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Emissions of nitrogen-containing organic compounds from the burning of herbaceous and arboraceous biomass: Fuel composition dependence and the variability of commonly used nitrile tracers

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Abstract Volatile organic compounds (VOCs) emitted from residential wood and crop residue burning were measured in Colorado, U.S. When compared to the emissions from crop burning, residential wood burning exhibited markedly lower concentrations of acetonitrile, a commonly used biomass burning tracer. For both herbaceous and arboraceous fuels, the emissions of nitrogen-containing VOCs (NVOCs) strongly depend on the fuel nitrogen content; therefore, low NVOC emissions from residential wood burning result from the combustion of low-nitrogen fuel. Consequently, the emissions of compounds hazardous to human health, such as HNCO and HCN, and the formation of secondary pollutants, such as ozone generated by NO_x, are likely to depend on fuel nitrogen. These results also demonstrate that acetonitrile may not be a suitable tracer for domestic burning in urban areas. Wood burning emissions may be best identified through analysis of the emissions profile rather than reliance on a single tracer species.

1. Introduction

Biomass burning is a major source of particulate matter and volatile organic compounds (VOCs) in Earth's atmosphere [*Crutzen and Andreae*, 1990; *Lobert et al.*, 1990; *Jain et al.*, 2006]. Nitrogen-containing VOCs (NVOCs) are an important class of molecules emitted by biomass burning. Species such as isocyanic acid (HNCO) and hydrogen cyanide (HCN) are hazardous to human health and can compose a significant fraction (up to 60%) of NVOC mass [*Lobert et al.*, 1990; *Burling et al.*, 2010; *Roberts et al.*, 2011; *Ren and Zhao*, 2015]. NVOCs such as acetonitrile (CH_3CN) and HCN are routinely used as tracers in field research and are believed to be primarily emitted by biomass burning [e.g., *Holzinger et al.*, 1999; *Li et al.*, 2000; *de Gouw et al.*, 2003; *Holzinger et al.*, 2005; *Burling et al.*, 2010].

NVOCs originate from the pyrolysis and combustion of nitrogen-containing precursors bound within the fuel [*Leppälahti and Koljonen*, 1995; *Burling et al.*, 2010; *Ren and Zhao*, 2015]. The majority of the fuel nitrogen is contained within proteins and free amino acids; however, some amount may be tied up in heterocyclic structures, such as pyrroline and pyridine, or in chlorophyll [*Leppälahti and Koljonen*, 1995; *Hansson et al.*, 2003, 2004; *Ren and Zhao*, 2015]. During pyrolysis, the nitrogen-containing components of fuel can volatilize and decompose to form a suite of NVOCs. In biomass combustion reactors, the primary products are NO, NH_3, HCN, and HNCO [*Hansson et al.*, 2003, 2004; *Ren and Zhao*, 2015]. The distribution of these species relies on a number of factors, including fuel composition, feed particle size, and combustion conditions including O_2 fraction, temperature, and pressure [*Leppälahti and Koljonen*, 1995; *Hansson et al.*, 2003, 2004; *Ren et al.*, 2010; *Ren and Zhao*, 2015].

Extensive literature has detailed the formation of NVOCs such as HCN and HNCO in combustion reactors; however, these systems operate at conditions that do not necessarily reflect those of wildfires or other ambient biomass burning sources. Laboratory studies focused on biomass burning under atmospherically relevant conditions that have provided rich, fuel-specific emission inventories for a suite of VOCs, including NVOCs [*Goode et al.*, 1999; *Yokelson et al.*, 1996; *Burling et al.*, 2010; *Veres et al.*, 2010; *Brilli et al.*, 2014; *Stockwell et al.*, 2015; *Hatch et al.*, 2015; *Gilman et al.*, 2015]. Several studies have investigated the variability of important nitrogen-containing compounds such as NO_x and NH_3 [e.g., *Goode et al.*, 1999; *Yokelson et al.*, 1996, 2013; *McMeeking et al.*, 2009; *Burling et al.*, 2010]; however, to our knowledge, none have systematically investigated NVOC composition and its relation to fuel nitrogen content.

Here we present measurements of biomass burning NVOCs from ground and mobile platforms. We compare the emission profile of residential burning with that of a crop residue fire to investigate differences in important NVOC tracers, such as acetonitrile. We interpret our results through extensive comparison with available literature data in order to provide perspective as to how NVOC emissions may vary in ambient biomass burning smoke and to investigate the applicability of NVOCs as general biomass burning tracers. Here we focus on the emissions from arboraceous (i.e., tree components, such as wood, leaves, and bark) and herbaceous (e.g., grasses and agricultural refuse) fuels.

2. Field Measurements

Mobile and ground measurements of VOCs emitted from crop residue and residential wood burning were performed using a newly developed high mass-resolution H_3O^+ chemical ionization time-of-flight mass spectrometer (H_3O^+ ToF-CIMS) [*Yuan et al.*, 2016]. The H_3O^+ ToF-CIMS employs a high-resolution mass analyzer to enable the determination of a VOC's exact mass, which in most cases allows assignment of a chemical formula. Basic details are summarized in the supporting information.

