

# Semicontinuous Measurements of Organic Carbon and Acidity during the Pittsburgh Air Quality Study: Implications for Acid-Catalyzed Organic Aerosol Formation

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Laboratory evidence suggests that inorganic acid seed particles may increase secondary organic aerosol yields secondary organic aerosol (SOA) through heterogeneous chemistry. Additional laboratory studies, however, report that organic acidity generated in the same photochemical process by which SOA is formed may be sufficient to catalyze these heterogeneous reactions. Understanding the interaction between inorganic acidity and SOA mass is important when evaluating emission controls to meet PM<sub>2.5</sub> regulations. We examine semicontinuous measurements of organic carbon (OC), elemental carbon (EC), and inorganic species from the Pittsburgh Air Quality Study to determine if we can detect coupling in the variations of inorganic acidity and OC. We were not able to detect significant enhancements of SOA production due to inorganic acidity in Western Pennsylvania most of the time, but its signal might have been lost in the noise. If we assume a causal relationship between inorganic acidity and OC, reductions in OC for Western Pennsylvania that might result from drastic reductions in inorganic acidity were estimated to be  $2 \pm 4\%$  by a regression technique, and an upper bound for this geographic area was estimated to be  $5 \pm 8\%$  based on calculations from laboratory measurements.

## Introduction

The category of carbonaceous aerosols includes elemental carbon (EC) and organic carbon (OC). Emissions of EC are primarily from fossil fuel combustion or burning of biomass. OC in the atmosphere is either from these same sources or the result of oxidation reactions of volatile organic compounds (VOCs) emitted mainly by motor vehicles and vegetation (1). The latter type of OC is associated with what is called secondary organic aerosol (SOA), and the identification of specific compounds that comprise SOA still poses many challenges (2).

A previously unaccounted pathway for increased SOA formation was proposed by Jang and co-workers (3, 4). They proposed that heterogeneous reactions in aerosols, such as

acid-catalyzed carbonyl chemistry, can lead to large increases in SOA formation primarily through polymerization mechanisms; a "multifold" increase in organic aerosol yields was observed in the laboratory for heterogeneous reactions of aldehydes and also in SOA yields for acrolein and isoprene reacting with ozone when an acid seed was present, compared with the case where the acid seed was absent (4).

The presence of acid aerosols in the atmosphere is well documented, with anthropogenic emissions of SO<sub>2</sub> and NO<sub>x</sub> responsible for a large fraction of the acidity in the form of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, respectively (5–9). The significant implication of the work of Jang et al. (4) is that if atmospheric acidity is reduced through emission controls of inorganic precursor species (e.g., SO<sub>2</sub>), acid-catalyzed formation of SOA may also be reduced, thereby resulting in an effective control for PM<sub>2.5</sub> mass concentrations.

Since the seminal work by Jang and Kamens (3), other laboratory studies have found that acidic particles can act as catalysts for increased SOA formation. Iinuma et al. (10) reported that in the ozonolysis of  $\alpha$ -pinene, organic aerosol concentration increased by as much as 40% when inorganic acid-seed aerosols were present. Jang and co-workers (11, 12) observed increased reaction rates and increased yields of SOA over the duration of their studies in the presence of acid catalysts as opposed to their absence. Limbeck et al. (13) found that the presence of sulfuric-acid catalysts increased the formation of polymers resembling humic-like substances when dienes were photooxidized. Tolocka et al. (14) observed oligomeric products in the reaction of  $\alpha$ -pinene and ozone and proposed reaction pathways for polymerization of organic molecules to proceed in the aerosol phase. Furthermore, Gao et al. (15) observed the presence of more high-molecular weight compounds in the presence of acid seed than with seeds that were not acidic.

Kalberer et al. (16), however, reported that polymerization can proceed without preexisting strong acid seed particles. In a laboratory study of the photooxidation of 1,3,5-trimethylbenzene and NO<sub>x</sub>, organic acids and nitric acid formed from the photooxidation reaction in amounts sufficient to catalyze acetal polymerization reactions. In addition, the polymerization reactions observed continued for more than 25 h, implying that polymerization reactions may occur during the entire lifetime of a tropospheric aerosol. Gao et al. (15) suggested this as a possible explanation for their observation of high molecular weight compounds formed even in the presence of nonacid seeds. In light of the potential implications of the work of Jang et al. (4) and Kalberer et al. (16), it is desirable to know if inorganic acidity is indeed responsible for increased SOA formation in the atmosphere. Current research has focused on laboratory studies, some at particularly high concentrations of VOCs, oxidants, or acidity. At this stage it is difficult to extend conclusions drawn from these studies to the complex atmospheric system.

A synthesis of field studies has likewise produced inconclusive results. From an analysis of 24-h filter-based measurements from the Speciation Trends Network, Chu (17) reported high levels of both sulfate and organic aerosols accompanied by ammonia deficiency during an episode on July 18th of 2001 on the East Coast. From this observation, the author suggested that SOA formation through heterogeneous reactions may be occurring during the summer. Using higher time-resolution data from the Aerodyne Mass Spectrometer, however, Zhang et al. (18) observed "negligible enhancement" of organics in the presence of acidic aerosols in Pittsburgh during 15 days in September 2002. As Zhang et al. (19) have reported, it may also be possible that the

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periods of high acidity and peak periods of secondary organic aerosol formation do not necessarily coincide in the same period, and 24-h measurements are unable to capture the separate diurnal patterns of these species.

