

Atmospheric Pressure Mass Spectrometry: A New Analytical Chemical Characterization Method for Dissolved Organic Matter in Rainwater

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The complex mixture of organic compounds in the atmosphere influences climate, air quality, and ecosystem processes. Atmospheric pressure electrospray ionization mass spectrometry (APESI-MS) was evaluated as a potential tool for direct measurement of the total suite of individual dissolved organic matter (DOM) compounds in rainwater. The APESI-MS response was linear to all DOM compounds of atmospheric significance examined as standard solutions. Urban precipitation samples from New Brunswick, NJ (USA) were analyzed by APESI-MS over the mass-to-charge (m/z) range 50–3000. Over 95% of the m/z ions detected were in the low m/z range (50–500). Over 300 unique m/z ions were detected across the 11 rainwater samples indicating the complexity of the mixture of DOM in rainwater. Forty percent of the organic bases (positive mode detection) and 22% of the organic acids (negative mode) occurred in at least 6 of the 11 rainwater samples. Ions corresponding to the m/z of carboxylic acids standards (nonanedioic acid; 1,4-butanedicarboxylic acid; pentanedioic acid; hydroxybutanedioic acid; and butanedioic acid) and to reduced N standards (allylurea; caffeine; imidazole; and N-2-propenylurea) occurred in at least one of the 11 rainwater samples. Total dissolved organic carbon (DOC) estimated from the APESI-MS analysis and measured by standard DOC methods were not statistically different.

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Introduction

Precipitation is an efficient removal mechanism for water-soluble chemical substances in the atmosphere. Since the early 1980s wet deposition has been collected and analyzed routinely in the U.S. to determine air quality trends and understand the effects of atmospherically derived inorganic chemical substances (sulfate, nitrate and ammonium) on receiving ecosystems (1–3). Although organic substances have not been included as chemical species to be monitored within atmospheric deposition networks, organic matter has been characterized chemically in urban rainwater for over the past century using a diverse array of analytical chemical methods (4). These early studies included analyses of bulk dissolved organic carbon (DOC) or nitrogen (DON), functional group composition (carboxylic acid, carbonyl, amines, amino acids, sugars), and individual molecules (PAH compounds, plus others). More recently studies of dissolved organic compounds in rainwater have increased the number of individual compounds identified, mainly as carboxylic acids, aromatic alcohols, carbonyl compounds, and reduced nitrogen compounds (e.g., refs 5–10). In addition, assessments of polar organic compounds in the atmosphere have considered compounds likely to be removed through cloud processing and wet removal processes (11–13). These studies demonstrate the possibility that many other organic chemical groups (polyols, ketoacids, hydroxy acids, hydroxy nitrates) are present in precipitation but go undetected as individual chemical substances and are lumped collectively as bulk dissolved organic matter (DOM).

Understanding the nature of organic matter in the atmosphere, including rainwater, is important for many reasons. Organic matter represents roughly half of the aerosol mass, influences cloud albedo, increases cloud condensation nuclei concentrations, contributes to atmospheric visibility impairment, tropospheric ozone production, acidity of rainwater, and nutrient enrichment of ecosystems, among others (6, 14–18). DOM present in the atmosphere is highly complex and poses a significant analytical chemical challenge. This is especially true from a materials mass balance framework where most or all of the DOM compounds require detection and quantitation. Few studies of rainwater DOM have related the individual compounds detected to the total dissolved organic matter. Recent work in North Carolina reported organic acids as the largest contributor (40%) to the total rainwater DOC with total aldehydes and amino acids contributing 8% and 2% of the total DOC (19, 20). Generally less than 40% of DOC in rainwater is identified (20). Fogwater DOC chemical mass balance studies can account for approximately 20% or less of constituent chemical compound classes (low molecular weight carboxylic acids, carbonyl compounds) (21–24).

No single analytical method has been able to detect and quantify single DOM compounds directly in a rainwater sample. Typically, extraction, preconcentration, and derivatization steps are required to detect trace DOM compounds in rainwater by conventional instrumentation (UV/VIS, electrochemical, gas chromatography/mass spectrometry, ion chromatography). The key limitation for molecular level and compound class level identification has been a combination of (1) the low level of DOC (and consequently of individual polar organic compounds) and (2) the analytical need for measuring compounds in a polar medium (e.g., rainwater).