Mobile measurements were conducted on board NOAA's Chemical Science Division (CSD) Mobile Laboratory (MoLab). The MoLab is a cargo van outfitted with meteorological instrumentation that provides temperature, relative humidity, wind speed, wind direction, altitude, and GPS coordinates. Additional instruments are mounted to the floor and sample ambient air through inlets that exit the MoLab's roof. Here we focus on data collected by the H_3O^+ ToF-CIMS and utilize measurements of CO from an off-axis integrated cavity output spectrometer (OA-ICOS, Los Gatos Research) to estimate VOC enhancement ratios (ER = ΔVOC/ΔCO, mol/mol).

Crop residue burning emissions were measured downwind of a corn field in Greeley, CO, on 24 February 2016. Residential wood burning emissions were measured in Aspen, CO, from 29 February to 4 March 2016. Aspen is a town located in a valley on the forested western slope of the Rocky Mountains (population ~7000); many homes utilize fire places and wood stoves for heating and leisure. In Aspen, residential wood burning plumes were identified based on enhancements of common biomass burning markers, such as carbon monoxide, methyl furan, and furfural (see discussion in section 4). We associate these plumes with residential burning due to their discrete occurrence downwind of homes. Acetonitrile was not significantly enhanced in residential burning plumes; consequently, this species could not be used for plume identification.

Ground measurements were conducted on the roof of NOAA's Earth System Research Laboratory in Boulder, CO, from 3 December 2015 to 3 January 2016. Boulder MoLab measurements were conducted from 17 to 23 February 2016. During ground measurements, the H_3O^+ ToF-CIMS sampled ambient air through an unheated, 10 m teflon sampling line mounted on the northside of the building. An external pump pulled air through the sampling line at a rate of 6 L min^{-1}. Burning plumes were identified by enhancements of methyl furan and furfural. No regional wildfires or prescribed burns were reported during the sampling period; thus, we associate these plumes with residential burning emissions. Maps illustrating the ground site locations and MoLab path are provided in Figure S1 in the supporting information.

3. Data Sets

We analyze data from literature in order to compare our field observations to those conducted under laboratory conditions. These data are from previous studies conducted at the Fire Sciences Laboratory (FSL) in Missoula, MT [*Burling et al.*, 2010; *Yokelson et al.*, 2013; *Stockwell et al.*, 2015; *Gilman et al.*, 2015; *Hatch et al.*, 2015]; all data are publicly available as supporting information or on NOAA's data server

(http://www.esrl.noaa.gov/csd/groups/csd7/measurements/2009firelab/). The FSL studies were performed to understand the emissions resulting from the combustion of North American fuels routinely burned by wildfires and human activity. Each fuel was burned under atmospherically relevant conditions and the emissions were monitored by a suite of instruments. These studies represent the most extensive inventory of fuel-specific biomass burning VOC emissions to date.

Yokelson et al. [2013] and *Gilman et al.* [2015] reported the emissions of 180 compounds from burning trees and shrubs using a number of VOC instruments including an open-path Fourier transform infrared (OP-FTIR) spectrometer, a proton-transfer-reaction mass spectrometer (PTR-MS), a proton-transfer ion trap-mass spectrometer (PIT-MS), and a gas chromatograph-mass spectrometer (GC-MS). *Stockwell et al.* [2015] reports the emissions of 125 compounds from grass, agricultural crops, and arboraceous biomass fires using a high-resolution proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). *Hatch et al.* [2015] reports an extended set of measurements from a subset of burns included in *Stockwell et al.* [2015] using comprehensive two-dimensional gas-chromatography time-of-flight mass spectrometery (GC × GC-ToFMS). Both *Stockwell et al.* [2015] and *Hatch et al.* [2015] conducted these measurements as a part of the FLAME-4 campaign [*Stockwell et al.*, 2014]. Fuel composition for burns reported by *Yokelson et al.* [2013] and *Gilman et al.* [2015] are provided by *Burling et al.* [2010], while those reported by *Stockwell et al.* [2015] and *Hatch et al.* [2015] are given by *Stockwell et al.* [2014]. Fuel composition was determined by analysis of subsamples using a commercial CHN analyzer.

We define NVOCs as gaseous compounds containing N-C bonds. In order to relate NVOCs across various experiments, we normalize NVOC mass to total VOC emissions (i.e., the NVOC fraction, f_{NVOC}). Here we focus on the emissions of nonmethane VOCs. We choose to present f_{NVOC} as opposed to other ratios (such as $\sum NVOC/CO_2$ or $\sum NVOC/CO$) because it is our intent to evaluate the contribution of NVOCs to the entire reactive VOC profile. We find that f_{NVOC} is more strongly tied to fuel composition than either $\sum NVOC/CO_2$ or $\sum NVOC/CO$. Furthermore, f_{NVOC} is likely less sensitive to other factors, such as MCE, that might affect the variability of NVOCs, CO, or CO_2. A discussion demonstrating these observations is provided in the supporting information.

