland ranged from 12 to 21 °C. Details on the sampling configuration and measurements are described elsewhere.^{20,21} Briefly, the AML sampled gas-phase compounds through a 1–2 μm polytetrafluoroethylene (PTFE) filter and 34 m of 0.95 cm ($3/8$ -in.) inner diameter perfluoroalkoxy (PFA) tubing at a flow rate of 11 standard liters per minute (SLPM). The inlet was periodically flooded (overblown) upstream of the filter with dry zero air (AirGas) to monitor instrument baselines. The AML also periodically measured outdoor air near the laboratory itself by disconnecting the long sampling tube. Acetaldehyde (CH_3CHO) and more than 200 other individual volatile organic compounds (VOCs) and intermediate volatility organic compounds (IVOCs) were measured in the east fan room by gas chromatography (GC) with mass spectrometry (MS) and flame ionization detection (FID).²¹ VOC and IVOC measurements are averaged to 60 min and have 2σ uncertainties of 10%.

The AML also sampled air in the Washburn Tunnel outside Houston, TX during two round-trip transits on 22 May 2009 as part of the Study of Houston Atmospheric Radical Precursors (SHARP) campaign. The AML conducted similar mobile measurements in the Central Artery I-93 Tunnel in Boston, MA, on 16 January 2008. Total sampling times (with a 1 m inlet) were 4 min in Houston and 9 min in Boston. Ambient temperatures were 21 °C in Houston and –5 °C in Boston.

Proton Transfer Reaction Mass Spectrometric Measurements. Fast 1-s measurements of VOCs were made with an unmodified proton transfer reaction mass spectrometer (PTR-MS, Ionicon) stationed in the AML. Ethylene glycol, with a molecular mass of $62 \text{ g} \cdot \text{mol}^{-1}$, was detected at mass-to-charge ratio $m/z = 45$ (Figure 1) following a dehydration fragmentation reaction (reactions 1 and 2) as first pointed out by Wisthaler et al.:²²

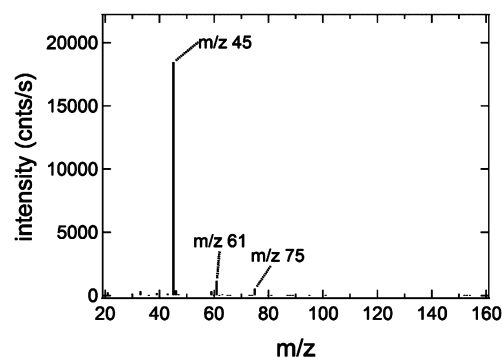
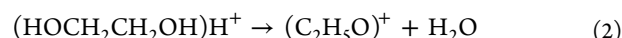
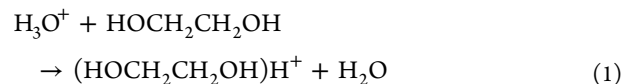


Figure 1. PTR-MS difference mass spectrum of air sampled from the headspace of in-service engine coolant. m/z 61 and 75 are not thought to be related to ethylene glycol.

CH_3CHO is also detected at m/z 45; thus the total m/z 45 signal observed reflects the sum of both compounds. Since CH_3CHO was simultaneously measured by in situ GC-FID, its contribution to m/z 45 can easily be removed to calculate the EG concentration. Except at night, the GC CH_3CHO concentrations rarely exceeded 25% of the m/z 45 values. The only other known contributors to m/z 45 are ethylene oxide (H_2COCH_2), which is an isomer of acetaldehyde, and a weak interference from protonated carbon dioxide (CO_2H^+). Ethylene oxide is an intermediate in the conversion of ethylene to ethylene glycol, and while there may be industrial sources, there is no evidence that vehicles emit ethylene oxide. The high m/z 45 concentrations could only have been caused by ethylene oxide if there were numerous vehicles transporting and leaking ethylene oxide at high emission rates in the tunnel. Endothermic charge transfer to carbon dioxide, forming CO_2H^+ , has been observed to occur within the PTR-MS.²³ The interference from CO_2 is small, and no increases in m/z 45 were observed during spikes of $[\text{CO}_2]$ of several hundred parts per million (ppm) in which there was little increase in $[\text{CO}]$ or other pollutants. Furthermore, CO_2 would not produce the slow time response observed during the high m/z 45 events. Previous PTR-MS measurements in urban areas may have overestimated CH_3CHO concentrations at times due to this interference by ethylene glycol.

