Phenols in Northeastern U.S. Aerosol Particles from Lignin and its Products in Seawater

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Abstract

Atmospheric particles collected during the ICARTT 2004 field experiment at ground based sites at Appledore Island (AI), New Hampshire, Chebogue Point (CP), Nova Scotia, and aboard the R/V Ronald Brown (RB) were analyzed using Fourier Transform Infrared (FTIR) spectroscopy to quantify organic mass and organic functional groups. Several of these spectra

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contain a unique absorbance peak at 3500 cm$^{-1}$. Laboratory calibrations identify this peak as poly-functional phenols. The phenol groups are associated with ocean-derived emissions based on correlations with tracer VOCs and ions, and Potential Source Contribution Function (PSCF) analysis. Based on the measured absorptivities, the project average phenol group concentrations are 0.24 $\mu$g m$^{-3}$ (4% of the total OM) at AI, 0.10 $\mu$g m$^{-3}$ (5% of the total OM) at CP, and 0.08 $\mu$g m$^{-3}$ (2% of the total OM) on board the RB. The complete spectra were decomposed into three primary factors using Positive Matrix Factorization (PMF) sufficient to explain more than 95% of the measured OM. At the three platforms the anthropogenic combustion factor contributed 40% (AI), 34% (CP), and 43% (RB) of the total organic mass; the biogenic factor contributed 20% (AI), 30% (CP), and 27% (RB). The ocean-derived factor contributed 40% (AI), 36% (CP) and 29% (RB) of the OM and showed similar correlations to tracers as the phenol group.

Introduction

The International Consortium for Atmospheric Research on Transport and Transformation field experiment (ICARTT-2004) was carried out during the summer of 2004 to study emissions, transport and chemical transformations of gas and aerosol species in the Northeastern U.S. and their impact on air quality and climate on regional to inter-continental scales. A major focus of the study was the contribution of organic carbon (OC) to the aerosol mass.(1) As a part of this experiment, aerosol particles were collected over a two-month period at ground sites at Chebogue Point and Appledore Island, and aboard the R/V Ronald Brown to quantify their organic fraction. In addition to aerosol particles, the sampling platforms also included a suite of high time resolution measurements including gas and particle phase physical and chemical properties, as well as meteorological parameters.(1–6) Pollution events at these sites were found to be highly episodic and were associated with specific emissions sources based on analysis of co-emitted tracers. At Chebogue Point, for example, US pollution outflow episodes accounted for 15% of the overall measurement period.(7) Distinct episodes associated with fresh and processed biogenic
emissions, biomass burning, and local anthropogenic sources were also frequently identified.(7) Onboard the R/V Ronald Brown, a factor analysis of the combined data on gas and aerosol species revealed that the aerosol organic mass measured during the study was predominantly of secondary anthropogenic origin.(3) In addition to these continental sources, possible marine sources of organic aerosol were also identified.(8) Back trajectory analysis indicated that forest fire plumes from Northern Canada and Alaska rarely mixed with the boundary layer and were a minor component of atmospheric measurements,(9–11) suggesting that aerosols in this region are dominated by regional sources.

Infrared spectroscopy provides a well-developed methodology for quantitative measurements of dominant functional groups in atmospheric aerosols that can be related to pollution sources.(12–15) For example, long chain hydrocarbons (alkanes and alkene groups) are usually characteristic of diesel and oil combustion,(16) carboxylic acids reflect SOA,(17) marine saccharides are a source of organic hydroxyl and amine mixtures,(18), and non-acid carbonyl groups have been detected in biogenic emissions and the products of biomass burning.(19, 20) In previous work, we presented the analysis of major functional groups in aerosol samples measured during the ICARTT experiment.(15) Example absorption spectra and corresponding functional group composition are illustrated in Figure 1 (a). A total of 197 ICARTT spectra (out of 322) contain a unique and sharp absorption peak at 3500 cm⁻¹ above the broad organic hydroxyl absorption that has not been observed at other urban or remote sites in prior FTIR sampling.(13–15, 21–24) In the present work we identify phenol as the functional group having this absorption feature and identify its sources during ICARTT 2004.