The metric used to quantify inorganic aerosol acidity has also varied across field studies. Sulfate has commonly used as a surrogate, but this may lead to problems because a large fraction of the sulfate may be neutralized by ammonia. Another common metric for acidity is the deficit of ammonia with respect to the quantity required to fully neutralize the strong acids (i.e., sulfate and nitrate) present in the aerosol (17, 19). Estimates of acidity from such an ion-balance approach are equivalent to the total extractable acidity obtained from pH measurements of aqueous extracts of particles (9). Also referred to as the aerosol strong acidity, this metric gives an indication of the total amount of hydrogen that can become available in the particle when removed from its present environment (9). However, the strong acidity often overestimates the actual particle acidity because some of the hydrogen is associated with bisulfate under ambient conditions.

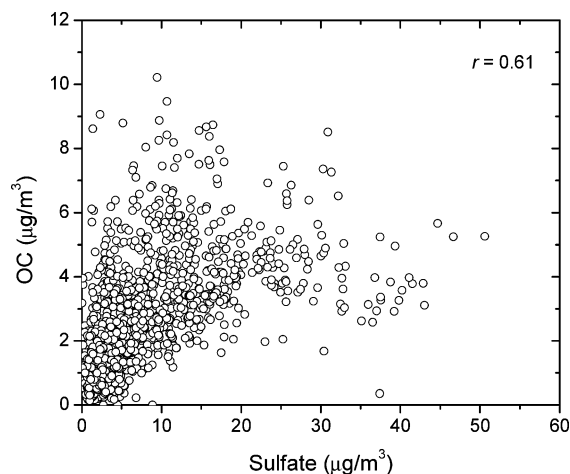
To address these issues, this work examines time-resolved (1–4 h) field measurements collected during the Pittsburgh Air Quality Study (PAQS) from July 2001 to July 2002 to determine the potential enhancement in OC concentrations during periods of high inorganic acidity in Pittsburgh. Measurements of inorganic species are combined with a thermodynamic model to calculate concentrations of aerosol free acidity, and this analysis is extended over a period of several seasons. In addition, some estimates are made as to the possible reductions in OC that can be achieved as a result of reductions in inorganic acidity.

## Experimental Section

Pittsburgh, PA, is located in the northeastern U.S., between the major agricultural and utility emissions in the Midwest and large urban and coastal areas in the East. Between July 2001 and July 2002, measurements of aerosols, gases, and meteorological conditions were made at the Pittsburgh Air Quality Study monitoring station. The site was located approximately 6 km east of downtown Pittsburgh, several hundred meters from the closest appreciable emission sources. From July 2001 to March 2002, the mean  $\text{PM}_{2.5}$  concentration was  $16.1 \mu\text{g}/\text{m}^3$ , with organic matter contributing on average 30% of this mass (20).

Continuous measurements of temperature, ultraviolet (UV) radiation intensity, relative humidity (RH), and gas-phase concentrations of  $\text{O}_3$ ,  $\text{NO}$ ,  $\text{NO}_x$ , and  $\text{CO}$  were made and documented by Wittig et al. (21). Two to 4 h measurements of OC and EC were made by an in-situ OC/EC analyzer (22–24). Using measurements of ozone,  $\text{NO}_x$ ,  $\text{CO}$ , and UV radiation collected by collocated samplers at the site, the EC-tracer method was used by Cabada et al. (23) to derive a primary OC/EC ratio for sources affecting the region and then to estimate the SOA concentration.

To estimate the concentration of  $\text{H}^+$ , or free acidity, 1–2-h measurements of sulfate, total nitric acid, and total ammonia were made with semicontinuous instruments and used as inputs to a chemical equilibrium model, GFEMN (25). A steam-jet aerosol collector (26) captured aerosols and gases of these chemical species in a humidified chamber; resulting aqueous droplets were collected and analyzed by ion chromatography (DIONEX models DX-120 and DX-600 for water-soluble cations and anions, respectively) using a method described by Jaffrezzo et al. (27) for the anion analysis. Additionally, a R&P 8400S measured inorganic sulfate by a flash-volatilization technique (28). Concentrations reported by these semicontinuous instruments were calibrated against a filter-based speciation sampler and implemented for simulation as described by Wittig et al. (29) and Takahama



**FIGURE 1.** Correlation plot of OC and sulfate concentrations from July 2001 to July 2002.  $r$  is the sample correlation coefficient.

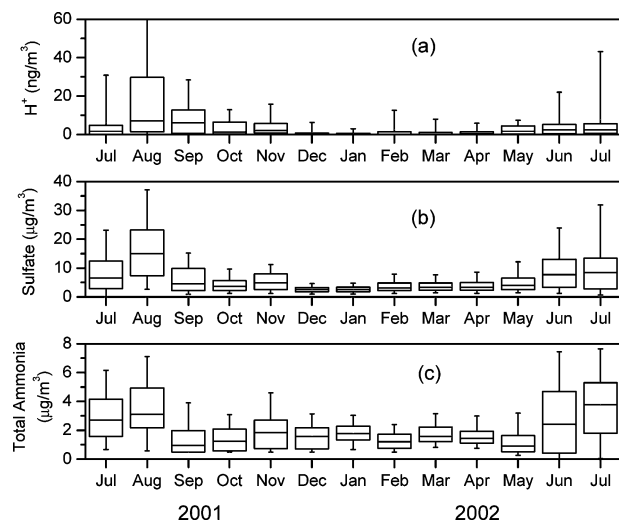
et al. (30). The thermodynamic calculations were made assuming particles were liquid, except when the measured growth factor (31) was near unity, indicating that the particles were solid. For these periods, the  $\text{H}^+$  concentrations were set to zero. The inorganic data were then averaged to match the sampling intervals of the in-situ OC/EC analyzer. Takahama et al. (30) showed that aerosol nitrate predictions from GFEMN agreed with observations within measurement uncertainties for most cases, which gives us some measure of confidence in our calculations of acidity.