Commercially available high pressure liquid chromatography/mass spectrometry (HPLC/MS) instruments (25) offer

TABLE 1. Ion Generation in APESI-MS

positive ion detection	
[M+H] ⁺	acid conditions
[M+Na] ⁺ , [M+K] ⁺	salts present
[M+NH ₄] ⁺	ammonium buffer present
[M+X] ⁺	X = solvent or buffer cation
[2M+H] ⁺	dimer formed at high analyte concentrations
[M+H+S] ⁺	solvent adducts
negative ion detection	
[M-H] ⁻	basic conditions
[M+X] ⁻	X = solvent or buffer

new possibilities for directly detecting DOM compounds in rainwater. Atmospheric pressure electrospray ionization (APESI) is a soft ionization method that is combined with quadrupole mass detection. Unlike GC/MS electron impact ionization, APESI is based on the dispersion of a liquid into small charged droplets in an electrostatic field (26). Because of this ionization process, APESI-MS provides molecular weight information as a mass-to-charge (*m/z*) ion. The molecular species detected depend on the nature of the sample and the analytical conditions, including solvent composition and pH (25, 27, 28). Table 1 gives an overview of potential ion generation that is important in the interpretation of APESI mass spectra. In addition to these molecular ion possibilities, most high molecular weight compounds produce multiply charged ions under APESI-MS (26–30). The multiply charged ion cluster is usually in the 500–3000 *m/z* range. Therefore, APESI-MS provides molecular information and has the unique requirement that samples must be introduced as solutions into the electrospray source region, making it an attractive direct method for detecting potentially all DOM compounds in precipitation samples.

The objective of this study was to develop and evaluate APESI-MS as a potential tool for the direct measurement of total DOM and individual DOM compounds in rainwater. Detector responses to DOM compounds of atmospheric significance were studied through analyses of standard solutions. Urban precipitation samples were collected and analyzed by APESI-MS to evaluate DOM compounds detected in terms of *m/z*, ion abundance, and occurrence in individual

rain events. A data handling protocol was developed for the *m/z* ions obtained from the APESI-MS. The APESI-MS method was compared to total DOC measured independently.

Experimental Section

Precipitation Collection. Precipitation was collected from a suburban site in the northeastern U.S. (New Brunswick, NJ; Latitude 40°28' N; Longitude 74°26' W; elevation 26 m). The site is a surface air quality and meteorological site supported by the NJ Department of Environmental Protection and is part of several other larger air monitoring networks, such as North American Research Strategy for Tropospheric Ozone - - Northeast Network (NARSTO-NE) (31) and the North East States for Coordinated Air Use Management (NESCAUM). Rainwater samples were collected between April and June on five dates in 1999 and six dates in 2000 using a precipitation collector (fitted with a stainless steel liner) that opens only during wetfall events (Aerochem Metrics Model 301, Bushnell, FL). Sample retrieval occurred within 2–4 h after rainfall stopped to minimize biological decomposition of DOM. Samples were filtered immediately through glass fiber filters (Whatman GFF; prebaked at 500 °C for at least 4 h to reduce organic contamination; pre-rinsed with E-pure water, Barnstead, Inc.) after temperature and pH were measured. Samples were stored frozen in polypropylene tubes until analysis.

Field blanks were prepared by placing 800 mL of E-pure water into the rainwater collector. After 17 h the water was sampled, filtered, and stored (frozen) until analysis using the same procedures used for rainwater samples. Procedural blanks consisted of E-pure water that was sampled and analyzed using the same procedures used for rainwater samples to check for contamination due to laboratory sample handling (pipetting, sample vials) and analysis.

Analytical Methods. APESI-MS. Direct analysis of DOM was conducted using an Agilent 1100 Liquid Chromatograph/Mass Spectrometer (LC/MS) consisting of an autosampler and quadrupole mass-selective detector equipped with an APESI source. The autosampler injected samples and standard solutions (20 µL) from individual vials into the LC system. In this initial study of total DOM in rainwater, no LC column was used; flow bypassed the analytical column and went directly to the APESI source region of the mass spectrometer.