**Experimental Section**

Submicron particles were collected on 37 mm teflon filters at Appledore Island (108 samples), Chebogue Point (115 samples), and the R/V Ronald Brown (99 samples) over time periods between 6 hr and 24 hr. Simultaneous field blanks were also collected for each sample. Details of the
sampling sites and filter storage and handling are described by Gilardoni and coworkers.\textsuperscript{(15)} FTIR absorbance of a detected organic species varies linearly with its mass loading and is independent of the mixture composition.\textsuperscript{(13, 14)} The bulk of organic mass in ambient aerosol samples comprises alkane (quantified between 2790-2930 cm\textsuperscript{-1}), carboxylic acid and non-acid carbonyl (1720 cm\textsuperscript{-1}), organic hydroxyl (3100-3400 cm\textsuperscript{-1}) and primary amine (1630 cm\textsuperscript{-1}) groups, with alkene (2980 cm\textsuperscript{-1}), aromatic (3050 cm\textsuperscript{-1}), and organosulfate groups (876 cm\textsuperscript{-1}, by rinsing) typically below the detection limit for many regional samples.\textsuperscript{(15)} Since FTIR absorption strength varies linearly with mass loading of organic functional groups, similarities in absorption spectra reflect similarities in the relative amounts of functional groups in ambient samples that in turn reflect similarities in possible primary and secondary sources.\textsuperscript{(25)} The Ward algorithm\textsuperscript{(26)} was used to hierarchically cluster normalized absorption spectra from non-duplicate samples into four main classes that contain different relative amounts of alkane, organic hydroxyl, carbonyl and acid groups. Increasing the number of branches subdivided these classes into smaller groups with minor differences in relative composition. The striking feature of the average spectra illustrated in Figure 1 (a) is that adjacent to the broad organic hydroxyl group absorption between 3100 and 3400 cm\textsuperscript{-1} is a narrow absorption peak at 3500 cm\textsuperscript{-1}, which has not been identified previously in atmospheric aerosol samples.

**Narrow absorption at 3500 cm\textsuperscript{-1}** To identify the source of absorption at 3500 cm\textsuperscript{-1} IR spectra for organic compounds maintained in standard reference libraries (27, 28) were examined to locate significant peaks between 3500±20 cm\textsuperscript{-1}. This criterion is satisfied by aromatic amines (for example, 1,2-benzene diamine and 4-tert-butyl benzene amine) and poly-functional phenols (for example, ethyl 3,4-dihydroxy benzoate and n-propyl 3,4,5-trihydroxy benzoate). The standard absorption spectra for these compounds are illustrated in Figure 1 (b). Calibration standards for the selected compounds were prepared from 1 mmol l\textsuperscript{-1} solutions in acetone that were atomized using a TSI model 3076 constant output recirculation atomizer. The polydisperse atomized samples were diluted by the addition of dry air at a mixing ratio of 1:1, and a flow rate of 1.5 SLPM was used to collect particles on 37 mm teflon filters. Multiple samples were prepared by collecting
aerosols for time periods between 20 and 60 min at 10 min intervals. The filters were stored in petri dishes under constant temperature and relative humidity for 24 hours prior to FTIR analysis to facilitate solvent evaporation. The net sample loading on each filter was determined gravimetrically using the difference in filter weights measured before and after loading. The filters were scanned using a Bruker Tensor 27 FTIR Spectrometer with a DTGS detector operating in the transmission mode. Each individual sample spectrum was determined by averaging 128 scans between 400 and 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) and subtraction of corresponding pre-sampling filter scans.(15). Mass concentrations of functional groups were calculated using an automated algorithm that determines baselines and performs Gaussian peak fits to the spectra.(22, 23)

