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Baseline measurements of ethene in 2002: Implications for increased ethanol use and biomass burning on air quality and ecosystems

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ABSTRACT

While it is well known that combustion of ethanol as a biofuel will lead to enhanced emissions of methane, ethene (ethylene), acetaldehyde, formaldehyde, and oxides of nitrogen (primarily NO) when compared to gasoline alone, especially during cold starts or if catalytic converters are not operating properly, the impacts of increases in atmospheric ethene levels from combustion of fuels with higher ethanol content has not received much attention. Ethene is a well known and potent plant growth hormone and exposure to agricultural crops and natural vegetation results in yield reductions especially when combined with higher levels of PAN and ozone also expected from the increased use of ethanol/gasoline blends. We report here some baseline measurements of ethene obtained in 2002 in the southwestern and south central United States. These data indicate that current ethene background levels are less than 1 ppb. Anticipated increases in fuel ethanol content of E30 or greater is expected to lead to higher atmospheric levels of ethene on regional scales due to its atmospheric lifetime of 1.5–3 days. These background measurements are discussed in light of the potential enhancement of ethene levels expected from the anticipated increases in ethanol use as a renewable biofuel.

1. Introduction

With the realization that fossil fuels are not renewable and therefore are a limited resource, it is clear that renewable energy sources must continue to grow in importance if we are to develop a sustainable energy policy. Combustion of either fossil fuels or biofuels has impacts on the environment, particularly on air quality, which will need to be addressed in order to insure an environmentally friendly, sustainable energy economy (Gaffney and Marley, 2009). Ethanol, produced from corn and sugar cane, has developed into a renewable biofuel source that can be used as a gasoline replacement in internal combustion engines. It is usually offered as an ethanol-gasoline blend denoted as an ethanol additive at some percentage of ethanol. Thus, E10 is a mixture of 10% ethanol and 90% gasoline and E85 would be an 85% ethanol and 15% gasoline mixture. Currently E10–E15 gasoline blends are commonplace across the United States with some states moving towards the widespread use of E85.

The combustion of ethanol in internal combustion engines leads to the emission of methane, ethene (ethylene), acetaldehyde, formaldehyde, and higher oxides of nitrogen (primarily NO) compared to gasoline alone (Gaffney and Marley, 2009; Poulopoulos et al., 2001). These emissions can lead to the enhanced atmospheric production of ozone and peroxyacetyl nitrate (PAN) (Tanner et al., 1988; Jacobsen, 2007; Ginnebaugh et al., 2010; Pereira et al., 2004). For example, it is well established that the reaction of OH radicals with acetaldehyde will lead to the formation of PAN via the following reactions:

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O$$

$$CH_3CO + O_2 \rightarrow CH_3COO_2$$

$$CH_3COO_2 + NO_2 \leftrightarrow CH_3COO_2NO_2(PAN)$$

PAN initially discovered via its observed ability to damage plants in Southern California is a potent phytotoxin (Gaffney and Marley, 2005). It is also a strong lachrymator as is its precursor acetaldehyde. Currently, controls on reactive hydrocarbon emissions have led to lower PAN levels in U.S. urban centers. However, increases in

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ethanol combustion are likely to lead to increased levels of acetaldehyde and nitrogen oxides (NO and NO_2) and, therefore, higher PAN levels (Jacobsen, 2007; Ginnebaugh et al., 2010).

The reactions of peroxy radicals with NO also lead to the formation of enhanced levels of ozone. Modeling studies of the anticipated use of very high ethanol fuel levels such as E85 have been shown to lead to higher ozone levels due to the higher NO emissions and photochemically active aldehyde emissions (Pereira et al., 2004; Ginnebaugh et al., 2010; Williams, 2004). Increases in both PAN and ozone levels are of concern due to their potential ability to impact plants, both natural and agricultural, leading to reduction of yields. PAN can also act to transport reactive nitrogen dioxide over larger distances thus leading to increases in regional ozone as well as the formation of peroxyacetic acid (CH_3COO_2H) in remote regions, where NO levels are low, through reaction of the peroxyacetyl radical with HO_2 radicals (Gaffney et al., 1989; Gaffney and Marley, 2005).

While it is well known that ethanol combustion will lead to enhanced ethene emissions, especially during cold starts or if catalytic converters are not operating properly, the impacts of increases in atmospheric ethene levels from combustion of fuels with higher ethanol content has not received much attention. Modeling efforts have indicated that ethene levels may be significantly higher if E85 use is widespread (Jacobsen, 2007; Ginnebaugh et al., 2010). Ethene is a well known and potent plant growth hormone and was originally noted as an air pollutant of concern due to its damaging effects on crops and horticulture (Burg and Burg, 1965; Ecker, 1995; Harvey, 1928; Stahl, 1969). Indeed, yield reductions of >50% have been found for ethene exposures to rice and wheat at levels of tens of ppb (Klassen and Bugbee, 2002).