TABLE 2. Response of APESI-MS to Standards (20 µL Injections) over the Concentration Range 0.025 to 1 µM^{a,b}

compound (<i>common name</i>)	molecular formula	molecular weight	slope	r ²
Negative Mode				
nitric acid	HNO ₃	63.0	1072	0.995
butanedioic acid (<i>succinic acid</i>)	C ₄ H ₆ O ₄	118.1	2703	0.982
pentanedioic acid (<i>glutaric acid</i>)	C ₅ H ₈ O ₄	132.1	3572	0.987
hydroxybutanedioic acid (<i>malic acid</i>)	C ₄ H ₆ O ₅	134.1	2496	0.997
1,4-butanedicarboxylic acid (<i>adipic acid</i>)	C ₆ H ₁₀ O ₄	146.1	4775	0.975
nitrobenzoic acid	C ₇ H ₅ NO ₄	167.1	14649	0.991
1,6-hexanedicarboxylic acid (<i>suberic acid</i>)	C ₈ H ₁₄ O ₄	174.2	9918	0.994
nonanedioic acid (<i>azelaic acid</i>)	C ₉ H ₁₆ O ₄	188.2	8971	0.992
average (SD)			6023 (4695)	
Positive Mode				
imidazole	C ₃ H ₄ N ₂	68.08	10881	0.999
N-2-propenylurea (<i>allylurea</i>)	C ₄ H ₈ N ₂ O	100.12	17147 ^c	0.983
N-butyl-1-butanamine (<i>N-dibutylamine</i>)	C ₈ H ₁₉ N	129.25	43801	0.996
3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione (<i>caffeine</i>)	C ₈ H ₁₀ N ₄ O ₂	194.2	15019 ^c	0.998
average (SD)			21712 (14954)	

^a Detection of particular compounds at the pg level is possible with the Agilent 1100 LC/MS (Agilent Technologies, Inc.). ^b Shown for each compound is whether it was detected in the positive or negative ionization mode, molecular formula, molecular weight, and linear regression statistics including slope (APESI-MS response/µM compound) and r². ^c [M+1] and [M+Na] ion.

The mobile phase (pH 3.5) was 50:50 v/v methanol/water (0.05% formic acid in E-pure water) with flow rate 0.22 mL min⁻¹. The APESI-MS measurements were performed in the positive and negative ionization modes with a fragmentor voltage of 40–80 V over the mass range 50 to 500 and 80 V over the mass range 500–3000. Nitrogen was the drying gas (350 °C, 10 L min⁻¹, 25 psig.). The capillary voltage was 3 kV. The electrospray ionization full-scan mass spectra (*m/z* 50–3000) were recorded on Agilent software (ChemStation version A.07.01) and then imported into EXCEL and ACCESS (Microsoft, Inc.) for statistical analysis and interpretation. Because of the low fragmentor voltage used in the ionization process, the APESI-MS generally does not fragment compounds but rather provides molecular weight information as a *m/z* ion (32).

The response of the APESI-MS to DOM compounds of atmospheric significance was studied through analyses of standards of known atmospheric occurrence prepared in E-pure water (Table 2). These encompass a range of compound classes including heterocycles, carboxylic acids, primary and secondary amines, amides, etc. The mixture of standard compounds (concentration range 25 nM to 1 μM) was analyzed in both the positive and negative modes.

For each rainwater sample, replicate injections (six) were made in both the positive and negative modes to establish a solid statistical basis for interpreting the *m/z* and ion abundance responses generated by the APESI-MS. All samples were analyzed over the *m/z* range of 50–500 *m/z*. Three precipitation samples only were analyzed for the higher range (500–3000 *m/z*) based on earlier rainwater analyses indicating that only a few DOM compounds occurred in that range.

The APESI-MS output for each sample was processed as follows to arrive at a final data set for analysis and interpretation. The mean ion abundance (± SD) for the replicate injections for each *m/z* (rounded to nearest integer) in each sample was calculated for the rainwater samples and for blanks. Each *m/z* with abundance statistically different from zero at the 0.05 level (t-test) (33) was retained. The rainwater samples then were corrected for procedural blanks by subtracting the ion abundance of any *m/z* found in the blanks from the same *m/z* in a sample. The SD of the corrected ion abundance for each *m/z* was calculated using propagation of error procedures (34). The final data set for a rainwater sample included the average (± SD) ion abundance for each remaining *m/z* with ion abundances that were statistically different from zero. Because of the generally increased variability in detecting compounds with ion abundances < 500, only *m/z* with ion abundances > 500 were included in the final data set.

Bulk Constituent Analysis. Rainwater samples were analyzed for the following bulk chemical properties: DOC (Shimadzu 5000A high-temperature combustion; (35)), dissolved inorganic nitrogen (DIN: ammonium (36), nitrite plus nitrate (37)), and DON determined by the difference between total dissolved N (Antek, Inc. 7000 TN Analyzer (18)) and DIN.