The modified combustion efficiency (MCE $= \Delta CO_2/(\Delta CO + \Delta CO_2)$) [*Yokelson et al.*, 1996]) was similar for all samples reported here: MCE $= 0.95 \pm 0.01$ [*Gilman et al.*, 2015], 0.95 ± 0.02 [*Stockwell et al.*, 2015], and 0.94 ± 0.02 [*Hatch et al.*, 2015]. MCE is an estimate of the relative amount of flaming and smoldering combustion.

Supplemental composition data for arboraceous fuels were extracted from the BAAD (Biomass And Allometry Database) introduced by *Falster et al.* [2015]. Measurements of the nitrogen content within the leaves ($n = 1303$), bark ($n = 261$), sapwood ($n = 425$), and heartwood ($n = 143$) are reported for selected samples. While the diversity of samples are limited (Figure S2), the observed trends in nitrogen content reflect those observed from previous studies [e.g., *Dickson*, 1989; *Martin et al.*, 1998; *Nordin et al.*, 2001; *Hansson et al.*, 2003]

4. Results

Figure 1 presents the mass spectra of emissions from residential burning measured in Aspen, CO, and crop residue burning measured in Greeley, CO. Oxygenated compounds such as methanol, ethanol, formic acid, and acetic acid dominate the mass spectra, which is consistent with laboratory and ambient smoke measured elsewhere [e.g., *Burling et al.*, 2010; *Yokelson et al.*, 2013; *Stockwell et al.*, 2015; *Gilman et al.*, 2015; *Hatch et al.*, 2015]. The fraction of acetonitrile significantly differs between the two sources (mass fraction = 0.01 in the crop residue fire and 7×10^{-4} in residential wood stove emissions). Figure 1 presents the temporal profile of acetonitrile while sampling each plume. For residential wood burning, acetonitrile shows minimal enhancement, which suggests that acetonitrile is not strongly associated with emissions from residential fuels in Aspen. In contrast, acetonitrile exhibits significant enhancements in the emissions from crop residue burning. For comparison, the enhancement ratio of acetonitrile from three residential burning plumes was ~1.4×10^{-4} (range $0.7-2.2 \times 10^{-4}$) while the enhancement ratio from the crop residue burning was 3×10^{-3}. These enhancement ratios are comparable to those measured by *Stockwell et al.* [2015] for burned lumberyard wood (ER = $0.2-2 \times 10^{-4}$) and burned giant cutgrass (ER = 3×10^{-3}), respectively.

At higher masses, m/z 97.028 ($C_5H_4O_2$-H^+) stands out as a significant VOC (mass fraction ~0.05). This mass is identified as furfural (2-furanaldehyde), which is the dominant species observed in laboratory smoke with
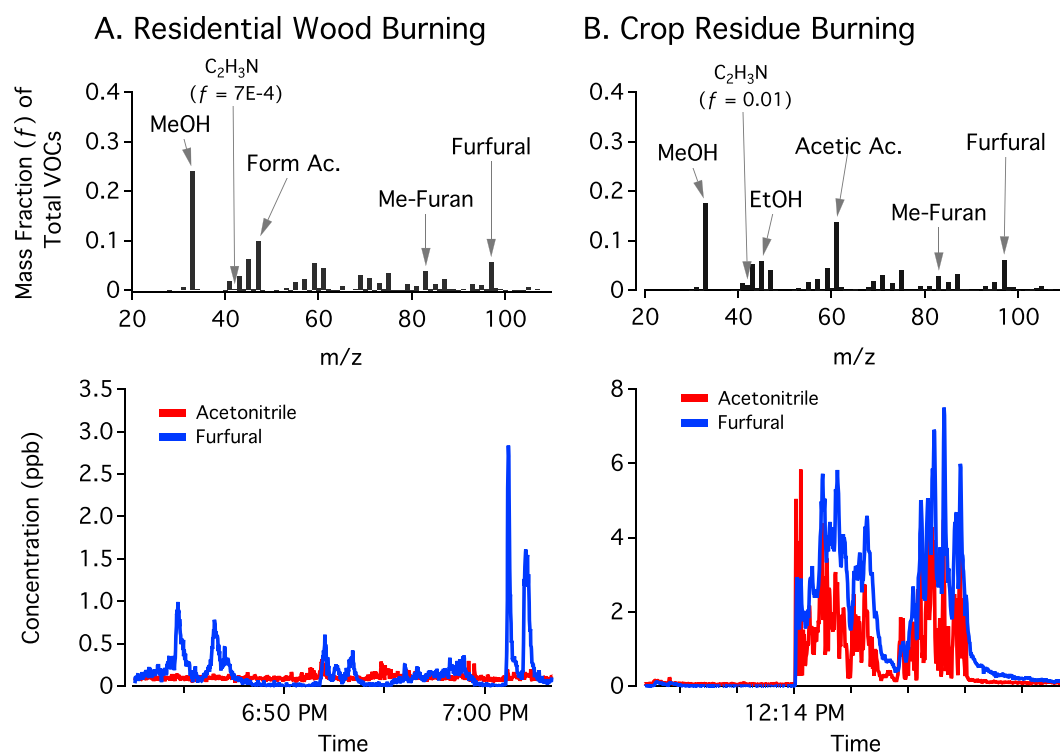
Figure 1. Normalized mass spectra and time profile of (a) residential burning emissions measured n Aspen, CO, and (b) crop residue burning emissions measured in Greeley, CO. The mass spectra are presented as the weighted fraction for each species.