The observed organic aerosol concentration field is relatively homogeneous in Western Pennsylvania (32) and most of the northeast U.S. Production of SOA takes place during the same time over a large area, and the system can be described by a box model to a first approximation (33). Therefore, the measurements represent the chemical processes taking place over a large area even if they are from a single location. This spatial homogeneity makes the PAQS data set suitable for this analysis because transport in and out of the region is a secondary effect.

## Analysis of Results

In the past, sulfate concentrations have been used as a surrogate for aerosol acidity (8). Figure 1 shows the relationship between OC and sulfate; the sample correlation coefficient ( $r$ ) of 0.61 indicates a mild correlation. Examining such a graph might suggest that during periods of high acidity, there are significantly larger quantities of organic aerosol that might be attributable to SOA from heterogeneous chemistry (17). However, there may be other possible explanations for this observation. First of all, each parcel of air has its own history of accumulated emissions. Air parcels coming from relatively clean areas tend to have lower pollutant concentrations, while air parcels coming from heavily populated and industrialized areas have higher concentrations. For example, sulfate and primary OC are both derived at least in part from stationary source combustion, which could explain some of the correlation between the two species. In addition, there are meteorological effects, such as the strength of atmospheric mixing, common to both sulfate and OC that may be causing the observed relationship in Figure 1.

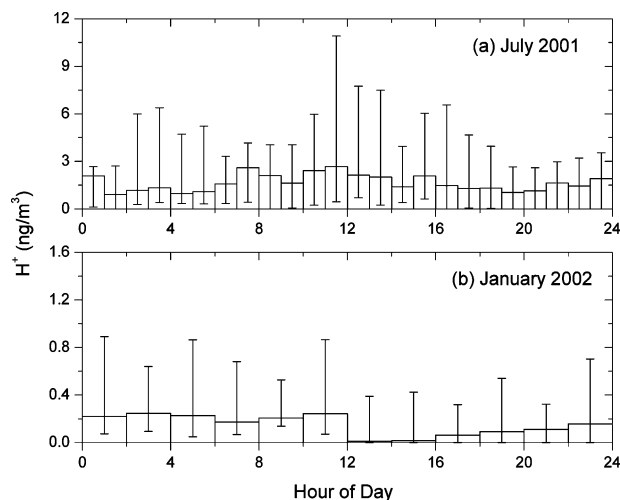
The use of free acidity ( $\text{H}^+$ ) calculated from thermodynamic principles has several advantages. Limbeck et al. (13) reported that free acidity and not the quantity of sulfate affects the formation of polymers. Furthermore, Cocker et al. (34) found that the presence of dry  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{HSO}_4$  seed particles did not affect the SOA production, but the organic aerosol yields depended on the composition



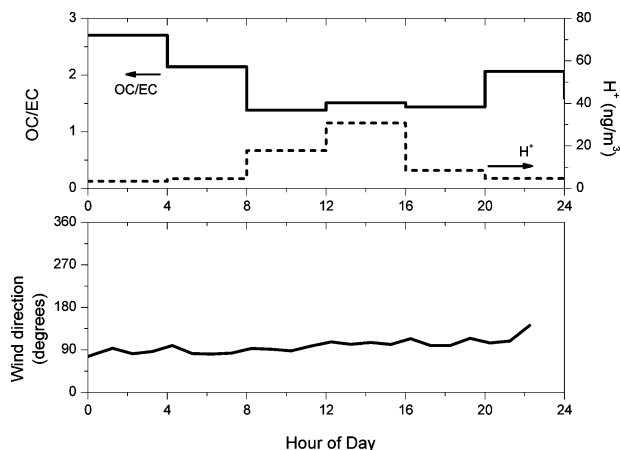
**FIGURE 2.** Boxplots of (a)  $\text{H}^+$ , (b) sulfate, and (c) total ammonia ( $\text{PM}_{2.5} + \text{gas}$ ) illustrating the seasonal variation of these species. Boxes enclose data within the 25th to 75th percentile range, black line in the box denotes median, and whiskers extend to the 5th and 95th percentile of the data.

of the seed aerosol when wet. Because the estimation of  $\text{H}^+$  by GFEMN is composition-dependent, the solution properties of the seed aerosol are taken into account when calculating the particle acidity. Sulfate and  $\text{H}^+$  are mildly but not strongly correlated ( $r = 0.68$ ) for our data set— $\text{H}^+$  is not only a function of the sulfate concentration but also the amount of neutralizing base (predominantly  $\text{NH}_3$  in this area), the presence of other acidic species (e.g., nitrate), and also the water content of the aerosol. Therefore, we proceed with the analysis as follows: (1) we use the  $\text{H}^+$  concentration as our metric of acidity, (2) we normalize the OC concentrations by the EC concentrations, which takes advantage of the fact that EC is mostly emitted by the same combustion sources as primary OC, and (3) we also examine wind directions in conjunction with the concentrations, as a change in wind direction can indicate a change in combustion source—each of which can have a different ratio of OC to EC emissions.