Results and Discussion

Standards. A variety of polar organic compounds with known occurrences in U.S. urban and rural airsheds were prepared as authentic standards (Table 2). The molecular ions corresponding to each compound were verified and the response factors calculated to establish precision and reproducibility over concentration ranges typical for the urban precipitation samples examined in this study. The mobile phase pH of 3.5 had hydrogen ion concentrations high enough that the monocarboxylic acids and dicarboxylic acids were dissociated and were detected as [M-1] *m/z* ions, as was the inorganic nitric acid standard. The reduced nitrogen compounds

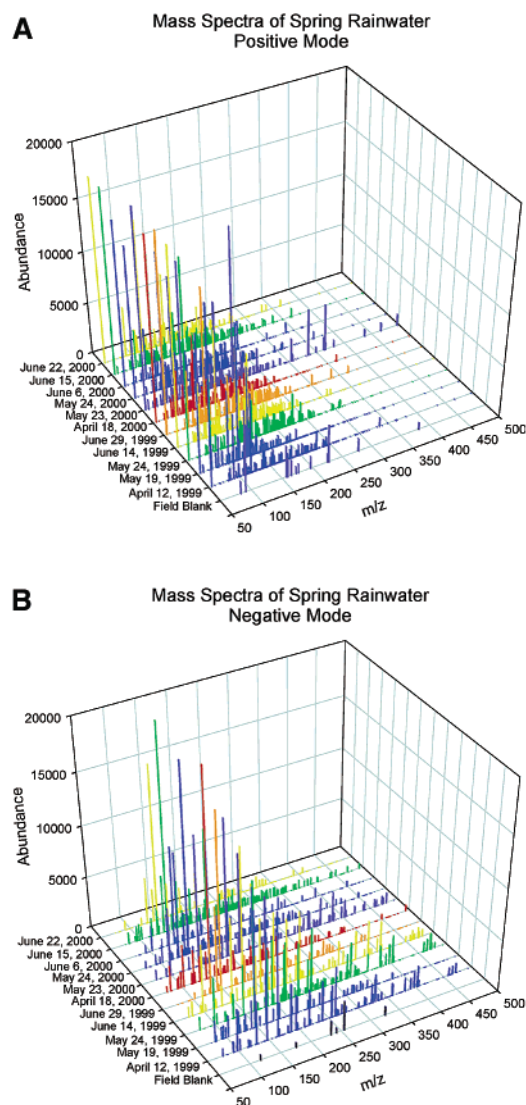


FIGURE 1. A) Mass-to-charge ratio (*m/z*) and abundance of ions detected in positive ionization mode with APESI-MS for field blank and 11 rainwater samples; B) Mass to charge (*m/z*) and abundance of ions detected in negative ionization mode with APESI-MS for field blank and 11 rainwater samples; *m/z* 62 (NO₃⁻) and 97 (HSO₄⁻) are not shown.

occurred as either [M+1] or sodium adduct [M+23] *m/z* ions. In cases where the reduced organic nitrogen compounds exhibited both [M+1] and [M+23] forms of the molecule, both ions were summed and response factors calculated accordingly. This approach to tracking reduced nitrogen compounds in solution is valid based on the linear regression statistics of slope and *r*² results (Table 2).

APESI-MS Rainwater Analysis. A large number of *m/z* ions were detected in the rainwater samples by APESI-MS as either bases (positive ionization mode) or acids (negative mode) indicating the complex chemistry of the rainwater (Figure 1A and B). The number of compounds detected in any one of the 11 rainwater samples ranged from 66 to 196 for the *m/z* range of 50–500 (see Table A Supporting Information). A total of 305 unique *m/z* were detected across the 11 rainwater samples, with a similar number detected in the positive and negative modes (141 and 164, respectively). Abundances for individual *m/z* ions ranged from 500 (minimum reported here) to 19,173 in the positive mode and to 22,511 in the negative mode (see Table A Supporting Information), indicating considerable variation in the concentrations of individual compounds within a sample. Nitrate