The PTR-MS m/z 45 measurements presented here use the instrumental response of CH_3CHO , quantified by dilution of a multicomponent gas standard (Apel-Riemer). In order to estimate the PTR-MS sensitivity response factor for ethylene glycol, we calculate the reaction rate constants for the proton transfer reaction of H_3O^+ with acetaldehyde and ethylene glycol

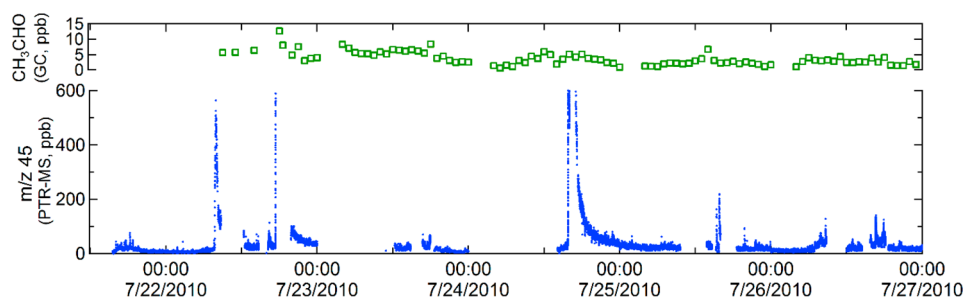


Figure 2. GC-FID CH_3CHO and PTR-MS m/z 45 measurements from July 22 to 28, 2010. Peak m/z 45 mixing ratios on July 22 and 24 are off-scale (1.4 ppm on both days). The EG mixing ratio can be calculated by the difference between these two measurements: m/z 45 (PTR-MS) – CH_3CHO (GC).

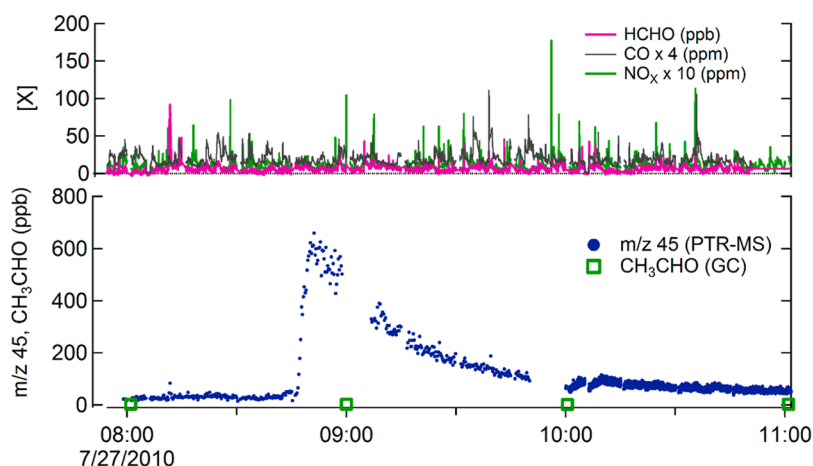


Figure 3. A high-EG event on July 27, 2010. The numerous “spikes” in the HCHO, CO, and NO_x time series are from diesel-fueled vehicles and high-emitting gasoline-fueled vehicles.

using classic ion–molecule theory, similar to that presented by Zhao and Zhang.²⁴ These calculations suggest that the PTR-MS sensitivity response factor for ethylene glycol is $\sim 10\%$ lower than that of acetaldehyde. Values for the dipole moment and polarizability for acetaldehyde and ethylene glycol are from the CRC Handbook of Chemistry and Physics.²⁵