**Acidity.** Periods of high acidity ( $\text{H}^+$ ) are generally found during the summer months with fewer instances occurring closer to the winter season (Figure 2a).  $\text{H}^+$  in the aerosol phase calculated by GFEMN results from an aqueous-phase charge balance of primarily  $\text{H}_2\text{SO}_4$ , and to a lesser extent  $\text{HNO}_3$ , with  $\text{NH}_3$ . Sulfate concentrations are higher during the summer than in the winter (Figure 2b) primarily because the conversion rate of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  is faster during the warm and sunny summer days. Lower sulfate levels in the winter imply that the total ammonia (gas +  $\text{PM}_{2.5}$  aerosol) available with respect to  $\text{H}_2\text{SO}_4$  is higher (Figure 2b,c). In general, this results in a large fraction of bisulfate ions during the summer and more sulfate ions during the winter; the free acidity reflects this difference. During the summer months, the  $\text{H}^+$  concentration is likely to be higher during the daytime (Figure 3a), while the opposite is true for the winter (Figure 3b). Diurnal variations in acidity may be caused by many factors. For example, during high periods of photochemical activity in the morning and early afternoon, production of nitric acid and sulfate may exceed their deposition rates, resulting in a rise in the concentrations of these species. It is likely that the strong diurnal pattern in acidity observed during the summer is primarily due to the photochemical production of sulfate. During the winter, however, a combination of aerosol composition and low RHs often induced solid-phase transitions in the aerosols (31), leading to lower concentrations of acidity during the afternoons.



**FIGURE 3.** Time-series plots of diurnal variations in acidity for (a) July 2001 and (b) January 2002. Bars represent the median and the error bars extend to the 25th and 75th percentile of the monthly data for each sampling period.

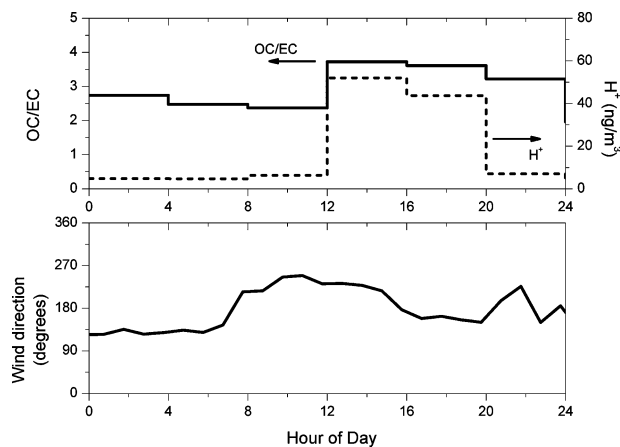


**FIGURE 4.** Time series of OC/EC,  $\text{H}^+$ , and wind direction for March 27, 2002.

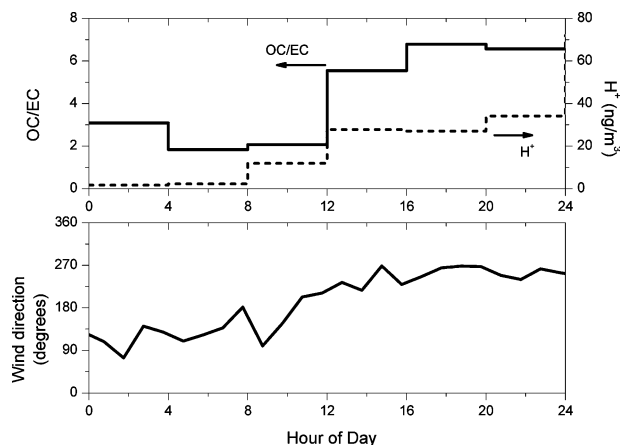
**OC/EC Ratio, Acidity, and Wind Direction.** Measurements of wind direction were used to determine if changes in OC/EC ratios could have occurred as a result of change in source signature. Time series plots of OC/EC ratios, acidity ( $\text{H}^+$ ), and wind direction were examined for periods in which the aerosol became increasingly acidic. In the examination of these time series from July 2001 to July 2002, 104 occurrences of significant increases in  $\text{H}^+$  were visually identified.

Possible evidence for acid-catalyzed SOA taking place in this region would be illustrated by an increase in the OC/EC ratio accompanying or following a period of high  $\text{H}^+$  concentrations, when the wind direction does not shift dramatically during this period. We might expect this result if the OC and EC emission source is constant (i.e. characteristic emission ratio of OC to EC remains the same), but OC/EC ratios increase as acid-catalyzed SOA formation proceeds. In general, there was no clear evidence that acid-catalyzed SOA formation was consistently observable in Pittsburgh during our study period. In fact, in some cases the OC/EC decreased when the aerosol became acidic, suggesting possibilities of other processes dominating the change in organic aerosol concentrations or simply the decoupled behavior of organic and inorganic aerosols. Figure 4 shows time-series from March 27, 2002, the wind direction is relatively steady, but between 4 a.m. and 2 p.m., OC/EC decreased from 2.1 to 1.4 at the same time that  $\text{H}^+$  increased





**FIGURE 5.** Time series of OC/EC,  $H^+$ , and wind direction for June 25, 2002.

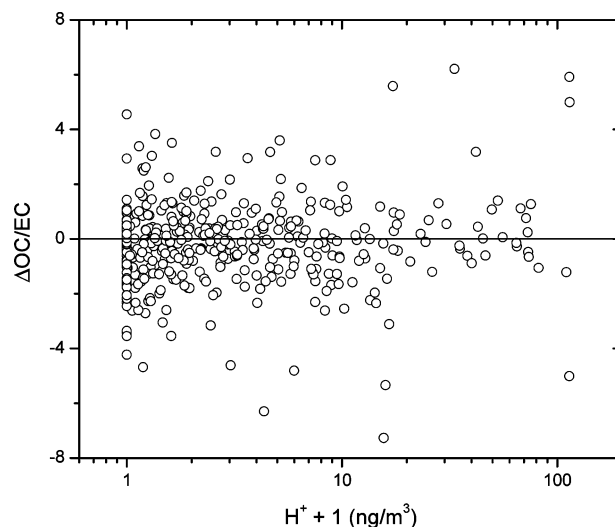


**FIGURE 6.** Time series of OC/EC,  $H^+$ , and wind direction for July 17, 2002.

from 5 to 18  $\text{ng}/\text{m}^3$ . Thirteen of the 104 instances of  $H^+$  increase exhibited this behavior, where the inorganic acidity increased and the OC/EC decreased simultaneously under conditions of constant wind direction.