FTIR spectra for the prepared laboratory standards of ethyl 3,4-dihydroxy benzoate and n-propyl 3,4,5-trihydroxybenzoate, illustrated in Figure Figure 1 (c), contain a narrow absorption peak at 3500 cm\(^{-1}\) that is very similar to the structure observed in ambient samples. In contrast, 1,2-benzene diamine and 4-tert-butyl benzene amine do not absorb sufficiently to produce and absorption signal above the noise in the spectra despite this structure’s presence in NIST database spectra. This difference can be explained by the detector sensitivities of the spectrometers in the 3000 to 3600 cm\(^{-1}\) range, matrix effects, as well as from differences in sample preparation. The NIST standards were scanned in the solid phase using the DOW-Kbr foresprism grating instrument, with a range of operation between 1300-3800 cm\(^{-1}\), and details on the detector used were not specified. The Bruker Tensor 27 model used in this work has an operational range from 400-4000 cm\(^{-1}\), with the DTGS detector having high sensitivity in the 2500-3500 cm\(^{-1}\) region.(29)

We conclude that the peak at 3500 cm\(^{-1}\) in the ambient spectra is due to absorption by phenol moieties. The reference spectrum of wood samples (containing multiple organic hydroxyl and phenolic groups from lignin structures) shows strong absorption between 3200-3500 cm\(^{-1}\) with a narrow peak at 3500 cm\(^{-1}\),(30, 31) consistent with the identification of the phenol group with the absorption at 3500 cm\(^{-1}\). The absorbance of the calibration standards varied linearly with the number of moles of bonds and mass loading independent of mixture composition and is shown in Figure Figure 2. A linear fit between absorbance and loading for the two standards yields a slope
of 0.092 $\mu$mol-bond area$^{-1}$ for n-propyl 3,4,5-trihydroxybenzoate (with correlation coefficient, R=0.97) and 0.154 $\mu$mol-bond area$^{-1}$ for ethyl 3,4-dihydroxy benzoate (R=0.77). We assume that an equimolar mixture of our standards represents phenols in the atmosphere, and the absorbance for ambient samples can be determined by an arithmetic mean. The inverse absorptivity is then 0.123 $\mu$mol-bond area$^{-1}$ at 3500 cm$^{-1}$, compared to 0.057 $\mu$mol-bond area$^{-1}$ for the broader peak associated with linear chain organic hydroxyls and other polyols.\(^{(23)}\) Deviation from the equimolar assumption in ambient standards would introduce an uncertainty of 25% in phenol abundance, in addition to an uncertainty between 5-22% due to interference by water, ammonia and primary amines in the 3300-3600 cm$^{-1}$ absorption region;\(^{(14)}\) however the impact on total OM would be negligible due to the relatively small contribution from phenol groups to the total OM. The lower inverse absorptivity (fewer bonds per unit absorption area) at 3500 cm$^{-1}$ for the phenol group than at 3050 cm$^{-1}$ for the aromatic group (8.7 $\mu$mol-bond area$^{-1}$) makes the latter group more difficult to resolve in the ICARTT samples even though it co-occurs with the phenol groups.

**Analysis of ambient ICARTT spectra** Positive Matrix Factorization (PMF) was applied to baselined FTIR spectra to decompose the complex ambient samples into a smaller number of primary components.\(^{(22, 23, 32)}\) Singular value decomposition was used to determine the optimum number of factors, and the robustness of the factor solution was examined by varying the rotation parameter FPEAK. Non-negativity constraints were imposed on the solution spectra and the infrared spectra of field blanks were used to estimate the uncertainty in measured absorbance. Sources associated with each factor were identified using correlations with co-measured VOCs from PTR-MS and GCMS measurements,\(^{(2–5, 7, 9, 11, 33–37)}\) X-Ray Fluorescence (XRF) metals (at Chebogue Point),\(^{(38)}\) and ions from PILS and impactor measurements (R/V *Ronald Brown*).\(^{(3)}\) Characteristic spectral signals and compositions for sources determined based on a synthesis of 19 different field projects were used as a consistency check.\(^{(39)}\) Hierarchical Ward clustering was used to segregate all ambient samples into a smaller number of clusters, each of which was dominated by a different combination of source factors. The Potential Source Contribution Function (PSCF) was used to determine the most probable geographic source regions for each source.
factor. Three day back trajectories ending at the sampling platforms were computed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model with hourly resolution at 50, 100 and 500 m above sea level and treated as a single ensemble to minimize the effect of selecting altitude. Periods in which the fractional contribution for each source factor was in the top 75th percentile were classified as high with the remainder classified as low, and the associated back-trajectories were grouped accordingly. The trajectories were interpolated into 15 min intervals and superposed on a domain centered around the sampling platform and gridded into a total of 250,000 cells. The probability for the location of source was then determined as the normalized total count of high period trajectories for each grid cell through which a threshold minimum of 500 trajectories traversed.