Concentrations determined by PTR-MS are the difference between measurements of ambient air and measurements of VOC-free air. The instrumental background of the PTR-MS was checked by use of dry zero air overblows and also by periodic sampling (every 67 min) of VOC-free air generated with a heated platinum catalyst connected to the PTR-MS by 1 m of $1/8$ -in. o.d. PFA tubing. After the onset of high-EG events, the background signal at m/z 45 increased and slowly returned to normal levels, indicating adsorption and subsequent desorption of EG onto/from the 34 m sampling tube and internal surfaces of the PTR-MS. This behavior was evident by a diminished time response of the m/z 45 signal during dry zero air overblows and when the PTR-MS switched to sampling air from its catalyst. When m/z 45 mixing ratios were high (over 20 parts per billion, ppb), the $1/e$ time response in the m/z 45 signal exceeded 1 min when the PTR-MS switched to sampling catalyst air (102 ± 5 s on July 27, 2010), compared to ~ 2 s for other VOCs measured (see Figure S1 in Supporting Information). Similarly, m/z 45 levels rapidly decreased during zero air overblows but remained elevated (Figure S2 in Supporting Information). Reversible sorption leads to errors in short time-scale measurements (e.g., 1 Hz) but likely cancels out when longer averaging times are considered (i.e., PTR-MS

measurements are likely low when [EG] is increasing and high when [EG] is decreasing). The time response of the sampling system and PTR-MS to CH_3CHO was comparable to that of other VOCs, evident from standard additions of CH_3CHO (Figure S3 in Supporting Information).

Several additional diagnostic tests demonstrate that the PTR-MS measurements of EG were indeed reflective of tunnel air and not long-term contamination of the filter, sampling tube, or internal surfaces of the PTR-MS. If the high m/z 45 measurements from the tunnel (described in the Results section) were solely caused by long-term desorption of EG from the sampling tube when sampling humid air, then sampling outdoor air would have yielded similarly high (20+ ppb) m/z 45 readings. At the conclusion of the study on July 27, 2010, the PTR-MS sampled outdoor ambient air with the same long sampling tube with a used filter (Figure S3 in Supporting Information). In contrast to the 35 ppb measured in the tunnel only 1.5 h earlier, the PTR-MS measured an m/z 45 mixing ratio of only 4 ppb, consistent with normal outdoor CH_3CHO mixing ratios. The low m/z 45 mixing ratios observed by the PTR-MS at night, which at times agreed with the CH_3CHO measurements by the GC within measurement uncertainties (see Results section), further demonstrate that the PTR-MS and sampling inlet were able to “recover” from the high concentrations of EG sampled during the day.

The PTR-MS was periodically offline for calibrations and other instrumental maintenance. During the 7 days of sampling, the PTR-MS was online for 39 out of 84 total hours of daytime measurements (07:00–19:00) and 70 out of 84 h of nighttime

measurements (19:00–07:00). Daytime and nighttime data were averaged to 1 and 14 s, respectively. Because of the uncertainty in the internal PTR-MS response to EG and the adsorption/desorption of EG to both the long sampling tube and the internal surfaces of the PTR-MS, we estimate the 2σ uncertainty of the time-averaged EG measurements as (+100%/–50%). This large uncertainty does not affect the conclusions of this paper. At the Caldecott Tunnel, the contribution of CH_3CHO (as measured by GC) to the total m/z 45 concentration (usually <25%) had only a minor impact on the overall uncertainty of the EG concentration.

RESULTS

Caldecott Tunnel Measurements of Ethylene Glycol.

The EG mixing ratios (PTR-MS m/z 45 minus GC CH_3CHO) in the Caldecott Tunnel during the day were typically between 10 and 40 ppbv but occasionally (approximately once per day) exceeded 100 ppbv. During the entire week of sampling (Figure 2), EG mixing ratios exceeded 100 ppb 12 times. These infrequent high m/z 45 concentrations were not mirrored by the concentrations of any other gas-phase or particulate pollutant, including CH_3CHO (by GC-FID), which never exceeded 13 ppbv. The rise times (0–50% of maximum concentration) of the high m/z 45 events varied from 1 to 4 min. The m/z 45 concentrations decayed immediately after peaking, with $1/e$ decay times that ranged from 2 to 25 min. The one exception to this was the high m/z 45 event on July 22 at 17:30, which persisted for 30 min before decaying. During the 39 h of daytime PTR-MS operation, 100,000 vehicles traveled through bore 1 of the tunnel (based on recorded traffic levels).²⁰ The ratio of vehicles to high m/z 45 events was thus 8300.