TABLE 3. Bulk Properties of Rainwater Samples Collected in New Brunswick, NJ^a

date collected	storm trajectory	rainfall amount, cm	temp, °C	pH	NO ₃ -N, μM	NH ₄ -N, μM	DOC-C, μM	DON-N, μM
April 12, 1999	SSW	2.2	5.0	4.4	27	16	62	7
May 19, 1999	W	0.4	19.0	4.8	21	20	50	9
May 24, 1999	SSW	4.4	18.5	4.4	16	22	137	7
June 14, 1999	W	0.4	22.0	4.7	21	22	77	12
June 29, 1999	SSW	0.5	26.0	4.4	22	8	78	10
April 18, 2000	WSW	1.4	5.0	4.4	42	34	106	21
May 23, 2000	W	0.1	18.0	3.8	78	20	230	12
May 24, 2000	W	2.4	18.0	4.5	34	34	150	8
June 6, 2000	WSW	0.6	14.5	4.2	13	6	36	2
June 15, 2000	WNW	0.1	20.0	4.4	44	39	120	15
June 22, 2000	WSW	0.5	23.0	4.4	25	13	60	3

^a PO₄ concentrations were always <0.1 μM.

and HSO₄⁻ were common, dominant inorganic ions present in all 11 rainwater samples (negative mode *m/z* 62 and 97, respectively) with mean ion abundances of 26,331 and 54,250, respectively (not included in the above statistics). Unless explicitly stated, data for these inorganic ions are not included in the data analysis in this paper.

The above statistics are for *m/z* between 50 and 500, which accounts for almost all of the compounds detected by APESI-MS in the rainwater samples. This is demonstrated by analysis in both the low (50–500) and high (500–3000) *m/z* range of three rainwater samples. In the high *m/z* range there were no compounds detected in the positive mode and eight or less (7, 8, and 2) *m/z* detected in the negative mode, with ion abundances > 500 (see Table A Supporting Information). This contrasts with the large number of *m/z* detected in the low *m/z* range in these rain samples. Throughout the remainder of this paper only data for *m/z* between 50 and 500 are considered.

Bulk Properties. The C and N concentrations of the bulk DOM in the 11 rainwater samples were similar to previously reported concentrations in rainwater (38, 39) (Table 3). Both nitrate and ammonium were important components of the inorganic-N (DIN) content of these rainwater samples. pH ranged from 3.8 to 4.8.

Field Blanks. Contamination due to field sampling and laboratory sample processing was minimal. Bulk concentrations in field blanks were as follows: 2 μM DOC-C, 0.3 μM NH₄, <0.1 μM NO₃. This is consistent with the results of the APESI-MS molecular level analysis of the DOM in the field blanks. There were only 12 *m/z* with ion abundances > 500 detected in the positive mode and 6 *m/z* with ion abundances > 500 in the negative mode; most of those had ion abundances less than 2000 (Figure 1).

Comparison of APESI-MS with Bulk DOC Measurements. Two approaches were used to compare the total DOC concentration in rainwater estimated from APESI-MS data to the bulk DOC concentration measured by standard methods (Table 3). In the first approach, total organic C content from APESI-MS data for 3 rainwater samples was estimated by applying the average (± SD) APESI-MS response factor for all standard organic compounds detected in the positive or negative mode (Table 2) to the ion abundance response for each *m/z* in a rainwater sample in either the positive or negative mode, respectively. A carbon weight per molecular weight conversion factor of 2.1 was used to account for H, O, N and other elements other than C (40). All *m/z* were assumed to be singly charged compounds. The total C content in the sample was then estimated by summing the C content of all compounds from both the negative and positive modes. The total DOC concentration in each of the three rainwater samples estimated from the above approach was not statistically different (95% confidence interval; Tukey

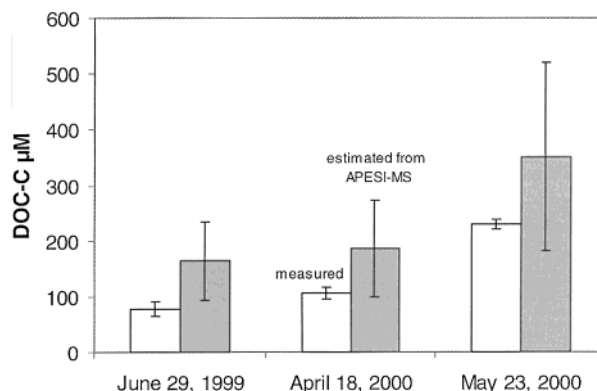


FIGURE 2. Total DOC concentration for three rainwater samples determined by high temperature combustion methods and estimated from APESI-MS are not statistically different. This suggests that the APESI-MS approach is not missing a large component of the complex mixture of organic compounds in rainwater. The range in APESI-MS response factors for different standards was used (mean ± SD; Table 2) which accounts for the large variation in the estimated APESI-MS total DOC concentrations for a sample. (see text for assumptions and details).