Figure 5 shows an example of a case where both the OC/EC and the acidity increased together, which was observed on June 25, 2002, during midday, and the wind direction was not extremely steady but on average from the same direction. The  $H^+$  concentration increased from its initial value of 6  $\text{ng}/\text{m}^3$  to 52  $\text{ng}/\text{m}^3$ , the latter being one of the highest values attained during the study period. Twenty-two of the 104 accounts of  $H^+$  increase were of the second type, where inorganic acidity and OC/EC increased together under conditions of constant wind direction.

Changes in OC/EC accompanied by significant changes in wind direction, however, could be indicative of a change in the primary OC to EC ratio emitted by different sources or SOA transported into the region. Figure 6 illustrates this case, which was observed on July 17, 2002. Between 4 a.m. and 12 p.m., the wind direction changed steadily (also with increasing variability), shifting by almost 180 degrees over an 8-h period. At noon, the OC/EC and  $H^+$  increased together, with  $H^+$  concentrations again reaching a high value of 28  $\text{ng}/\text{m}^3$ , which may be possible evidence of acid-enhanced formation of SOA over Pittsburgh, but this may also be indicative of a source region rich in both primary organics and acidic aerosols. Thirty-eight of 104 counts of acidification were of this last type, where the inorganic acidity and OC/EC both increased during the same period but under varying wind direction.



**FIGURE 7.** Correlation plot of changes in OC/EC between periods  $k$  and  $k-1$  and acidity at  $k$ . A constant of 1  $\text{ng}/\text{m}^3$  is added to the  $H^+$  for displaying  $H^+ = 0 \text{ ng}/\text{m}^3$  values on a logarithmic scale.

In the 31 out of 104 cases remaining, there was no detectable change in OC/EC with increase in acidity. These observations may be explained by several means, including the decoupled behavior of inorganics and organics, the acidity perturbing organic aerosol concentrations by an immeasurable amount, or the positive and negative changes in OC/EC due to simultaneous atmospheric processes summing to an amount within measurement uncertainty.

Calculations of air mass back-trajectories with the HYSPLIT (NOAA) software on selected periods generally confirmed that measured wind directions at the site were indicative of source region. For example, 6-h back-trajectory calculations showed that during June 25, 2002, the air parcels that arrived at Pittsburgh at 10 a.m. and 2 p.m. both originated from the West. During the July 17, 2002, episode, however, the air parcel that arrived in Pittsburgh at 10 a.m. was transported from the Southeast, while the air parcel that arrived at 2 p.m. was transported from the Southwest after following a circuitous path around and over the city.

To formalize this analysis, observed changes in OC/EC and acidity were grouped according to wind directions that were relatively constant and those that were different between two successive sampling intervals. For this analysis, the data were averaged into regularly spaced intervals of 4 h. Wind directions that were different were determined by a test of statistical significance on the mean wind directions between two successive sampling periods. The change in mean wind direction was considered different if rejected by a two-sample  $t$ -test at an  $\alpha = 0.05$  significance level and was considered relatively constant otherwise. Though the wind direction data are by no means random or independently sampled, Ott and Mage (35) showed that the mean and variance calculated by the central limit theorem are good approximations when applied to data exhibiting serial correlation; therefore, our simple algorithm is acceptable. Figure 7 shows the change in OC/EC as a function of the geometric mean acidity between two successive periods  $k$  and  $k-1$ , for the case in which the change in wind direction between the two periods was relatively constant. If acid-catalyzed SOA formation were detectable in Pittsburgh, we would expect a positive correlation between the two variables, particularly in the region of high  $H^+$  concentrations. However, as evident in Figure 7, there is little observable correlation ( $r = 0.10$ ) between inorganic acidity and increase in OC/EC.

The change in OC/EC shows a similar lack of correlation with other measures of acidity. One such metric is the  $H^+$

concentration from the previous time interval—we might expect that this metric is important if the response of increase in OC/EC to availability of  $H^+$  is on the order of hours; indeed, Kalberer et al. (16) suggest that the OC increase due to acidity could occur over the lifetime of the aerosol. The correlation between  $\Delta OC/EC$  and  $H^+$  from the previous time interval is 0.07, which is lower than the correlation of  $H^+$  of the current time 4-h interval. In contrast, Czoschke et al. (36) report time scales for polymerization on the order of seconds. In the event that the acid-catalyzed SOA formation is rapid and proceeds with any amount of increase in  $H^+$ , we might expect a positive correlation between  $\Delta OC/EC$  and  $\Delta H^+$  over the same time periods. The sample correlation with changes in OC/EC from this analysis was 0.07.