An expanded view of a high-EG event is shown in Figure 3. On July 27, 2010, the m/z 45 mixing ratio was between 15 and 40 ppb until 08:46, when it increased over 4 min to 660 ppbv, followed by a slow decrease over the next hour. CH_3CHO mixing ratios measured by GC-FID were below 4 ppb both before and after this high m/z 45 plume. Individual plumes from diesel vehicles whose vertical tailpipes emitted exhaust close to the overhead sampling inlet are identified by the numerous “spikes” in several pollutant time series, especially NO_x .²⁰ The rise time (0–50% of maximum concentration) of these pollutant increases, including m/z 45 from CH_3CHO , from diesel vehicles was much shorter, less than 2 s. Temporally wider plumes of approximately 1 min total duration with higher concentrations of VOCs, including m/z 45 from CH_3CHO , were from occasional high-emitting gasoline-fueled vehicles whose low tailpipes emitted exhaust near road level.

In contrast to daytime measurements, when the PTR-MS m/z 45 readings were often 1–3 orders of magnitude higher than the GC CH_3CHO values, at night the PTR-MS m/z 45 mixing ratios, which presumably still had contributions from both acetaldehyde and EG, were usually within a factor of 2 of the GC acetaldehyde values. Acetaldehyde (by GC-FID) was not measured between 01:00 and 04:00, but concentrations from 22:00 to 01:00 and from 04:00 to 06:00 were usually between 0.5 and 2.5 ppb, compared to m/z 45 concentrations that ranged from 1 to 6 ppbv between 22:00 and 05:00. For example, the average m/z 45 mixing ratio between 01:00 and 04:00 on July 27, 2010, was 4 ± 2 ppb (see Figure S4 in Supporting Information), compared to average acetaldehyde (GC) mixing ratios of 2 ppb from 20:00 to 01:00 and from 04:00 to 07:00. Lower EG emission rates due to decreased

ambient temperatures and markedly lower traffic rates are the presumed explanation for the lower EG mixing ratios at night, which can be smaller than the measurement uncertainty.

Outdoor Measurements of m/z 45. Limited outdoor measurements of m/z 45 at the Caldecott Tunnel site were consistent with ambient acetaldehyde mixing ratios (~ 4 ppb) and did not suggest the presence of EG. This is not surprising, given the infrequency of high-EG events measured inside the tunnel and the limited time devoted to outdoor measurements. EG was detected, however, in a “grab” sample of air collected near a small puddle of suspected engine coolant. On July 25, 2010, during a short time period of outdoor sampling, a pickup truck parked approximately 10 m downwind of the AML and idled for a minute before driving away. The vehicle left behind a small spill of a liquid that did not resemble motor oil. To sample the vapor above the liquid, a small plastic container was positioned 15 cm above the liquid for five seconds and then at 16:43 loosely placed over the AML’s inlet (i.e., the long tube used for tunnel sampling was not used here). The m/z 45 concentrations recorded by the PTR-MS slowly increased over the next 16 min (Figure 4). At 17:00, the container was

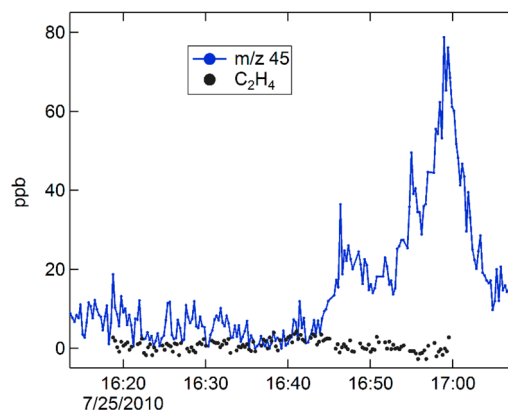


Figure 4. Measurements of m/z 45 (PTR-MS) and C_2H_4 in a sample of air collected above liquid leaked from a vehicle. Sampling of the air sample commenced at 16:43.