molecular formula $C_5H_4O_2$ [e.g., *Stockwell et al.*, 2015; *Hatch et al.*, 2015; *Gilman et al.*, 2015]. Cyclopentene-dione, an isomer of furfural, has been observed in biomass smoke previously; however, its emission factor has been measured to be 1–2 orders of magnitude lower than that of furfural [*Gilman et al.*, 2015; *Hatch et al.*, 2015]. *Gilman et al.* [2015] found that furfural and other furan species were unique components of wildfire smoke that did not have significant contributions from urban sources in Boulder. We use furfural as a tracer for biomass burning emissions in order to assess the variability of acetonitrile in ground measurements conducted in Aspen and Boulder. To our knowledge, no studies have discussed the use of furfural (and likewise, *m/z* 97) as a tracer for biomass burning when using methods of proton-transfer ionization. In the supporting information, we demonstrate the resolution of furfural from other isobaric species detected by H_3O^+ ToF-CIMS and discuss the limitations of *m/z* 97 as a biomass burning marker when using low mass-resolving instruments, such as the PTR-MS.

In Boulder, furfural exhibits a discernible diurnal pattern characterized by high evening concentrations (Figure 2). This temporal pattern is consistent with previous measurements of residential biomass burning in urban areas [e.g., *Szidat et al.*, 2007; *Poulain et al.*, 2011; *Brown et al.*, 2016]. We note that differences exist between weekday and weekend trends. Weekend concentrations exhibit a gradual rise throughout the day, while weekday concentrations begin to rise at 4:00 PM. This contrast likely reflects differences in home occupation on weekend days vs those during weekdays. A similar weekday diurnal profile was observed in Aspen (Figure S3). Other furan species, such as *m/z* 69.034 ($C_4H_4O-H^+$, furan) and *m/z* 83.049 ($C_5H_6O-H^+$, methylfuran), show very similar diurnal patterns.

Unlike furfural, acetonitrile has a large, highly variable ambient background of ~0.1 ppb (black trace, Figure 2). In order to evaluate the variability of acetonitrile plumes, we present the diurnal pattern of acetonitrile enhancements (i.e., acetonitrile signal — ambient background). The ambient background is calculated using a low-pass filter. The weekday pattern of acetonitrile enhancements differs from that of furfural; the evening peak is absent and the variability does not exhibit structure that would suggest a clear diurnal source. During the weekend, large enhancements of acetonitrile were observed during the midday and early morning; however, other biomass burning markers (such as furfural) do not exhibit the same response.
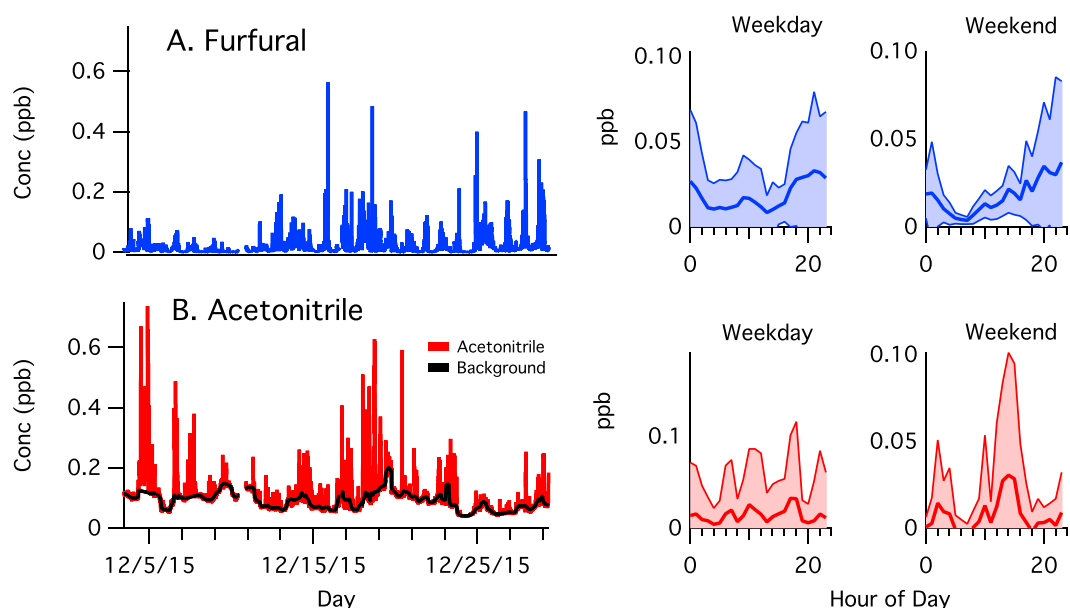
Figure 2. Time series and diurnal profiles of (a) furfural and (b) acetonitrile concentrations measured in Boulder, CO. In order to evaluate the variability of fresh acetonitrile plumes, the diurnal pattern for acetonitrile was calculated after subtracting the ambient background (black trace). The ambient acetonitrile background calculated using a low-pass filter. The envelopes surrounding each profile represent the standard deviations from the mean.

