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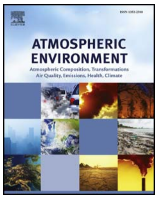

Quantification of amine functional groups and their influence on OM/OC in the IMPROVE network

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ABSTRACT

Recently, we developed a method using FT-IR spectroscopy coupled with partial least squares (PLS) regression to measure the four most abundant organic functional groups, aliphatic C-H, alcohol OH, carboxylic acid OH and carbonyl C=O, in atmospheric particulate matter. These functional groups are summed to estimate organic matter (OM) while the carbon from the functional groups is summed to estimate organic carbon (OC). With this method, OM and OM/OC can be estimated for each sample rather than relying on one assumed value to convert OC measurements to OM. This study continues the development of the FT-IR and PLS method for estimating OM and OM/OC by including the amine functional group. Amines are ubiquitous in the atmosphere and come from motor vehicle exhaust, animal husbandry, biomass burning, and vegetation among other sources. In this study, calibration standards for amines are produced by aerosolizing individual amine compounds and collecting them on PTFE filters using an IMPROVE sampler, thereby mimicking the filter media and collection geometry of ambient standards. The moles of amine functional group on each standard and a narrow range of amine-specific wavenumbers in the FT-IR spectra (wavenumber range 1 550–1 500 cm^{-1}) are used to develop a PLS calibration model. The PLS model is validated using three methods: prediction of a set of laboratory standards not included in the model, a peak height analysis and a PLS model with a broader wavenumber range. The model is then applied to the ambient samples collected throughout 2013 from 16 IMPROVE sites in the USA. Urban sites have higher amine concentrations than most rural sites, but amine functional groups account for a lower fraction of OM at urban sites. Amine concentrations, contributions to OM and seasonality vary by site and sample. Amine has a small impact on the annual average OM/OC for urban sites, but for some rural sites including amine in the OM/OC calculations increased OM/OC by 0.1 or more.

1. Introduction

Amines are organic molecules that contain nitrogen bonded to two or fewer hydrogen atoms. They are abundant in the atmosphere and present in both gas and particle phase. About 150 amines and about 30 amino acids, an amine that contains a carboxylate acid group, have been identified in the atmosphere (Ge et al., 2011). Gas-phase amines are emitted from both natural and anthropogenic sources. Examples of natural sources include vegetation, biomass burning, volcanoes, and the ocean; while anthropogenic sources include animal husbandry, waste incinerators, food industries, cooking, tobacco smoking, motor vehicles, and CO_2 sequestration (Ge et al., 2011; Cape et al., 2011). Although gas-phase amine ($R\text{-}NH_2$) concentrations are orders of magnitude lower than ammonia (NH_3), both compounds are ubiquitous in the atmosphere and participate in secondary formation of aerosols (You et al., 2014). The partitioning behavior of amines is strongly dependent on aerosol composition such as the water content and acidity, which can change the form of amines into protonated aminium or aminium salts (e.g., Pratt et al., 2009; Pankow, 2015).

Like gas-phase amines, particle phase amines are ubiquitous in the atmosphere. They have been measured in various locations around the world, including urban and rural areas of the US using chromatography, mass spectrometry, ultraviolet, fluorescence, infrared and electrochemical detectors (Ge et al., 2011). Multi-hour filter-based sampling coupled with Fourier transform infrared spectroscopy (FT-IR) has shown that amines can contribute up to 10% of organic matter in various locations world-wide (Russell et al., 2011) and short-time scale aerosol mass spectrometry measurements (AMS) have shown they may contribute up to ∼20% of the organic content of ambient particles during winter inversions (Silva et al., 2008). Therefore, the quantification of amine in ambient aerosol is important for understanding their role in atmospheric chemistry and their contribution to organic matter

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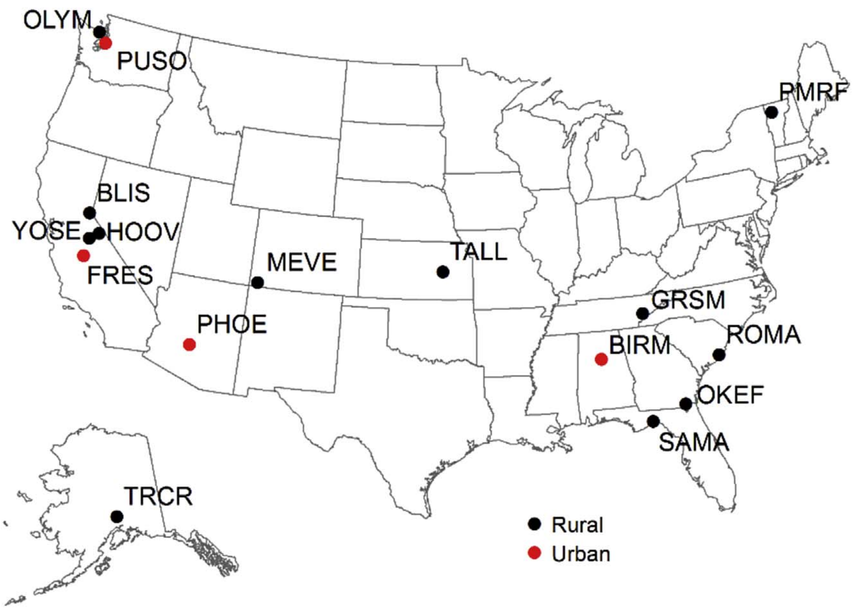

Fig. 1. Map of IMPROVE sites. Four letter site IDs are identified by full name in Table 1.