removed and the tunnel sampling tube was reconnected. Mixing ratios of C_2H_4 , which is a volatile component of gasoline, did not increase during the sampling, indicating that the liquid was unlikely to be gasoline and likely to be engine coolant.

During unrelated near-roadway measurements in Barcelona, Seco et al.²⁶ observed a single episode of elevated m/z 45 measurements that were not correlated with combustion tracers (NO_x or CO) or photochemical indicators,²⁷ though the chemical identity (acetaldehyde vs EG vs ethylene oxide) could not be determined.

Tunnel Measurements in Houston and Boston. Mixing ratios of m/z 45 measured during the four transects in the Washburn Tunnel ranged from 5 to 10 ppb above the ambient background value (Figure 5). Separate, interference-free CH_3CHO measurements were not available, complicating the quantification of the relative contributions of EG and CH_3CHO to the observed m/z 45 signal. Upon exiting the tunnel, the m/z 45 signal decayed to the ambient level in only a few seconds, identical to the time response of other pollutants measured by the PTR-MS (e.g., toluene), suggesting that at most a small portion of the total m/z 45 signal was from EG. In contrast, when high m/z 45 concentrations were sampled at the

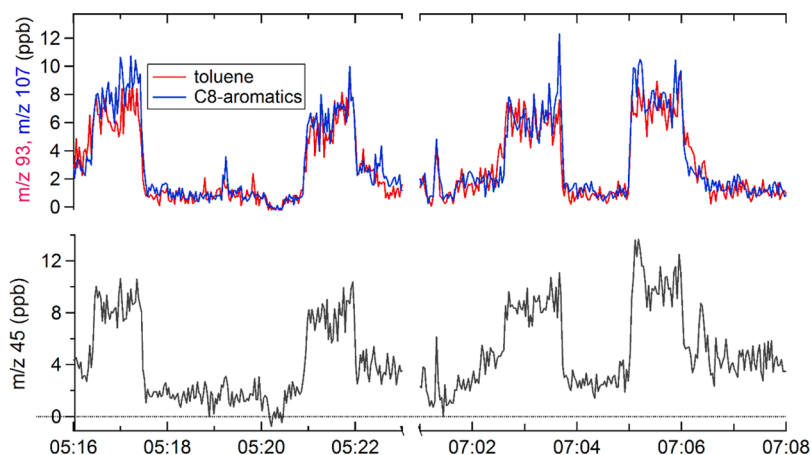


Figure 5. Mobile measurements in Houston on May 22, 2009. Washburn Tunnel measurements are indicated by the four periods of elevated concentrations (05:17, 05:21, 07:03, and 07:06). Time response of the PTR-MS to m/z 45 was equivalent to its time response to m/z 79 (toluene) and m/z 107 (C8-aromatics), indicating that the m/z 45 signal was mostly from acetaldehyde with only a small contribution from ethylene glycol.

Caldecott Tunnel, over 2 min was required for m/z 45 levels to decay to baseline values when the PTR-MS switched to sampling catalyst-prepared zero air.

Similar measurements in Boston's Central Artery Tunnel at much colder temperatures (outdoor temperature -3 °C) showed increases in m/z 45 of only 2–6 ppb. As in the Washburn Tunnel, the time response of m/z 45 was similar to that of other VOCs measured by the PTR-MS, suggesting that acetaldehyde was the main contributor to m/z 45.