Results

Quantification of Phenols in ICARTT The concentrations of phenol and non-phenol hydroxyl groups are compared in Figure 3 (a), grouped by Ward cluster. The narrow phenol group absorption peak at 3500 cm$^{-1}$ could not be decoupled from the broad organic hydroxyl group background in 38% of the total spectra quantified and was determined to be below the detection limit. The detection limit increases with the hydroxyl to phenol ratio and varies between 0.06-0.11 µg m$^{-3}$ for ICARTT. Organic hydroxyl groups compose 70% of the OM in Cluster 1 (31 total spectra) with the remainder comprised of alkane and primary amine groups. Spectra in this cluster contain the largest phenol absorption peaks, which yield the largest absolute concentration (mean and standard deviation of 0.56±0.15 µg m$^{-3}$) and contribution to total organic hydroxyl group mass (15-23%) from phenol groups. Cluster 2 (48 spectra) is characterized by a large carbonyl fraction, which contributes 34% of the mass, a correspondingly smaller fraction of organic hydroxyl groups (19%), and the smallest relative phenol group absorption. The average phenol group concentration is 0.13±0.05 µg m$^{-3}$, composing 13% of the organic hydroxyl group mass. Clusters 3 (46 spectra) and 4 (58 spectra) consist of 35% alkane groups with different ratios of
carboxylic acids and hydroxyl groups constituting the remaining OM. The average phenol concentration for clusters 3 and 4 is $0.19 \pm 0.04 \, \mu g \, m^{-3}$ (14-16% of organic hydroxyl group mass) and $0.14 \pm 0.04 \, \mu g \, m^{-3}$ (11-14% of organic hydroxyl group mass), respectively. The linear correlation between phenol and non-phenol hydroxyl group concentrations is very strong ($R > 0.75$) for each of the clusters suggesting that both functional groups have the same sources.

**Sources of Phenol Groups** The project mean and standard deviation for the phenol group concentration at Appledore Island is $0.24 \pm 0.18 \, \mu g \, m^{-3}$, which composes 5-11% of the total OM. The phenol group concentration shows a moderate correlation ($0.25 < R < 0.50$) with methyl chloride, methyl bromide, and carbonyl sulfide. Local wind directions vary between 0 and 90 degrees (North East, corresponding to the direction of the Gulf of Maine) for periods of elevated phenol group concentration (greater than $0.4 \, \mu g \, m^{-3}$) with elevated wind speeds of $5.8 \, m \, s^{-1}$ (project average $5.60 \, m \, s^{-1}$) during those times. At Chebogue Point the average phenol group concentration is $0.10 \pm 0.06 \, \mu g \, m^{-3}$, which constitutes 5-9% of the total OM. Moderate correlations ($0.25 < R < 0.5$) exist for phenol group concentrations only with formaldehyde and pentanone concentrations. The local wind direction for periods of elevated phenol group concentrations is between 150 and 210 degrees (South-South West, corresponding to the directions of the Gulf of Maine and North American mainland) with average wind speeds of $3.3 \, m \, s^{-1}$ ($3.1 \, m \, s^{-1}$ project average). For the R/V *Ronald Brown* the average phenol group concentration is $0.08 \pm 0.09 \, \mu g \, m^{-3}$, composing only 2-6% of the total OM, and has no correlations of $R > 0.25$ with any of the measured tracer compounds. Periods of elevated phenol group concentrations (higher than $0.10 \, \mu g \, m^{-3}$) correspond to average wind speeds of $5.5 \, m \, s^{-1}$ ($4.9 \, m \, s^{-1}$ for entire project). The ship was located in an area between 42N and 44N, and 69W and 71W during these periods with local winds from directions between 30 and 130 degrees (East) again corresponding to the Gulf of Maine. A majority of filter samples at Appledore Island (66%) and Chebogue Point (64%) contained phenol concentrations above the detection limit, compared to only 32% of the samples from the R/V *Ronald Brown*.