Throughout the Boulder ground campaign, isolated plumes of acetonitrile are observed without enhancement of other VOCs. We hypothesize that these plumes resulted from solvent sources in Boulder. During MoLab measurements, major enhancements of acetonitrile were observed downwind of pharmaceutical and academic laboratories. Measurements and a brief description of this source are presented in the supporting information (Figure S4). We note that the isolated plumes of acetonitrile are unlikely to result from long-range transport of aged biomass burning emissions since these plumes exhibit narrow peaks and short timescale structure.

Overall, the correlation between the time profiles of acetonitrile and furfural is poor ($R^2 = 0.14$). Even when furfural is significantly enhanced, acetonitrile shows low response. These ambient measurements suggest that acetonitrile is not strongly associated with fresh residential burning emissions in Boulder, which is consistent with the conclusions drawn from measurements of residential burning plumes in Aspen (Figure 1).

5. Discussion

5.1. NVOC Dependence on Total Fuel Nitrogen Content

Acetonitrile is commonly used to identify air masses impacted by biomass burning [*Holzinger et al.*, 1999; *de Gouw et al.*, 2003]; however, its absence from residential burning emissions in Boulder and Aspen limits its use as an effective tracer for this source. Similarly, its absence brings to question the degree to which other NVOCs may vary between different burning plumes. The following section explores NVOC variability as a function of fuel nitrogen content.

Figure 3 illustrates the dependence of f_{NVOC} on fuel nitrogen content for all herbaceous and arboraceous samples reported by (a) *Yokelson et al.* [2013] and *Gilman et al.* [2015], (b) *Stockwell et al.* [2015], and (c) *Hatch et al.* [2015]. In general, f_{NVOC} increases with higher fuel nitrogen content. These results are consistent with previous studies that have demonstrated a dependence of NO_x, HCN, and NH_3 emissions on fuel nitrogen content [e.g., *Hansson et al.*, 2004; *McMeeking et al.*, 2009; *Burling et al.*, 2010; *Ren and Zhao*, 2015]. The observed trends do not strongly differ between the two categories (e.g., Figure 3b), suggesting that NVOCs emitted from arboraceous and herbaceous precursors follow similar fuel nitrogen dependencies.