DISCUSSION

Mechanism of Ethylene Glycol Emissions. Direct emission of gaseous EG from vehicles with malfunctioning cooling systems is the assumed source of the infrequent high m/z 45 events in the Caldecott Tunnel. As discussed in the Results section, there was only one high m/z 45 event per ~ 8300 vehicles. There are several possible mechanisms by which EG could be directly emitted in the gas phase. Leaks in the water pump's shaft seals, radiator cap, rubber transport hoses, or the radiator itself would allow the coolant to boil at its nonpressurized boiling point (107 °C at 1 bar) rather than its intended elevated boiling point of 130 °C at a pressure of 2 bar. Leaks of engine coolant past a faulty engine head gasket into the engine cylinders—especially during the exhaust stroke—would lead to EG emissions from the engine that likely would not be fully removed by the catalytic converter. Depending on the mechanism of EG emission from a vehicle, it is quite possible that an EG-emitting vehicle would not have elevated emissions of “traditional” tailpipe pollutants like VOCs, in agreement with the observed lack of correlation between the high m/z 45 events and other pollutants measured.

Unlikely alternative sources of the high EG signals include the following: (1) EG from the mobile lab itself, which is unlikely since the engine was off during the measurements, the inlet was leak-tested, and high m/z 45 was not measured while sampling outdoor air near the AML; and (2) EG from winter-grade windshield washer fluid, which would still be a vehicular source of EG. Similar infrequent spikes of m/z 59 concentrations, which could result from emissions of propylene glycol used by some newer cooling systems, were not observed in any of the three tunnels.

In addition to the infrequent high-EG emission events, the presence of additional longer-term emission mechanisms is

required to explain two observations: (1) the sustained elevated EG concentrations of ~ 20 – 40 ppb observed on hour time scales during most days in the Caldecott Tunnel, in between the high m/z 45 events, and (2) the ~ 20 min time response of the [EG] decays following high concentration events, which is much longer than the PTR-MS/sampling tube response time to EG of 2 min and the tunnel ventilation time of a few minutes (see Supporting Information). The most likely longer-term EG sources are (1) emissions from vehicles' cooling systems at a rate much lower than that from vehicles with malfunctioning cooling systems and (2) evaporation/desorption of liquid EG from tunnel road, wall, and ceiling surfaces that was previously leaked from vehicles' cooling systems, similar to the EG observed above the suspected engine coolant leak described in the Results section. Due to its lower vapor pressure compared to water, EG accounts for only 0.6% of the vapor above a 50% by volume aqueous solution of EG at 100 °C. Only a small mass of ethylene glycol is required, however, to produce high gas-phase concentrations. For example, 32 000 m³ (the total volume of the tunnel) of air with an EG mixing ratio of 100 ppb contains only 8 g of EG.

Ethylene Glycol Emission Rate Estimates. We estimate the emission rate of EG in the Caldecott Tunnel by two separate methods.

Steady-State Method. We estimate the emission rate of EG required to sustain a steady state concentration using eq 3:

$$E_{\text{EG}} = [\text{EG}]_{\text{ss}} k_{\text{vent}} V \quad (3)$$

where E_{EG} is the EG emission rate (in grams per second), $[\text{EG}]_{\text{ss}}$ is the steady-state concentration of ethylene glycol (in grams per cubic meter), k_{vent} is the ventilation rate of the tunnel (0.01 s⁻¹; see Supporting Information), and V is the volume of the tunnel (32 000 m³). An emission rate of 0.024 g·s⁻¹ is required to sustain a steady-state EG mixing ratio of 30 ppb, as observed between 06:00 and 18:00 on July 26. Given that on average there are 31 vehicles in the tunnel at a time (see Supporting Information), this corresponds to an average emission rate of 0.77 mg·s⁻¹·vehicle⁻¹ while in the tunnel. Scaling up this emission rate to annual emissions per vehicle leads to unrealistically high values: it suggests that each vehicle emits on average 1.3 kg of EG per year, compared to a total mass of EG in each vehicle of only 2–7 kg. For this calculation we assumed 470 h of driving per vehicle per year.