Other metrics of acidity were also considered. Though the calculation of free acidity takes into the account the chemical composition, ambient RH, and associated water uptake by the aerosol, the pH provides additional information about the availability of  $H^+$  in solution as it indicates the quantity of  $H^+$  relative to the amount of water in solution. The sensitivity of the pH to the water content of the aerosol provides a means to examine periods when highly concentrated acidic particles exist for short durations, in which case the  $H^+$  contribution to the total  $H^+$  burden may not be significant, but ultrafine aerosol solutions highly concentrated in  $H^+$  may exist. Defining the pH as  $-\log[H^+]$  where  $[H^+]$  is the molarity of  $H^+$  in the solution, the pH for pure sulfuric acid at 35% RH is  $-1.1$ , according to calculations with AIM (37). The mean pH for all 4-h periods was 0.8, with a minimum of  $-0.9$  and 374 periods out of 1715 dropping below 0, often during the afternoons when RH was lowest. Despite the low values of pH attained, the correlation of  $\Delta OC/EC$  with pH with the current time period is  $-0.10$ , with the previous time period is  $-0.07$ , and with  $\Delta pH$  is  $-0.02$ . The negative values of correlation are as expected, as lower pH indicates higher acidity, but the absolute magnitudes of the correlations are not large. When the hydrogen ion activity, considering only nonidealities caused by the inorganic fraction of the aerosol, instead of its concentration is used to define pH, the correlations with  $\Delta OC/EC$  increase in some cases but remain small—the correlation of  $\Delta OC/EC$  and pH at the current time is  $-0.16$ , with  $\Delta OC/EC$  and pH from the previous time is  $-0.08$ , and  $\Delta OC/EC$  with the  $\Delta pH$  is  $-0.09$ .

There is also a possibility that the polymerization reactions that occur in the presence of acid catalysts are irreversible, or not reversible in atmospherically relevant time scales, and neutralization of the acidity will not lead to reductions in OC. To account for this effect, the relationships examined above were reanalyzed for periods only when the acidity increased. By this method, the strongest correlations observed were between  $\Delta OC/EC$  and the three metrics of acidity of the current time period. The correlations were 0.17,  $-0.18$ , and  $-0.28$  for  $H^+$  and pH defined by the hydrogen ion molarity and activity, respectively. These relationships are stronger than when data points for all changes in acidity are considered, but the correlations are still weak. Zhang et al. (19) showed that during nucleation events in Pittsburgh, unneutralized  $H_2SO_4$  existed for short periods in the morning during nucleation events, but rapid SOA formation and condensation occurred several hours after nucleation after the  $H_2SO_4$  had been largely neutralized by  $NH_3$ . Indeed, our analysis suggests that normalizing the airborne  $H^+$  concentrations by the water content showed little improvement in correlations of acidity with  $\Delta OC/EC$ .

### Estimating the Effect of Acidity on OC Concentrations

Though our method of analysis did not produce evidence of acid-catalyzed heterogeneous chemistry leading to increased SOA concentrations in Pittsburgh, it is possible that the effect of acidity on SOA was masked by the myriad of other

**TABLE 1. Sample Correlations of Measurements (with No Lag and Also When Lagged by One 4-h Time Period) with OC/EC**

variable	lag = 0	lag = 1
$H^+$	0.30	0.25
NO	$-0.25$	$-0.21$
$NO_x$	$-0.34$	$-0.28$
CO	$-0.17$	$-0.14$
$O_3$	0.41	0.37
UV	0.12	0.25
temperature	0.22	0.21
sulfate	0.25	0.23
1/NO	0.44	0.32
1/ $NO_x$	0.48	0.38
1/CO	0.16	0.14

atmospheric processes occurring simultaneously. Therefore, we wish to know what the upper limit of the effect that reducing inorganic acidity might have on OC concentrations over this area in the event that SOA enhancement is still occurring. For this purpose, we use two approaches: (1) predicting changes in OC from a regression model and (2) calculating the reduced OC for an assumed scenario.

**Regression Analysis.** To determine the contribution of  $H^+$  in explaining the variability in OC/EC, a regression model was constructed. Candidate regressors for the model were preselected based on our physical understanding of atmospheric chemistry—ozone, ultraviolet radiation, and high temperatures are favorable for SOA production; CO, NO, and  $NO_x$  are tracers of combustion (23). VOC concentrations are also important variables for the formation of SOA, but VOC measurements were not available in the time-resolution necessary so they were not considered.  $H^+$  was also included as a candidate regressor, as it is the variable of primary interest. Sample correlation coefficients of these variables and their lagged values with OC/EC are presented in Table 1. Because a sampling duration of 2–4 h is long compared to time scales of many atmospheric processes, we find that correlations of time-integrated OC/EC concentrations are stronger with explanatory variables measured during the same time period (lag = 0), rather than the variable's value at the previous sampling interval. In general, the correlations are consistent with our understanding of atmospheric chemistry. The photochemical cycle ultimately consumes NO and  $NO_x$  in the process of producing ozone, the primary oxidant of reactive organic gases that are precursors to SOA. Therefore, the ozone and the inverse concentrations of NO and  $NO_x$  show some correlation with OC/EC. UV, which initiates the photochemical reactions, is the only variable in Table 1 whose previous time value shows a stronger correlation with OC/EC than its present value. The sample correlation coefficient of OC/EC with carbon monoxide is negative, because emissions of CO indicate an increase in emissions of EC and primary OC, lowering the OC/EC ratio when SOA is present. Though higher temperatures are thought to be favorable for SOA formation, temperature is not strongly correlated with OC/EC.  $H^+$  shows a stronger correlation than sulfate, and it is the relationship between OC/EC and acidity around which we wish to build our regression model.