The relationship between f_{NVOC} and fuel nitrogen content varies among the different studies (slope = 0.024–0.061). *Hatch et al.* [2015] (31) and *Gilman et al.* [2015] (14) report more NVOCs than *Stockwell et al.* [2015] (7); thus, these differences in slope partially reflect detection of additional NVOCs as well as
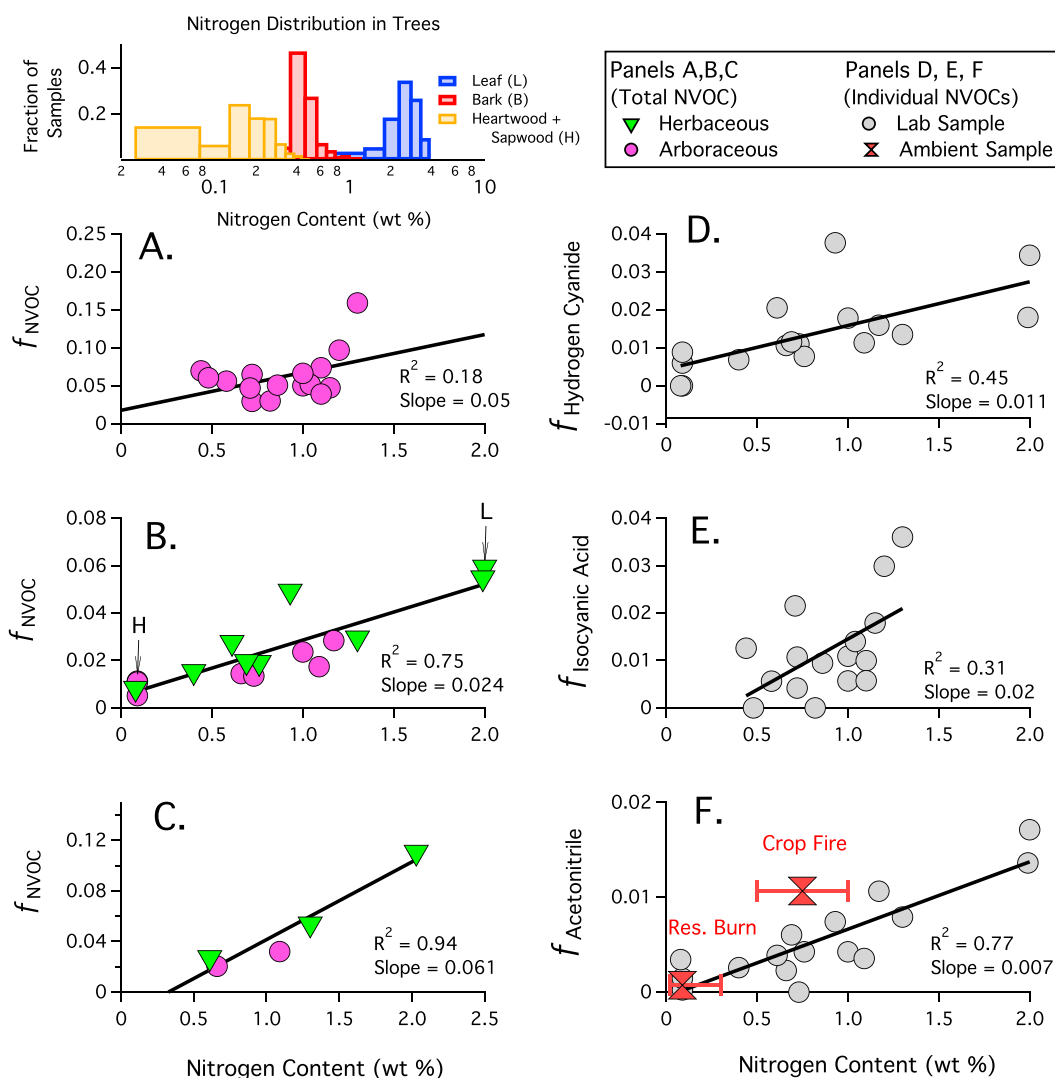
Figure 3. Fraction of NVOCs (f_{NVOC}) emitted from burning of herbaceous and arboraceous material, a function of wt % N in fuel. Data originated from (a) *Yokelson et al.* [2013] and *Gilman et al.* [2015] (b) *Stockwell et al.* [2015], and (c) *Hatch et al.* [2015]. (right column) Fraction of (d) hydrogen cyanide (HCN), (e) isocyanic acid (HNCO), and (f) acetonitrile (CH_3CN) relative to all VOCs for lab samples and the ambient plumes. The histograms at the top left illustrate the distribution of nitrogen from tree samples reported in the BAAD data set [*Falster et al.*, 2015]. Samples that are predominantly composed of heartwood (H) and leafy material (L) are highlighted in Figure 3b. The fraction of acetonitrile ($f_{acetonitrile}$) for residential wood (Res. Burn) and residue crop burning (Crop Fire) are shown in Figure 3f.

uncertainties associated with the number of samples analyzed in each study. Individual NVOCs follow the trends observed for f_{NVOC} (Figures 3d–3f). Acetonitrile and hydrogen cyanide emissions exhibit strong correlation with fuel nitrogen content. Limited measurements of isocyanic acid were available; however, the positive correlation is consistent with observations made elsewhere [e.g., *Hansson et al.*, 2004].

NVOC emissions from arboraceous fuels exhibit notable intersample differences. Samples burned by *Stockwell et al.* [2015] and *Hatch et al.* [2015] include fuels from temperate forests in Missoula, MT, chaparral in the San Jacinto Mountains in Riverside, CA, and commercial lumberyards in the United States and Honduras. The forest samples were composed of the boughs of trees with an unknown proportion of foliage:wood, while those from commercial lumberyards only contained wood. The samples from the lumberyards contained the lowest fraction of nitrogen of all reported samples (0.09%) and resulted in the lowest observed f_{NVOC}. In contrast, samples collected directly from forest environments exhibited a range of fuel nitrogen content, with some samples exhibiting concentrations as high as 1.2 wt %. We note that the variation in f_{NVOC} may be a useful metric to constrain the amount of nitrogen contained within fuels measured in the field.

The differences in f_{NVOC} between forest and lumberyard samples most likely result from the unequal distribution of nitrogen within the fuel. The nitrogen content of a tree varies anatomically [*Hansson et al.*, 2003; *Falster et al.*, 2015]; this observation is reflected in measurements archived in the BAAD database [*Falster et al.*, 2015] (Figure 3 histograms). In general, heartwood and sapwood have less nitrogen than bark, twigs, and leaves. The lumberyard samples described previously are largely composed of heartwood, while those removed directly from forests contain all elements of the organism, including nitrogen-rich leaves. For reference, the lumberyard samples (heartwood, H) and a predominantly leafy fuel (giant cutgrass, L) are highlighted in Figure 3b. We note that the observed variation in fuel nitrogen content between freshly forested samples and those from lumberyards is unlikely to result from differences in growing and storage conditions. Studies of kiln drying have demonstrated that the nitrogen content within the center of wood samples does not change significantly after felling, drying, and storage [*Theander et al.*, 1993; *Terziev and Boutelje*, 1998].