Carbon Balance Method. We estimate fuel-based emission factors²⁸ for EG using the carbon balance method (eq 4). We note that EG is not necessarily a tailpipe emission; application of the carbon balance method here assumes that the ratio of EG emissions to fuel consumption can be inferred from the ratio of EG to (CO₂ + CO) concentrations.

$$EF_{EG} = 0.84\Delta[EG]/(\Delta[CO_2] + \Delta[CO]) \quad (4)$$

where EF_{EG} is in units of grams of EG per kilogram of fuel, $\Delta[EG]$ is the background-subtracted (inside tunnel minus outside) mass concentration of EG in the tunnel (in milligrams per cubic meter), $\Delta[CO_2]$ and $\Delta[CO]$ are the background-subtracted mass concentrations of CO₂ and CO in the tunnel (in grams of carbon per cubic meter), and 0.84 is the carbon mass fraction of gasoline (vs 0.87 for diesel). Using the average daytime (09:00 to 18:00 PDT) concentrations during the 7 days of sampling in the Caldecott Tunnel, we calculate an emission factor of 580 mg EG/kg of fuel while in the tunnel.

Similar to the results from the steady-state estimate, scaling up these emission factors to national emissions by use of fuel-sales information leads to unrealistically high numbers: Multiplying by 3.5×10^{11} kg of fuel sold in the United States in 2012²⁹ leads to a calculated annual U.S. emission rate of 200 Gg/yr. For comparison, the total mass of EG in the cooling systems of all vehicles in the United States is approximately 1 Tg (250×10^6 vehicles \times 3 L/vehicle \times 1.1 kg/L). This calculated emission rate therefore requires that approximately 20% of the total mass of EG in vehicles' cooling systems escapes to the atmosphere every year, comparable to the result from the steady-state method and also unreasonably high. Excluding the large m/z 45 plumes over 50 ppb reduces this emission factor by only 65%.

These unrealistically high estimated EG emission rates can be rationalized by an examination of the following potential explanations: (1) There were unknown contamination issues with the sampling system, for example, the presence of liquid EG in the sampling path. (2) The measured EG concentrations in bore 1 of the Caldecott Tunnel were not representative of the entire volume of the tunnel. (3) The EG emission rates in bore 1 of the Caldecott Tunnel are actually as high as calculated by either the steady-state or carbon balance method but not representative of "normal" driving emissions and therefore cannot be used to estimate emissions at a national level.

The several measurements of outdoor air do not support explanation 1. Outdoor air was sampled by the PTR-MS *without* the long sampling tube every day, usually for at least 30 min at a time. The low m/z 45 mixing ratios (<10 ppb) observed are consistent with CH₃CHO mixing ratios and indicate that the PTR-MS itself and the tubing within the AML did not suffer long-term contamination. As described in the Results section, outdoor air was only sampled once *with* the long PFA sampling tube, 95 min after measuring 35 ppb inside the tunnel, and yielded an outdoor m/z 45 mixing ratio of only 4 ppb. While we cannot conclusively rule out the possibility that the sampling tube was contaminated at other times during the week of measurements, it appears unlikely given the evidence presented above.

Explanation 2—that the measured concentrations were not spatially homogeneous throughout the tunnel—appears reasonable, given the small portion of vehicles that presumably are high emitters and that it is unlikely that evaporating liquid EG on the tunnel surfaces would be evenly distributed in the tunnel. Explanation 3 also appears plausible given the uphill

grade in bore 1. Sustained uphill driving, in the 4% grade of the 1 km tunnel itself and the preceding 4 km at grades of 4–6.5%, can lead to higher engine loads, specific powers, engine temperatures, and an increased likelihood of cooling system failure, which would lead to increased EG emissions. Future emissions measurements at a range of driving conditions would be required to verify this potential explanation.

