On the primary emission of formic acid from light duty gasoline vehicles and ocean-going vessels

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HIGHLIGHTS

- HCOOH emission factors were measured for mobile vehicles and ocean-going vessels.
- HCOOH emission factors were higher during the cold start phase of a typical drive cycle.
- On a global scale HCOOH primary emissions are small compared with secondary sources.

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ABSTRACT

We present determinations of fuel-based emission factors for formic acid (EF_{HCOOH}) from light duty gasoline vehicles (LDGVs) and in-use ocean-going vessels. Emission ratios, from which the emission factors were derived, were determined from LDGVs through measurement of HCOOH and carbon dioxide (CO_2) in the exhaust of a fleet of eight LDGVs driven under the California Unified Cycle at the California Air Resources Board's Haagen-Smit Laboratory. Emission ratios from in-use ocean-going vessels were determined through direct measurement of HCOOH and CO_2 in ship plumes intercepted by the R/V Atlantis during the 2010 California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign within 24 nautical miles of the California coast. The eight car fleet average EF_{HCOOH} was 0.94 ± 0.32 (1σ) and 0.57 ± 0.18 mg (kg fuel)$^{-1}$ for the cold start and hot running phases of the drive cycle, respectively. This difference suggests that catalytic converter performance and the air/fuel equivalence ratio are important metrics contributing to EF_{HCOOH}. EF_{HCOOH} was determined to be 1.94 ± 1.06 mg (kg fuel)$^{-1}$ for a single diesel vehicle driven under highway driving conditions, higher on average than any individual LDGV tested. In comparison, HCOOH primary emissions from in-use ocean-going vessels were substantially larger, averaging 20.89 ± 8.50 mg (kg fuel)$^{-1}$. On a global scale, HCOOH primary emissions from fossil fuel combustion are likely to be insignificant relative to secondary production mechanisms, however primary emissions may contribute more significantly on a finer, regional scale in urban locations.

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1. Introduction

Field measurements have demonstrated that organic acids are ubiquitous in the troposphere and are present in both the gas and aerosol phase (Keene and Galloway, 1988; Chebbi and Carlier, 1996; Khare et al., 1999; Veres et al., 2011). Organic acids can contribute to particulate and rain water acidity (Galloway et al., 1982) and have been shown to be a major component of secondary organic aerosol

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(SOA) mass loadings (Lee et al., 2003), thus impacting particle hygroscopicity. As a result, there is renewed interest in determining the relative strengths of primary and secondary sources of organic acids and the importance of anthropogenic and biogenic processes. Formic acid (HCOOH) has been shown to be ubiquitous in both remote and urban environments (e.g., Chebbi and Carlier, 1996). Despite being one of the most abundant trace gases in the atmosphere, quantitative source attribution of HCOOH has remained elusive.

Laboratory measurements, confirmed by field observations indicate that HCOOH is directly emitted to the atmosphere from terrestrial vegetation (Kesselmeier, 2001), as a by-product of both biomass burning (Veres et al., 2010) and biofuel and fossil fuel combustion (Kawamura et al., 1985; Kawamura and Kaplan, 1987), and from agricultural (Shaw et al., 2007) and soil emissions (Sanhueza and Andreae, 1991). In addition, HCOOH has been shown to be produced in the photooxidation of a wide range of terrestrial, marine, and anthropogenic volatile organic compounds (VOC) (Orlando et al., 2000; Larsen et al., 2001; Butkovskaya et al., 2006a,b; Paulot et al., 2009) as well as the direct ozonolysis of biogenic (Jacob and Wofsy, 1988) and anthropogenic alkenes (Hatakeyama et al., 1986; Herndon et al., 2007). The production of HCOOH following the heterogeneous reaction of hydroxyl radicals with organic aerosol has also been suggested to be an important, yet unconstrained source of HCOOH (Vlasenko et al., 2008; Paulot et al., 2011). The relative strength of any individual source is regionally specific, underlining the importance of quantitative source functions, reaction rates, and product yields.

Atmospheric observations have suggested that in urban locations, direct anthropogenic emission of HCOOH can comprise as much as 25% of the total production rate (Grosjean, 1992). Radiocarbon analysis of gas-phase formic acid suggests that biogenic processes account for as much as 55% of HCOOH in urban regions and as much as 100% in remote areas (Glasius et al., 2001), although no distinction between primary and secondary processes could be made. On a global scale, Paulot et al. (2011) constructed a bottom-up inventory for HCOOH sources and sinks that suggests that over 85% of the globally, annually averaged HCOOH source can be attributed to photochemical production, and direct anthropogenic emissions of HCOOH are insignificant on the global scale (<1% of total sources). However, it is expected that direct emissions of HCOOH may play a more important role regionally, especially around mega-cities.