**PMF of ambient spectra** The ICARTT aerosol samples were typically collected for 6-24 hours and contain contributions from multiple sources. PMF analysis provides a technique for
de-convoluting mixed samples by extracting correlated variables corresponding to similarities in sources, transport, and chemistry.\textsuperscript{(4, 7, 22, 23, 42)} For the three sets of spectra, solutions utilizing between three and six factors were found to reproduce 90-110\% of the measured organic mass for each sample and to produce factors with smooth spectral shapes that were similar to known organic standards. A two factor solution reproduced less than 80\% of the measured OM on average and the use of more than seven factors resulted in factors with a low signal to noise ratio and a large over-estimation in OM (as much as 30\%) due to poor representation of the carboxylic COH and ammonium absorption peaks. Three unique types of factors persisted in all solutions that represented 90-110\% of the measured OM, and these findings were identified as fossil-fuel combustion, terrestrial biogenic, and ocean-derived. Varying the rotation parameter produced a highly robust solution with negligible differences in the residual (Q) matrix therefore a value of FPEAK=-0.4 was selected to minimize correlations between individual factors in each solution. Linear correlations between the calculated OM from a three factor solution and measured OM show excellent agreement, with slopes of 0.98 (Appledore Island), 1.2 (Chebogue Point), and 1.0 (\textit{R/V Ronald Brown}) and \textit{R} between 0.90 and 0.92 in each case, indicating that the three factor solution reproduces the structure of the measured spectra without introducing systematic errors. Project average functional group compositions, contributions to OM, and strong tracer correlations for the three factor solution are illustrated in Figure Figure 4 and their time-series for the duration of sampling are illustrated in Figure Figure 5.

\section*{Discussion}

Gas phase phenols and methyl halides in the atmosphere have been attributed to products of lignin (wood) burning,\textsuperscript{(43–45)} indicating that forest fires (or local biomass burning) are possible sources of the phenol groups measured in the atmosphere. The similarity between the absorption peak at 3500 cm\textsuperscript{−1} in the spectrum for lignin pulp and ICARTT cluster 1 spectra (Figure Figure 1) further suggests that the phenolic groups are derived from plant material or its combustion. However,
typical atmospheric biomass burning tracers such as acetonitrile, acetone, and potassium\(^7, 22\) show no correlation (R<0.25 in all cases) to the phenol group concentration. In addition to being wood burning tracers, methyl halides also have marine sources\(^{(46)}\) as does formaldehyde\(^{(47)}\). Local meteorology at each of the three platforms (elevated wind speeds and direction) indicates that air masses containing phenols originated over the Gulf of Maine rather than the North American land mass. Based on these factors, we propose that lignin-derived phenols during ICARTT were most likely re-suspended as sea-spray to the atmosphere after deposition to the ocean from riverine and atmospheric sources\(^{(18, 48)}\). Dissolved lignin and lignin-derived phenols have been measured in seawater samples\(^{(49)}\) and their source in the North Atlantic Ocean has been attributed to be a combination of riverine input\(^{(50)}\), sediment re-suspension, and aerosol deposition of biomass burning products\(^{(51)}\) (with any single mechanism insufficient to explain the observed ocean concentrations). These mechanisms result in a higher lignin concentration in near-coastal and surface waters, consistent with the higher amounts of phenol groups observed at the coastal sites.