Currently there is not a considerable amount of data available on what the regional background (baseline) ethene levels are in the U.S. This is likely due to the fact that current analytical methods used to measure volatile organic hydrocarbons have focused on the $>C_2$ hydrocarbons, or have looked at methane alone. As well, current measurement methods used for reactive hydrocarbons have sought to obtain rapid response analysis by using proton-transfer mass spectrometry (PTRMS). These methods, while very useful for the volatile organic compounds $>C_2$, do not determine ethene as it has the same mass number as molecular nitrogen and carbon monoxide. Background level ethene measurements require the use of canister sampling coupled with GC/FID analysis or absorption spectroscopic methods such as IR photoacoustic or high resolution long path FTIR spectroscopy, and these methodologies have not been routinely used. Past measurements of ethene range from the low ppt to high ppb, with levels in Los Angeles and Texas reaching the low ppm in the 1950–60s (Stahl, 1969). More recent measurements of ethene in the troposphere have been made at surface sites and from aircraft and have ranged from a few ppt to tens of ppb (e.g. Blake et al., 2003; Goldstein et al., 1996). Measurements of tropospheric ethene have been attempted on a large scale by using infrared solar occultation with satellite measurements of the Atmospheric Chemistry Experiment FT spectrometer (ACE-FTS, Herbin et al., 2009). The satellite results yield ethene data from 6 km and above, which indicate northern high latitude wintertime maximum ethene values above 50 ppt with some values at 200 ppt levels during 2005–2006 (Herbin et al., 2009). As ethene is ground sourced from both vegetative emissions and combustion, the ACE-FTS data aloft indicate that the boundary layer ethene concentrations should be significantly higher, due to its decrease by dilution and reaction before reaching 6 km and higher in the free troposphere.

We report here some baseline measurements of ethene obtained in 2002 in the southwestern and south central United States. Noting that in 2002 ethanol use was only 1% of the mobile fuel used nationwide and most of that use was in areas where ethanol addition to the gasoline was mandated as an air quality control strategy (U.S. Energy Information Energy, 2012), the canister based data presented here should serve as a reasonable regional baseline for the mid-southern U.S. for future evaluations of atmospheric ethene trends and for modeling of the impacts of increased use of ethanol as a gasoline fuel replacement. This will be of particular importance as the nation continues to move towards using mobile hydrocarbon fuels with higher ethanol content. These ethene measurements are discussed in light of the potential enhancement of ethene levels expected from the anticipated increases in ethanol use as a renewable biofuel.

2. Experimental methods

Air samples were collected at 261 sites located in New Mexico, Texas, Louisiana, Arkansas, Oklahoma, Kansas, and Mississippi (Fig. 1) from April 28 to May 3, 2002. Sample sites were chosen to be not obviously impacted by local sources of hydrocarbons. Two liter air samples were collected by hand in electropolished stainless-steel evacuated canisters at ground level and shipped to the University of California, Irvine for analysis of ethene and other non-methane hydrocarbons by using GC/FID. Details on this methodology have been described in detail previously (Barletta et al., 2005; Blake et al., 2003). All but one of the samples were taken at a significant distance from any nearby major highways to minimize local source impacts. One sample collected fairly close to a highway was found to have high ethene (2.4 ppb) as well as elevated ethyne (3.9 ppb), benzene (0.4 ppb), and toluene (1.6 ppb) indicating that a significant impact from the highway had occurred. That data point has been removed from the data analysis as it does not represent a regional value. Complete details on the data set are given in Appendix I, including location of sample (longitude and latitude), date and time sampled (CST), and concentrations for ethene, ethyne, benzene, and toluene in ppt.

3. Results

The regional distribution of atmospheric ethene levels observed during this period is shown in Fig. 2 and a frequency distribution of the results is shown in Fig. 3. The time of sampling versus the ethene levels are given in Fig. 4. These samples were collected across the region under a variety of meteorological conditions from

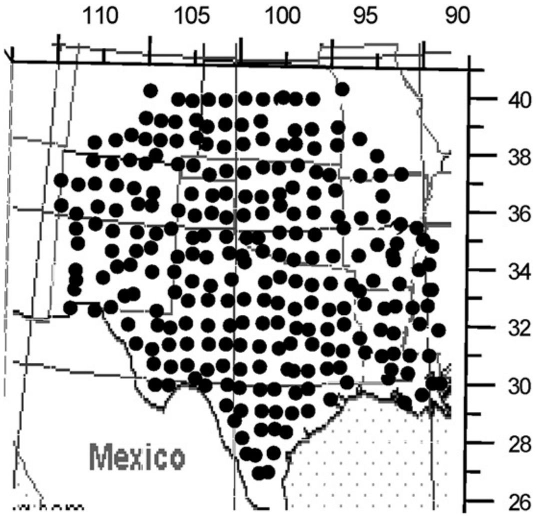

Fig. 1. Location of the 260 sample sites in the southwestern and south central U.S.