Here, we focus exclusively on the primary emission of HCOOH from light duty gasoline vehicles and in-use ocean-going vessels to provide directly measured, fuel-based emission factors for HCOOH (EF_{HCOOH}) for use in regional chemical transport models. The early measurements of Kawamura et al. (1985, 1987) describe primary emissions of organic acids from fossil fuel combustion but more recent measurements are not available to provide quantitative values for input into chemical transport models. Mechanistically, Zervas et al. (2001) demonstrated that HCOOH is produced in spark ignition engines from fuel blends comprised of a wide range of aromatic and oxygenated compounds. The exhaust concentration was shown to increase with the air/fuel equivalence ratio suggesting that excess oxygen enhances HCOOH production. Zervas et al. (2001) suggested that HCOOH could be formed following the oxidation of formaldehyde and/or other volatile organic compounds in engine exhaust or in the 3-way catalytic converter. However, at present, EF_{HCOOH} from light duty gasoline vehicles and in-use ocean-going vessels are not available to properly constrain HCOOH emission inventories. In their absence, current constraints on HCOOH emissions from mobile vehicles are mostly derived from measurements of the emission ratios of HCOOH relative to carbon monoxide (CO) in the Hampton Roads Bridge Tunnel studies of

Talbot et al. (1988), where HCOOH emission was determined to be 2.1×10^{-4} HCOOH per CO. It is important to note that these measurements were made prior to 1988. Substantial changes to fuel composition and emissions control technology in the past 15 years have almost certainly changed the HCOOH emissions rate. There currently are no experimental constraints on the emission rates of organic acids from ocean-going vessels.

In what follows we report the first measurements of real-time, fuel-based HCOOH emission factors from light duty gasoline vehicles and ocean-going vessels. In this study, a fleet of LDGVs were driven under the California Unified Cycle (UC) at the California Air Resources Board's Haagen-Smit Laboratory, where HCOOH, carbon monoxide (CO) and carbon dioxide (CO_2) were detected with high time resolution (≤ 1 s) in the diluted exhaust. The study was conducted on eight LDGVs (Table 1) requisitioned from the California on-road vehicle fleet in 2011. The average age of the test fleet was approximately ten years. HCOOH mixing ratios were quantified *via* chemical ionization time-of-flight mass spectrometry (CI-ToFMS) at 2 Hz, allowing for real-time measurement of HCOOH mixing ratios throughout the drive cycle. The simultaneous measurements of CO and CO_2 allow for fuel-based emission factors to be calculated for the overall drive cycle as well as for specific phases of the UC cycle.

Fuel-based emission factors for ocean-going vessels were determined from measurements of HCOOH and CO_2 within plumes intercepted during the 2010 CalNex campaign by the R/V *Atlantis* as it operated within the coastal waters of Southern and Northern California. The same CI-ToFMS instrument was used to make direct measurements of HCOOH both during day and night. Emissions from a total of 12 ship plumes are reported here, all of which were sampled within ten minutes of emission.

2. Experimental

2.1. CI-ToFMS measurements of formic acid

Formic acid was detected in real-time using a chemical ionization time-of-flight mass spectrometer (CI-ToFMS). The instrument used here has been previously described for the detection of gas-phase HCOOH (Bertram et al., 2011) and details of the acetate ion chemistry can be found in Veres et al. (2007). The sample flow entering the ion-molecule reaction region (IMR) was restricted to 1.7 slpm using a critical orifice. Utilizing acetate reagent ion chemistry, HCOOH was detected as $HCOO^-$, following negative ion proton transfer. Acetate reagent ions were generated by mixing 10 sccm of ultra-high purity (UHP) nitrogen that was bubbled through a reservoir of acetic anhydride with 1.5 slpm of UHP N_2 and passing the mixture through a ^{210}Po ionization source (NRD P-2021). Individual mass spectra were sampled at 66 kHz for the duration of the study and the raw spectra were time averaged and saved at a rate of 2 Hz. The CI-ToFMS was calibrated twice daily at the start and finish of each testing run using a calibrated HCOOH permeation source (Kin-Tek, SRT-2, 108 ng min^{-1} at 70 °C).

Table 1
Manufacturer, model, and year of the eight light duty gasoline vehicles tested.

Manufacturer	Model	Year
Chevrolet	Cavalier	2001
Chevrolet	S-10	2002
Chrysler	Grand Cherokee	2002
Nissan	Pathfinder	2003
Toyota	Solara	2003
Toyota	Tacoma	2003
Ford	Taurus	1997
Ford	Windstar	1998