Kramer test (33)) than the DOC concentration measured directly by standard methods (35) (Figure 2). Although the total DOC concentration estimated from the APESI-MS data involved a number of approximations, the relative similarity of these estimates to the concentration measured using standard methods for bulk DOC suggests that the APESI-MS approach is not missing a large component of the complex mixture of organic compounds in rainwater. The generally higher (although not statistically significant) DOC estimate from APESI-MS compared to the bulk DOC may reflect detection of inorganic ions other than nitrate and sulfate (which were removed from the APESI-MS calculation).

As a further indication that the APESI-MS method is detecting most of the dissolved organic compounds in rainwater we compared the sum of all *m/z* abundances (unitless) (positive plus negative modes) for each of the 11 rainwater samples with the total DOC measured by standard methods. There was a statistically significant linear relationship between these two measures ($r^2 = 0.72$; $p = 0.05$).

Interpretation of Mass/Charge Ion Abundances. The complex chemistry of the 11 spring rainwater samples is illustrated by the many organic compounds present as organic bases (positive mode analysis) or organic acids (negative mode) (Figure 1A,B). Although chemically complex, the rainwater samples exhibit common *m/z* ions as indicated by the frequency of occurrence of *m/z* ions detected in the rainwater samples. Twenty-two *m/z* ions were detected in all 11 rainwater samples (Figure 3A plus 3B). There was

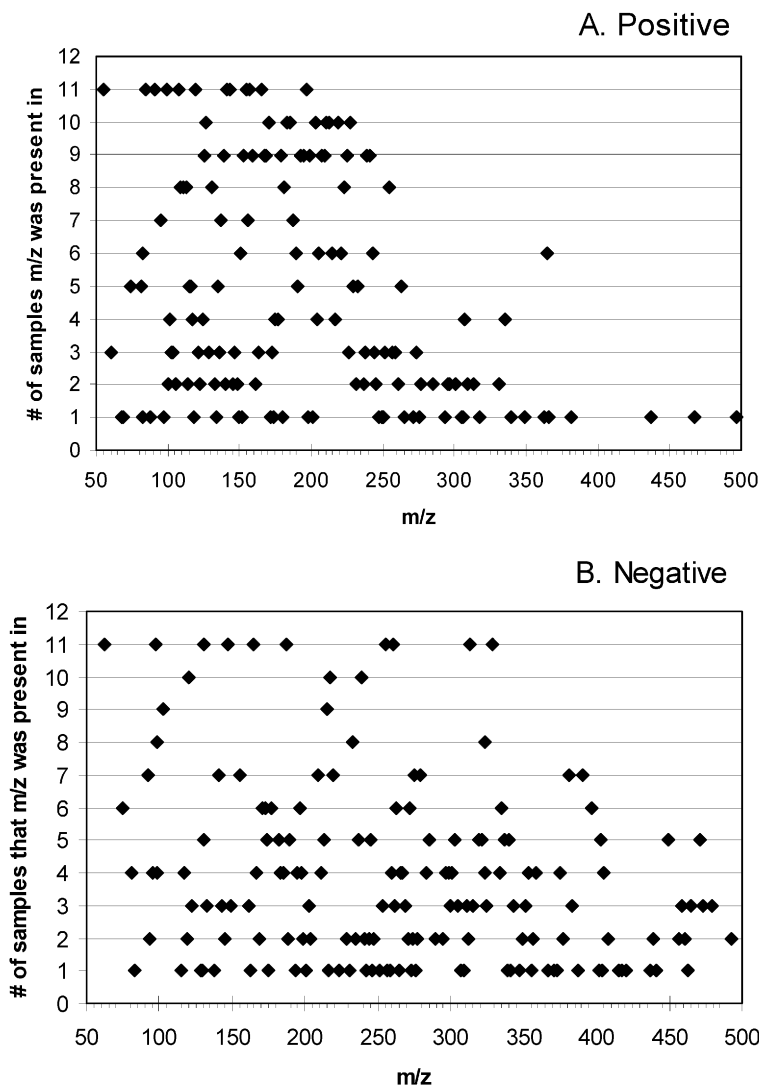


FIGURE 3. Frequency of occurrence of m/z ions detected by APESI-MS in 11 rainwater samples in A) positive ionization mode and B) negative ionization mode. The m/z for NO_3^- (62) and HSO_4^- (97) are included.