**Source Factors** Figure 4 illustrates the functional group composition of the three persistent factors identified at each platform. The factors show consistent compositions in each case at the three platforms with comparable contributions from each functional group. Correlations of factor concentration with VOC tracers of emission sources\(^{(7, 37)}\) with a linear correlation coefficient R>0.25 are used to associate each factor with the most probable source. The first factor is identified as ocean-derived based on its correlation to oceanic tracers such as methyl halides\(^{(52, 53)}\) and carbonyl sulfide\(^{(54)}\) (with 0.5>R>0.25), and the location of its potential source regions. The R/V *Ronald Brown* factor correlates to chloride and oxalate ion concentrations (0.5>R>0.25) and no VOCs. Organic hydroxyl groups dominate the marine factor and compose between 70% and 80% of the OM. Alkane and primary amine groups compose approximately equal fractions of the remaining OM, between 10% and 15% with minor contributions from carbonyl containing groups. The absorption spectra of the marine factor (Figure 5 (a)) are dissimilar between the ground sites and the R/V *Ronald Brown*. All three platforms show a broad absorption in the organic hydroxyl region with negligible ammonium, but the spectra for the ground sites have large absorption
peaks at 3500 cm$^{-1}$, consistent with the larger fraction of samples with detectable phenol group concentrations at these sites. Phenol groups compose 42% (Appledore Island), 35% (Chebogue Point), and 19% (R/V Ronald Brown) of the total organic hydroxyl group mass in the marine factor. OM has been shown to be transferred from the organic matter components in the ocean to atmospheric particles by wave-induced bubble bursting.\(^{18, 55}\) This mechanism also provides a way to transfer phenol groups, which originated from lignin-burning and were deposited to the ocean surface, to atmospheric particles. The project mean concentration and standard deviation for this factor is 1.77±0.31 µg m$^{-3}$ at Appledore Island (between 14% and 73% for individual samples), 1.12±0.18 µg m$^{-3}$ at Chebogue Point (between 11% and 58%), and 1.34±0.24 µg m$^{-3}$ aboard the R/V Ronald Brown (between 3% and 45%). Phenol concentrations show two very distinct relationships (Figure 3) to the marine factor, with slopes of 0.30±0.06 and 0.08±0.03 and R>0.7 in both cases. The higher slope corresponds to samples from air masses from the Gulf of Maine (high phenol concentration) while the lower slope corresponds to samples from air masses from over land or the Atlantic Ocean, consistent with higher lignin-derived phenol concentrations in the coastal waters of the Gulf of Maine.

The second factor is attributed to fossil fuel combustion. The project average concentration for this factor is 1.66±0.32 µg m$^{-3}$ at Appledore Island (between 12% and 69% for individual samples), 1.17±0.18 µg m$^{-3}$ at Chebogue Point (between 4% and 81%), and 2.94±0.81 µg m$^{-3}$ aboard the R/V Ronald Brown (between 26% and 92%). The combustion factor is dominated by saturated alkane groups (contributing between 80-90% of the total mass) typically produced by the use of petroleum products.\(^{7, 16}\) Carboxylic acid groups compose 10% of the mass and are associated with secondary aerosol formed by the oxidation of combustion products. The factor correlates strongly (R>0.5) with tracers of combustion and urban pollution such as long and branched chain alkanes, benzene, toluene, and dichlomethane in the gas phase.\(^{7}\) At Chebogue Point the combustion factor correlates to crustal elements Ca, Br, and Zn (that are tracers of dust) (R>0.5), and weakly to S and P (0.5>R>0.25), indicating a possible secondary contribution.\(^{22}\) The absorption spectra for this factor are illustrated in Figure 6 (a). All three platforms
show a large ammonium absorption at 3200 cm$^{-1}$, consistent with spectra observed in other urban environments.$(23, 39)$ The time series (Figure 5) shows episodes of high concentration at the ground sites between July 10-July 17, and July 27-July 30 on board the R/V *Ronald Brown*, corresponding to measured episodes of elevated continental urban outflow.$(7, 15)$