While leaves and needles represent a small portion of a tree's total mass, a large fraction of the whole-tree nitrogen resides within these components [e.g., *Ovington*, 1957; *Devine et al.*, 2013]. To demonstrate this, we calculate the fraction of whole-tree nitrogen associated with the foliage of evergreen trees common to the U.S. Pacific Northwest. *Gholz et al.* [1979] parameterized the mass of foliage, wood, branches, and bark with equations based on tree trunk diameter. Assuming a trunk diameter of 40 cm, foliage accounts for ~5% (range 0.9–9%) of above ground biomass. If we assume that the nitrogen content of foliage is ~2.5%, while all other components have a nitrogen content of ~0.25% (Figure 3), we calculate that foliage from these species may contain 33% (range 8–50%) of whole-tree nitrogen. These estimates are consistent with the total fraction of foliar nitrogen observed in ponderosa pine (~50%) [*Devine et al.*, 2013].

These differences in nitrogen content likely have atmospheric implications as there may be differences between the emissions of NVOCs in scenarios where heartwood and sapwood are the primary fuel (e.g., wood stoves, residential biomass burning) versus those in which leaves, stems, bark, and litter are burned (e.g., wildfires, prescribed and agricultural burning). This is discussed further in section 5.3. We note that these observations do not imply that all wood stove emissions lack NVOCs. In rural or developing regions, individuals may burn any number of fuels, including nitrogen-rich litter, twigs, or dung [*Stockwell et al.*, 2016]. Consequently, one must account for regional fuel when evaluating NVOC emissions from residential burning.

5.2. Effects of Fuel Nitrogen Speciation on NVOC Emissions

Figure 3 demonstrates that total fuel nitrogen content is a major determinant of NVOC emissions. Other factors, such as temperature and combustion efficiency, have been previously shown to affect VOC emission factors [e.g., *Yokelson et al.*, 1996; *Hansson et al.*, 2003, 2004]. The laboratory samples analyzed in Figure 3 were burned under similar conditions. Samples that were not included in this analysis, such as peat (decomposed plant matter), burned with MCE < 0.85. These samples contained ~2% nitrogen and were found to emit an f_{NVOC} that was >50% lower than fuels with similar fuel nitrogen content. Consequently, samples with equivalent total nitrogen content may not share the same f_{NVOC} if the burning conditions are substantially different.

One plausible, yet understudied, cause of NVOC variability is the speciation of nitrogen precursors contained within biomass. *Hansson et al.* [2003, 2004] demonstrated that HCN and NH_3 emissions in the exhaust of deoxygenated fluidized bed reactors were linked to differences in fuel precursors. *Hansson et al.* [2004] compared the HCN/NH_3 ratio resulting from the pyrolysis of Scots pine bark to those of model protein compounds such as whey protein isolate, soya beans, and yellow peas. The largest differences in NVOC emissions occurred between whey protein and bark, which exhibited substantially different amino acid distributions. *Hansson et al.* [2003] examined the NVOC emissions from the pyrolysis of individual proteins and found that the products from poly-L-proline exhibited a higher HCN/NH_3 ratio (9.5) than those from poly-L-leucine (2.2). Both proteins contain amino acids that are common in arboraceous biomass; thus, it is likely that differences in protein and amino acid distributions between species could lead to substantially different NVOC distributions.

Figure S5 illustrates the distribution of NVOCs emitted from the burning of tree samples from (a) *Gilman et al.* [2015] and (b) *Stockwell et al.* [2015]. In samples with low total nitrogen content (e.g., chipped hardwood and cooking stove fuel), NVOC emissions are dominated by hydrogen cyanide (HCN). In contrast, samples with high nitrogen content (e.g., ceanothus and juniper) exhibit larger fractions of higher carbon nitriles such as acetonitrile (C_2H_3N) and acrylonitrile (C_3H_3N). NVOCs containing oxygen (e.g., isocyanic acid and methyl nitrite) did not exhibit strong fuel dependencies.

The cooking stove fuel and chipped hardwood samples are comparable to the lumberyard samples described previously; thus, these samples are largely composed of low-nitrogen heartwood and sapwood. In contrast, juniper and ceanothus contain many of the nitrogen-rich twigs and leaves. The presence or absence of leaves is potentially a contributing factor in the emissions of higher carbon nitriles. This inference is supported by the observation that amino acid distributions vary in different tree components [*Näsholm and Ericsson*, 1990; *Nordin et al.*, 1998, 2001]. For example, *Nordin et al.* [2001] demonstrated that arginine (contains 4 N) dominated the pool of amino acids in the needles and bark of unfertilized Scots pine (*Pinus sylvestris* L.), while glutamine (contains 2 N) was the major amino acid in wood. Given that the pyrolysis of different proteins may yield different HCN/NH_3 ratios, we hypothesize that the mechanisms that control the variation of NVOC distributions in *Hansson et al.* [2003, 2004] may also affect nitrile distributions between arboraceous samples containing solely wood versus those that also contain leaves (Figure S5). More detailed studies may help to elucidate these mechanisms and provide a better understanding of plant-specific NVOC distributions.