a higher degree of similarity among rainwater samples in the organic bases than in the organic acids. For example, 40% of the organic bases occurred in 6 or more of the 11 rainwater samples, while only 22% of the organic acids occurred in 6 or more samples. Also, the organic base m/z ions clustered predominantly in a lower and narrower mass range (m/z 55 to 250) compared to the m/z ions corresponding to the organic acids (m/z 70 to 400).

Identification of specific compounds and calculation of their concentrations in the rainwater samples requires determining the APESI-MS response factor for specific compounds and comparing the behavior (e.g., retention time, different mobile phase conditions) on LC columns of authentic compound standards and the corresponding m/z ion in the rainwater samples. This is currently underway. In the meantime, we have examined the m/z ions in the rainwater samples for matches with those of our standard m/z ions and used corresponding response factors (Table 2) for preliminary identification and concentration calculations.

The m/z ion corresponding to caffeine was present in nine New Brunswick, NJ, rainwater samples (Figure 4) with estimated concentrations of $1.4 \pm 0.5 \mu\text{M C}$. Only a few samples contained m/z ions in the positive mode that correspond to the other reduced nitrogen atmospheric standard compounds analyzed to date (allylurea 1 sample;

imidazole 1 sample; N-2 propenylurea 2 samples). However, there were numerous m/z ions detected in the rainwater samples that we have not yet analyzed standards for but that correspond to organic compounds reported previously in atmospheric samples (e.g., heterocyclic N compounds such as ethylpyridine, methenamine, bipyridyl, aminopyridine, phenylpyridine (41)).

The m/z ions of organic acids present in the New Brunswick, NJ, rainwater corresponded well with the dicarboxylic acid standard m/z ions (Figure 4). These correspond to the C4 to C9 homologues. The m/z ion corresponding to nonanedioic acid was present in all rainwater samples. There was a decreasing frequency of occurrence for m/z ions corresponding to pentanedioic acid and the C4 dicarboxylic acid homologues. Dicarboxylic acids are considered to originate both from primary emissions and secondary gas-to-particle conversion processes. These organic acids have been identified in rainwater as dissolved organic matter (reviewed by refs 4, 10, 11) and measured as common polar organic compounds associated with urban particulate matter (e.g., refs 9, 41–44). Our estimated concentrations are similar to those reported previously in Los Angeles, CA rainwater for butanedioic acid (this study; reported in ref 43) (1.4 ± 0.2 ; $4 \pm 7 \mu\text{M C}$), pentanedioic acid (2.1 ± 1 ; $1.6 \pm 2.9 \mu\text{M C}$), and 1,4-butanedicarboxylic acid (1.0 ± 0.4 ; $0.7 \pm 1.6 \mu\text{M C}$) and approximately 10 times greater for nonanedioic acid ($3 \pm$