The third factor is attributed to secondary organic aerosol formation from oxidation of biogenic emissions. The average concentration is $0.87 \pm 0.12 \mu g \text{ m}^{-3}$ at Appledore Island (between 2% and 45% for individual samples), $0.98 \pm 0.14 \mu g \text{ m}^{-3}$ at Chebogue Point (between 9% and 53%), and $1.24 \pm 0.22 \mu g \text{ m}^{-3}$ aboard the R/V *Ronald Brown* (between 1% and 41%). This factor is characterized by a large carbonyl and primary amine fraction and correlates strongly to biogenic terpenoid compounds (isoprene, $\alpha$ pinene, $\beta$ pinene, and camphene) and as well as oxygenated VOCs (such as MEK and MVK) that have biogenic sources.$(7, 56)$ A lack of correlation with combustion tracers such as K, acetone, and acetonitrile support the identification of this factor as secondary biogenic particles rather than biomass burning emissions. The time series at the ground sites do not contain any singular events dominated by this factor but show a diurnal pattern with alternating high and low concentrations in 12 hr samples consistent with photochemical aerosol formation.$(5)$ The R/V *Ronald Brown* samples show a large contribution from the biogenic factor on July 27 and 28, consistent with observed high isoprene oxidation events.$(3)$ Biogenic factor spectra illustrated in Figure 6 (b) show a much smaller ammonium absorption than the combustion factor. The broad peak between 3000 and 3500 cm$^{-1}$ resulting in a smaller alkane group fraction is coupled with a high non-acid carbonyl group absorption (approximately 3-4 times the magnitude in the other factors). Phenol groups do not contribute significant mass to either the combustion or biogenic factors.

**Source Regions** PSCF analysis of air mass back trajectories for each factor identified at the ICARTT sites provides a consistency check on the locations of identified sources. The probable source regions for the phenol-containing factor are located in North American coastal waters and disperse areas of the Atlantic Ocean, consistent with the attribution of this source to ocean-derived particles. PSCF has poor resolution in the grid cells immediately surrounding the measuring site.
due to insufficient variability between air mass trajectories. Repeating the analysis using 24 hr and 36 hr back-trajectories did not improve the resolution between local (Gulf of Maine) and long-range (Atlantic) ocean sources for the marine factor suggesting that phenol sources are located closer upwind to the measuring sites with negligible contributions from long range transport. The combustion factors have high-probability source regions over New England, Nova Scotia and shipping lanes in the Atlantic Ocean; however, the large urban areas on the East coast are not strongly indicated. This is consistent with the episodic nature of Northeastern U.S. pollution, as back-trajectories associated with both high and low aerosol concentrations tend to traverse the same locations. High probability source regions for the biogenic factor are located in New England and the United States-Canada border; but these regions cannot be distinguished from the combustion source regions within the uncertainty of the method. The two continental factors associated with biogenic and combustion sources tend to co-vary in time, which is not surprising since their sources are located in similar regions. A factor based analysis of VOCs at Chebogue Point suggested source regions consistent with our results.\(^7\)

We conclude that lignin and the products of lignin degradation and lignin burning deposited to seawater (from riverine input, sediment suspension and airborne deposition) are a source of phenol groups in ambient aerosols in near coastal regions contributing as much as 0.6 \(\mu g \text{ m}^{-3}\) (10 \% of total OM) for some periods and regions of the ICARTT 2004 experiment. A factor based analysis of ambient spectra is consistent with this result as the phenol group constitutes between 19 and 42\% of the ocean-derived factor and a negligible fraction of the anthropogenic combustion and biogenic factors. The strong phenol group signature present in ICARTT samples is unique to the Northeastern US region, based on ambient sampling by FTIR to date.\(^{13–15, 21–24}\) The apparently unique feature of coastal waters in this region results from a combination of two factors: (1) they are located downwind of heavily forested regions with frequent boreal fires; and (2) they have a high riverine input from waterways that have substantial forest lignin content. The location and persistence of the phenol feature is supported by the detection of an absorption signal at 3500 cm\(^{-1}\) during the ICEALOT 2008 cruise above the R/V \textit{Knorr}, in three samples collected between
March 23 and March 26 as the ship crossed the St. Lawrence seaway south of Newfoundland.(23)