First, all variables were averaged to regular intervals of 4 h. Because we do not have knowledge of the functional dependence of the OC/EC ratio on other variables a priori, we began with a subset of candidate regressors from Table 1 with the strongest correlations (i.e. all variables from the current time period except for UV, for which the previous time period was also included) and transformed variables such that the assumption of linearity would approximately hold among the response and predictor variables. Then, we used a stepwise, forward-selection approach to variable

**TABLE 2. Regression Coefficients, Standard Errors, and *t*- and *p*-Values Calculated from Ordinary Least-Squares Regression**

coefficient	units	value	std error
$\beta_0$		1.3	0.1
$\beta_1$		0.55	0.02
$\beta_2$	( $\mu\text{g}/\text{m}^3$ ) <sup>-1</sup>	3.2	0.7
$\beta_3$	(ppb)	-0.30	0.02
$\beta_4$	( $\text{W}/\text{m}^2$ ) <sup>-1</sup>	0.0071	0.0012
$\beta_5$	(°C) <sup>-1</sup>	0.0043	0.0015

selection with alternatives scored according to the Akaike Information Criterion (AIC). Variables that exhibited strong correlation with variables already included in the model were not considered to avoid problems with multicollinearity, and variables whose regression coefficients were not significant were removed. We obtained a model of the following form

$$\log(\text{OC}/\text{EC})_k = \beta_0 + \beta_1 \log(\text{OC}/\text{EC})_{k-1} + \beta_2 \text{H}^+ + \beta_3 \log(\text{NO}_x)_k + \beta_4 \text{UV}_k + \beta_5 T_k + \epsilon_k \quad (1)$$

where OC/EC is the OC/EC ratio,  $\text{H}^+$  is the hydrogen ion concentration in the aerosol and our metric of inorganic acidity,  $\text{NO}_x$  is the concentration of the oxides of nitrogen, UV is the ultraviolet radiation intensity,  $T$  is the temperature, and  $\epsilon$  is the disturbance term. The  $\beta$ 's are regression coefficients. The subscripts  $k$  and  $k-1$  denote the time intervals for which the variables are specified, i.e., OC/EC at  $k-1$  specifies the OC/EC ratio lagged by one time interval. Lagged values of the dependent variable are introduced as regressors to reduce serial correlation in the residuals that may arise out of unaccounted influence of omitted explanatory variables (38). Even with the lagged dependent variable included the residuals still exhibited serial correlation according to the Breusch-Godfrey test (39, 40). Therefore, residuals from ordinary least squares regression were parametrized by a mixed autoregressive moving average process of order  $p, q$  [ARMA( $p, q$ )]; an ARMA(3,3) exhibited an acceptable fit to the residuals. The regression coefficients were then estimated by feasible generalized least squares (41).

The estimated regression coefficients,  $\hat{\beta}$ 's, are shown in Table 2. As eq 1 is an empirical construct, it should be mentioned that these regression coefficients are only applicable for the Western Pennsylvania region for conditions experienced during our study period. The correlation of fitted values with observed values of  $\log(\text{OC}/\text{EC})_k$  is 0.77, with over 1250 data points included in the regression. The regression coefficients of all regressors included in the model are significant from zero at the  $\alpha = 0.01$  significance level because variables that were not significant were removed in the model selection process and also because the sample size is large. It is important to point out that statistical significance does not necessarily imply causality. The signs of the regression coefficients are as expected, and they agree with the signs from the sample correlation coefficients of each variable with OC/EC.  $\beta_2$ , the regression coefficient for  $\text{H}^+$ , is of particular interest, as this parameter indicates the sensitivity of OC/EC to inorganic aerosol acidity. Because this coefficient relates the  $\text{H}^+$  concentration to the logarithm of OC/EC, its value is difficult to interpret directly unless used in the context of prediction. For instance, assuming that (1) a causal link exists between free acidity and OC/EC in the atmosphere and that (2) the value of all other variables are held fixed while the acidity is perturbed, we can use this statistical model to examine an extreme case where all effects of acidity are removed from additional OC formation by setting  $\text{H}^+ = 0$ . If EC remains constant, then the ratio of the predicted OC/EC to the fitted OC/EC should give an estimate of the decrease

**TABLE 3. Estimated Overall Reduction in OC as a Function of the Acidity Threshold and the Threshold's Corresponding Percentile in the Cumulative Distribution Function of  $\text{H}^+$**

acidity threshold, ( $\text{H}^+$ )* ( $\text{ng}/\text{m}^3$ )	percentile of $\text{H}^+$ distribution	overall reduction in OC (%)
25.0	96	$0.4 \pm 2.6$
4.1	75	$1.3 \pm 4.0$
0.9	50	$2.3 \pm 4.9$
0.1	25	$3.4 \pm 5.5$
0.0	0	$5.4 \pm 7.9$

in OC concentrations. For our scenario of reduced acidity, the predicted decrease in OC is about  $2 \pm 4\%$  overall. Thus, we find that the sensitivity of OC to  $\text{H}^+$  is small.

**Scenario Analysis.** Laboratory studies have cited observations of SOA enhancement by as much as 40% under conditions of high inorganic acidity (10, 42). If such a magnitude of enhancement were occurring in the atmosphere, it is of interest to know what the effect of perturbing the current levels of inorganic acidity might be. For instance, if we assume that the enhancement is occurring above an assumed threshold acidity ( $\text{H}^+$ )\*, reducing the acidity during those periods to values below the threshold would result in a new set of OC concentrations,  $\text{OC}'$ , in the following way

$$\text{OC}' = \text{OC}_p + \text{SOA}_0 / (1 + \phi)$$

where

$$\phi = \begin{cases} 0.4 & \text{for } \text{H}^+ \geq (\text{H}^+)^* \\ 0 & \text{for } \text{H}^+ < (\text{H}^+)^* \end{cases}$$