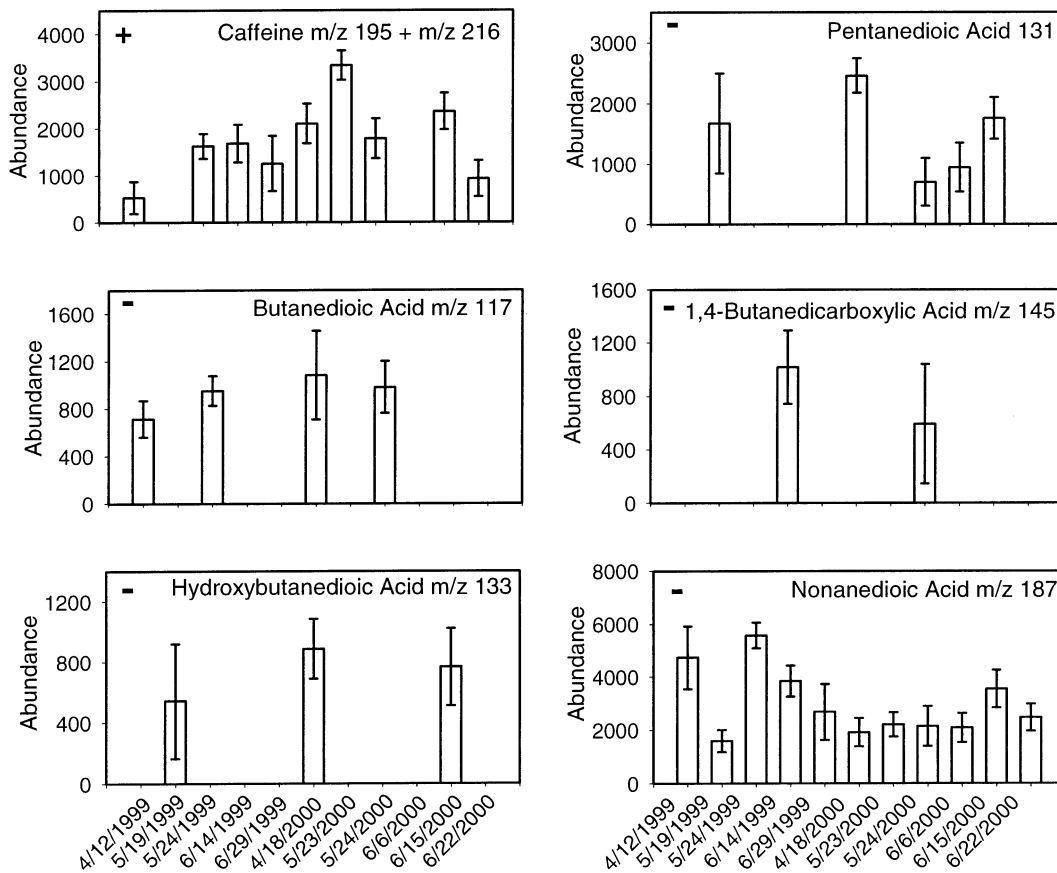


FIGURE 4. Abundance (mean \pm SD) of selected ions in the 11 rainwater samples detected by APESI-MS. Detection in the positive or negative ionization mode is indicated by a + or -, respectively, in the upper left corner of the graph. The compound name of the authentic standard that corresponds to the m/z ion is indicated on each graph.

1.3; $0.4 \pm 0.4 \mu\text{M}$ C). The m/z ion corresponding to the nitrobenzoic acid standard (primary emission from diesel exhaust) was not detected in our rainwater samples. Additional m/z ions detected in the negative mode correspond to various amino acids (e.g., aspartic acid, leucine, arginine), carboxylic acids (e.g., 1,2-benzene dicarboxylic acid) and other compounds previously reported in atmospheric samples (e.g., refs 41). We are currently investigating the response of the APESI to standards of these compounds.

The total concentration of all DOC compounds ranged from 36 to 230 μM DOC-C (Table 3). Previous studies have suggested that no one compound comprises more than a small percent of the total DOC in rainwater (6, 19, 43, 45). Using APESI-MS to look at the total suite of compounds further supports this idea (Figure 1A,B). Not only are there a large number of compounds (over 300 unique m/z were detected), but the maximum concentration of any one of these compounds is likely to be less than a few μM given the maximum ion abundance of any single compound in a sample ($\sim 20,000$; Table A Supporting Information) and the APESI-MS response factors for a range of compounds (Table 2).

The current study suggests that APESI-MS can provide considerable, new insight into the complexity of the mixture of compounds that comprise the bulk DOM in rainwater by providing molecular level information on the following: 1) the number and the m/z distribution of compounds in a sample, 2) whether a particular compound has primarily basic or acidic functional groups, and 3) the concentration of individual compounds. This information can then be used to study differences in the patterns of occurrence and concentration of the suite of compounds both within and among rainwater samples. Further development of this

method for rainwater and other aquatic samples is underway, including its application to studies of DOM bioavailability.

Acknowledgments

This material is based upon work supported by the National Science Foundation Environmental Biogeochemistry Program under Grant No. 9807621, NOAA NJ Sea Grant No. R/E-9706 (NJSG-01-467), and NJDEP No. SR99-030. The authors thank these funding agencies for their support. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation, NOAA NJ Sea Grant or the NJ Department of Environmental Protection.

Supporting Information Available

Table summarizing results of APESI-MS analysis of 11 rainwater samples including lowest and highest m/z detected, number of m/z in each sample, maximum and average ion abundances. Results for negative and positive mode analyses are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review June 4, 2002. Revised manuscript received September 23, 2002. Accepted October 18, 2002.

ES025848X