Similar calculations using the Houston and Boston tunnel data are complicated by the lack of separate acetaldehyde measurements that would quantify the contribution of EG to the total observed m/z 45 measurements from the PTR-MS. If the Houston and Boston m/z 45 data were purely from acetaldehyde, this would correspond to CH₃CHO emission factors of 60–100 mg of CH₃CHO/kg of fuel for the Washburn tunnel and 20–50 mg of CH₃CHO/kg of fuel for the Central Artery Tunnel. For comparison, the Caldecott acetaldehyde emission factor for light-duty vehicles, calculated from the GC acetaldehyde data by the carbon balance method, is 24 mg/kg.²¹ Given the differences in vehicle fleets, driving conditions, ambient conditions, and previously observed intercity differences,³⁰ it is not unreasonable for the Houston and Boston tunnel fleets to have higher CH₃CHO emission factors than the Caldecott fleet, but these differences do leave room for a contribution to the observed m/z 45 from EG.

In order for vehicular EG emissions to be comparable to reported industrial EG emissions of 0.8 Gg/yr,⁹ an EG emission factor of approximately 2.4 mg/kg fuel is required, which would be consistent with the observations from the Houston tunnel data if 3% of the total m/z 45 signal were actually from EG with the rest from CH₃CHO. This emission factor and 3% value are neither supported nor refuted by the Houston PTR-MS data and are not suggested as recommended vehicular EG emission rates, but they do suggest the potential for vehicular EG emissions to be competitive with industrial EG emissions.

EG emissions are likely most important only on small spatial scales and under particular circumstances. Emissions of EG are likely highest from older vehicles, which are more likely to have malfunctioning engine cooling systems, and under conditions that increase engine load and engine temperature (e.g., uphill driving).

Atmospheric Importance of Ethylene Glycol Emissions. As discussed earlier, oxidation of EG in the atmospheric aqueous phase (e.g., clouds) can lead to the formation of glyoxylic acid, oligomers, oxalic acid, and oxalate (C₂O₄²⁻), all of which can form SOA following evaporation of liquid water. Globally, oxalic acid accounts for a modeled 40–90% of SOA formed from in-cloud oxidation, with glyoxylic acid and oligomers each accounting for 10–20% of in-cloud SOA.¹⁸ Since total in-cloud SOA concentrations are comparable to SOA formed from gas–particle partitioning,^{18,31} it follows that oxalic acid accounts for a significant portion of total SOA, possibly exceeding 20% based on the findings of Liu et al.¹⁸ Using the multiphase model CAPRAM, Tilgner and Herrmann³² found that oxidation of industrial ethylene glycol emissions accounted for 10% of oxalic acid formation in their urban scenario. The remaining oxalic acid formation was from oxidation of aromatic VOCs (65%), ethene (13%), and dienes (11%). Their model's emission inputs (from Middleton et al.³³) do not include vehicular EG emissions. If vehicular EG emissions are actually comparable to industrial emissions, then it follows that EG may be a more important precursor of oxalate and SOA in urban areas than indicated by Tilgner and Herrmann.³²

Globally, oxidation of biogenically emitted isoprene produces 42 Tg C/year of glycolaldehyde.¹⁶ Given the much lower range of possible EG emission rates, it follows that vehicular emissions of EG are a minor global source of glycolaldehyde and aqueous SOA. Further constraining the importance of EG as precursor of SOA on smaller spatial scales (e.g., in urban areas) requires improved emissions estimates from a wider range of meteorological and driving conditions and, ideally, top-down quantification methods.

■ ASSOCIATED CONTENT

● Supporting Information

Additional text that describes sampling ethylene glycol and estimating ventilation rate in the Caldecott Tunnel and relative concentrations of SOA precursors in tunnel air, and six figures showing time response of PTR-MS, zero air overblow data, measurements of tunnel air and outdoor air, mixing ratios at night and during street-sweeping, and relative mass concentrations. This material is available free of charge via the Internet at <http://pubs.acs.org/>

■ AUTHOR INFORMATION

Corresponding Author

*E-mail ezrawood@chem.umass.edu; phone 413-545-4003.

Present Addresses

▲(J.P.F.) Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

▽(T.R.D.) Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh, PA 15213.

■(D.R.G.) Department of Chemical and Environmental Engineering, School of Forestry and Environmental Studies, Yale University, New Haven, CT 06511.

Notes

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