(OM), where OM is OC plus hydrogen, oxygen, nitrogen and sulfur heteroatoms.

In filter based particulate matter sampling, OM is typically estimated from organic carbon (OC) measurements using an OM/OC value of 1.8 for rural sites (Pitchford et al., 2007), and 1.4 for urban sites (White and Roberts, 1977). However, OM/OC has been shown to vary by site, season, and atmospheric conditions using various techniques, such as air quality models (Simon et al., 2011), linear regression on IMPROVE and CSN data (Malm et al., 2011), mass and light extinction reconstruction in IMPROVE (Lowenthal, and Kumar, 2003), and calculations from measured organic compounds (Turpin and Lim, 2001). The variability in OM/OC has also been measured by FT-IR on filter samples (Russell, 2003; Ruthenburg et al., 2014), using extractions of filter samples (El-Zanan et al., 2009) and by HR-AMS (Aiken et al., 2008). FT-IR techniques has shown promise in measuring OM/OC on each filter sample in a large sampling network, the Interagency Monitoring of Protected Visual Environments (IMPROVE, Ruthenburg et al., 2014), and can be applied to other monitoring networks such as the Southeastern Aerosol Research and Characterization (SEARCH) and EPA's Chemical Speciation Network (CSN) due to the low cost and non-destructive nature of the analysis on routinely collected filters. Recently we used FT-IR spectra of laboratory standards with known amounts of functional group mass and partial least squares (PLS) regression to measure four functional groups which make up a large portion of OM; alkane CH, alcohol OH, carbonyl and carboxylic acid OH (Ruthenburg et al., 2014). PLS is commonly used to calibrate spectral data that are highly collinear (i.e., have overlapping peaks) (Wold et al., 2001), as is the case for FT-IR spectra of aerosol samples (Dillner and Takahama, 2015; Weakley et al., 2016). The functional group measurements were used to estimate OM and OM/OC in IMPROVE samples collected at seven sites in 2011. In this work, we extend our method to include the amine functional group and apply it to samples collected at 16 IMPROVE sites in 2013. Amine measurements using FT-IR have several challenges including (1) some of the spectral bands of interest are obscured by large peaks from OH and the Teflon filter material, (2) uncertainty in the peak assignment of the amine functional group in the spectral region most useful for amine quantification, (3) other atmospherically relevant compounds absorb in the same region as amine, and (4) the position of the amine bands shift depending on the composition of the molecule to which it is attached (Kettle et al., 1989; Kumar et al., 2006; Venyaminov and Kalnin, 1990). To address these challenges, we evaluate multiple amine and amino acid compounds for use as standards and select for our calibration a narrow spectral band which has been established as being due to amines and that has limited absorbance by other species. The calibration is evaluated in ambient samples using a peak height method, which is independent of PLS and a broad spectral range PLS calibration. Amine functional group concentrations were measured in 1795 samples, and site and seasonal variability in amine concentrations are reported. The impact that the measured amine concentrations have on OM/OC is highlighted.

2. Methods

To measure amine functional group in ambient samples, laboratory standards with known amounts of amine functional group are prepared. FT-IR spectra of all laboratory standards and ambient samples are collected. Spectra of about two-thirds of the amine laboratory standards along with the moles of amine functional group on the standards (based on mass measurements) are used to develop a partial least squares (PLS) regression calibration. The calibration is tested with the remaining laboratory standards. The calibration is applied to ambient samples and the results are compared to a simple peak height analysis to evaluate whether the PLS model results are based on observable differences in the spectra.

2.1. *Description of the ambient samples*

Ambient samples were obtained from January to December 2013 at 16 IMPROVE sites (1795 samples) as show in Fig. 1 and listed by name in Table 1. IMPROVE samples were collected every third day beginning at midnight local time and ending 24 h later. Samples were collected at a nominal flow rate of 22.4 L min^{-1} on PTFE filters (Pall Corporation, 25 mm diameter) with $PM_{2.5}$ sampling inlets as part of the routine operation of the IMPROVE network. A detailed description of the samples can be found elsewhere (Reggente et al., 2016).

2.2. *Preparation of laboratory standards*

A credible basis for calibrating a spectroscopic method (i.e., FT-IR, X-ray fluorescence) is to use standards with known amounts of analyte that mimic the physical characteristics (of the analyte and the substrate), the chemical nature and the sampling geometry of the samples to be measured (Indresand et al., 2013; Ruthenburg et al., 2014). For FT-IR measurements of functional groups in ambient particulate matter