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Supporting Information Available

Details on source regions for the ocean-derived factor from PSCF analysis are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure 1: ICARTT spectra clusters, database standards, and laboratory standard spectra showing phenol absorption at 3500 cm$^{-1}$. (a) Representative spectra from ward clusters 1 (blue), 2 (green), 3 (orange), and 4 (red) are shown along with their corresponding functional group composition as alkanes (blue), hydroxyl (pink), carbonyl (teal), amines (orange), and acid (green) illustrated in pie charts 1-4. (b) Reference spectra for 1,2-benzene diamine (red), 4-tert-butyl benzene amine (orange), ethyl 3,4-dihydroxy benzoate (purple), n-propyl 3,4,5-trihydroxy benzoate (blue), and lignin (grey). (c) Laboratory standard spectra in the same colors as panel (b).
Figure 2: Calibration lines for IR absorption by phenols at 3500 cm$^{-1}$. Triangles are n-propyl 3,4,5-trihydroxy benzoate samples and circles are ethyl 3,4-dihydroxy benzoate samples. Dashed lines show linear fits for individual standards and the solid line shows the average calibration assuming an equimolar mixture.
Figure 3: (a) Comparison between phenol and non-phenol hydroxyl concentrations for ambient ICARTT samples. Squares are from Appledore Island, Triangles from Chebogue Point, and Circles from R/V Ronald Brown. The markers are colored according to hierarchical clusters illustrated in figure Figure 1. Dashed lines show best linear fits. (b) Comparison of phenol concentration with PMF marine factor. Higher line corresponds to air masses from the Gulf of Maine and lower line corresponds to Atlantic/Over land air masses.
Figure 4: Compositions of the PMF factors, respective time-averaged concentrations, and primarily correlated tracers by sampling platform. Relative contribution from above detection limit functional groups in the pie charts is from organic hydroxyl (pink), alkane (blue), non-carboxylic carbonyl (teal), amine (orange), and carboxylic acid (green) and listed top to bottom respectively. Average concentration for each factor is in $\mu g \ m^{-3}$. Elemental and VOC tracers correlated with $R > 0.5$ (bold) and $0.5 > R > 0.25$ are listed.
Figure 5: Time series for PMF factors at (a) Appledore Island, (b) Chebogue Point, and (c) R/V Ronald Brown during ICARTT 2004. The combustion factor is indicated in red, biogenic factor in yellow, and marine factor in blue.
Figure 6: Baselined FTIR absorption for the (a) marine factor, (b) combustion factor, and (c) biogenic factor. Spectra are shown in red for Appledore Island, green for Chebogue Point, and black for the R/V Ronald Brown.
Supplemental Information

The phenol group containing source factor at the three ICARTT platforms is identified with an ocean-derived source based on correlations with tracers summarized in Figure 4. PSCF analysis based on air back mass back trajectory analysis is illustrated in Figure S1, and indicates that the most probable source regions for this factor are located in North American coastal waters and disperse areas of the Atlantic Ocean, consistent with the inferred ocean source. Since the marine factor has winds from the North East (AI), South-South West (CP), and East (RB); the most proximate common overlap of these upwind areas are the waters of the Gulf of Maine.
Figure S1: Most probable source regions as determined by PSCF analysis for the ocean-derived factor identified using correlations to VOC tracers at (a) Appledore Island, (b) Chebogue Point, and (c) aboard R/V Ronald Brown. Wind sectors corresponding to events with the top 25th percentile of marine factor contribution are indicated on each plot.