5.3. Application of NVOC Fuel Dependency to Field Measurements

Based on NVOC trends with fuel nitrogen content, the difference in acetonitrile concentrations between the residential wood and crop residue burning emissions described in section 4 can be explained by differences in fuel composition. Emissions from residential burning in Boulder and Aspen likely result from the combustion of wood stove fuels that are similar in composition to the lumberyard samples described by *Stockwell et al.* [2015] (total nitrogen content ∼0.1 wt %). The crop residue fire was ignited in a harvested corn field. The nutrient content of residual corn stalks has been studied previously but varies depending on fertilization and harvesting scenarios [*Hoskinson et al.*, 2007]. From available data, we assume a nitrogen content of ∼0.75 wt % [*Hoskinson et al.*, 2007] and assign error bars based on a range of observed corn stover nitrogen contents [*Dwyer et al.*, 1995; *Hoskinson et al.*, 2007; *Johnson et al.*, 2010; *Barten*, 2013].

The fraction of acetonitrile ($f_{acetonitrile}$) in residential and agricultural burning emissions is presented in Figure 3f and compared to $f_{acetonitrile}$ observed in laboratory smoke from *Stockwell et al.* [2015]. The residential burning emissions exhibit an $f_{acetonitrile}$ comparable to low nitrogen-containing lumberyard samples ($f_{acetonitrile} = 7 \times 10^{-4}$). In contrast, the agricultural fire exhibited an $f_{acetonitrile}$ similar to samples containing higher fuel nitrogen content ($f_{acetonitrile} = 1 \times 10^{-2}$). The consistency with laboratory measurements indicates that ambient measurements of acetonitrile and other NVOCs are also likely to vary as a function of fuel composition.

We note that the ambient measurements described here represent case studies where relatively well-defined fuels were burned. Emissions from wildfires and prescribed burning will typically involve the combustion of many plants with varying degrees of fuel nitrogen. Furthermore, the mechanism by which plants are burned may also affect NVOC emissions. In forested wildfires, leaves and needles are readily consumed; however, the trunk may survive depending on fire intensity. Consequently, additional work is needed to assess the variability of NVOCs in response to forest-scale nitrogen content and fuel consumption.

6. Conclusions

Nitrogen-containing volatile organic compounds (NVOCs) emitted from the burning of arboraceous and herbaceous biomass exhibit a strong dependence on fuel nitrogen content. For every percentage increase in fuel nitrogen content, the percentage of total VOCs identified as NVOCs increases by ∼2.3–6%. Consequently, emissions of common ambient biomass burning tracers, such as acetonitrile, vary depending on fuel composition. The total fuel nitrogen content is a primary determining factor in the fraction of NVOCs emitted; however, combustion conditions and nitrogen speciation likely impact NVOC distributions.

These results highlight the importance of understanding the variability of fuel composition. Regions with high nitrogen-containing vegetation, such as agricultural crops or peat [*Akagi et al.*, 2011; *Hatch et al.*, 2015; *Stockwell et al.*, 2016] could emit greater amounts of health-impacting compounds, such as isocyanic acid and hydrogen cyanide [*Roberts et al.*, 2011] and impact regional air quality through enhanced ozone formation due to elevated NO_x emissions [*Burling et al.*, 2010]. Further investigations into the relationship between fuel composition and NVOC emissions should lead to useful parameterizations in atmospheric models.

These results also demonstrate the need for caution when using NVOCs, such as acetonitrile, as definitive tracers for biomass burning emissions. When studying wildfire emissions, the high nitrogen content in the leaves, stems, and bark will likely result in the emission of NVOCs that can be robustly used as burning tracers.

In contrast, wood stove emissions will likely lack NVOCs; therefore, relying on acetonitrile may lead one to underestimate the extent to which burning emissions impact VOC or aerosol composition. Here we show that furfural accounts for a large fraction of total VOC mass measured by the H_3O^+ ToF-CIMS ($\sim$5%) and that it is a suitable wood burning tracer in urban regions. Furfural has a short atmospheric lifetime under typical atmospheric OH concentrations of $\sim 1 \times 10^6$ molecules cm^{-3} ($\sim$7 h); thus, furfural may not be useful as a tracer for aged emissions. When investigating the impacts of aged wood burning emissions on air quality and climate, one may need to study the evolution of the entire emission fingerprint in order to extract information related to a plume's age. The presence or absence of furfural (and other furans) may help to constrain atmospheric aging, as these compounds are unlikely to survive a day of atmospheric processing.

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