$\text{OC}_p$  is the primary OC concentration,  $\text{SOA}_0$  is the original SOA concentration,  $\phi$  is the magnitude of enhancement, and  $\text{H}^+$  is the free acidity concentrations calculated for PAQS. Primary OC and SOA were not directly measured during the study, but the EC-tracer method is one approach that is used to estimate their concentrations (23), and we use those estimates here. The functional dependence of SOA enhancement on aerosol acidity has only been recently elucidated by a semiempirical approach (43), but in general the experiments by Limbeck et al. (13) qualitatively suggest a monotonic dependence on free acidity. Here we simply assume a step function, though we are left with the task of arbitrarily defining an acidity threshold to classify aerosols as acidic or not acidic. For our preliminary analysis, we used the reported aerosol volumes for  $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$  seeds and relative humidity conditions reported in the experiments of Jang and Kamens (3) and calculated the  $\text{H}^+$  concentrations using a chemical equilibrium model, AIM (37). The nonacidic seed aerosols ( $(\text{NH}_4)_2\text{SO}_4$ ) were neutral ( $\text{H}^+ = 0 \mu\text{g}/\text{m}^3$ ), and their acidic seed aerosols (mixed- $\text{H}_2\text{SO}_4$ - $(\text{NH}_4)_2\text{SO}_4$  particles) ranged in  $\text{H}^+$  from 0.025 to  $0.22 \mu\text{g}/\text{m}^3$ . Thus we assume a threshold of  $(\text{H}^+)^* = 0.025 \mu\text{g}/\text{m}^3$ , above which our aerosols are considered acidic.

The observed OC concentration, annually averaged from July 2001 to July 2002 is around  $2.5 \mu\text{g}/\text{m}^3$ . If we assume that emission reductions in precursor gases (e.g.,  $\text{SO}_2$  and  $\text{NO}_x$ ) to inorganic acidity results in the removal of acid-catalyzed SOA production, the annual average OC would be reduced by approximately 2% of this amount, though 80% of the reductions would occur during the summer months of July–August 2001 and June–July 2001, when aerosol acidity concentrations are the highest. Because the enhancement of SOA may actually become significant at acidities below our chosen threshold, we report the % reduction in average OC as a function of the assumed  $(\text{H}^+)^*$ . Table 3 shows the assumed  $(\text{H}^+)^*$  and the percentile to which it corresponds



in the distribution of observed  $H^+$  concentrations and the calculated percent reduction in annual average OC. The percent reduction is calculated as  $(1 - OC' / (OC_p + SOA_0)) \times 100\%$  and averaged for the entire study period; the mean and standard deviation of this value is reported. The threshold of  $0.025 \mu\text{g}/\text{m}^3$  initially selected corresponds to the 96th percentile of the  $H^+$  distribution, indicating that only in 4% of our observations,  $H^+$  concentrations exceeded this threshold. In the extreme case where SOA is reduced during all periods in which the acidity was nonzero (corresponding to the 0th percentile), the overall OC reduction would conservatively be estimated at  $5.1 \pm 7.9\%$ , which is only slightly higher than that predicted by the regression model.

## Discussion

We examined the changes observed in OC/EC, acidity, and wind direction from July 2001 to July 2002 using time-series plots and using scatter plots of changes in OC/EC and acidity conditioned on changes in wind direction. Based on this analysis, we observed 104 cases in which the acidity increased noticeably; 22 of which showed possible indications of acid-catalyzed chemistry and 38 of which showed evidence of either acid-catalyzed chemistry or transport and mixing. Chu (17) sites an episode on July 18th, 2001, in which high concentrations of sulfate not fully neutralized by ammonia were accompanied by low UV intensity and high OC concentrations in the Eastern U.S., suggesting acid-catalyzed SOA formation as a possible explanation for this observation. We also observed concurrent increases in acidic aerosols and organic aerosol concentrations at the PAQS monitoring site, but this was a rare phenomenon during our study period. Furthermore, examination of different metrics of acidity and OC/EC ratios showed at most an overall correlation of  $-0.28$ . The implication from this study is that acid-catalyzed SOA is not occurring most of the time, or that the "effect size" of acid-catalyzed SOA formation is not large enough to be observed consistently above the noise of other mechanisms. These mechanisms may include the combination of transport and mixing of primary emissions that can contribute to changes in OC/EC in addition to that caused by SOA formation and the net influence of uncertainties in our measurements.

There are many factors that could contribute to the measurement uncertainty and error, some which are more random and others which confer a systematic bias. One possible error of the latter type is the potential for conversion of polymeric products to light-absorbing carbon which would be misclassified as EC; this could underestimate the contribution of SOA to the OC/EC ratio. However, the peak temperature in the fourth helium mode used by the in-situ carbon analyzer to analyze the samples used in this analysis was  $870^\circ\text{C}$ —this protocol was found to under-report the EC concentration compared to other methods for laboratory-generated levoglucosan and  $\alpha$ -pinene SOA samples, possibly through the premature evolution of EC (44). Thus, there may be measurement error resulting from the operational definition of the OC-EC split and the analysis protocol used for the study, but this error may not necessarily bias the OC/EC ratio to be systematically low in the presence of SOA.

The question remains whether this observation is specific to the monitoring site, or if it can be extended to regions outside of Pittsburgh. Stanier et al. (45) observed that nucleation events were regional in nature, which implies that  $\text{H}_2\text{SO}_4$ , the main component involved in nucleation of new aerosols in this region (46) and also the primary source of inorganic aerosol acidity, is also generated regionally. During the summer when SOA concentrations are higher (23), the OC concentration is also spatially homogeneous (32), suggesting that primary OC and SOA formation is regionally distributed. Therefore, we expect that our conclu-

sion can be extended to the Western Pennsylvania region and that acid-enhancement of SOA would also be unobservable in the area.

Assuming that acid-catalyzed SOA formation has occurred within the noise of our signal, we estimated possible reductions in OC concentrations that might result from a reduction in inorganic acidity using two methods. One was an empirical approach that estimated the possible response of OC/EC to  $H^+$  from field measurements, and the other method was based on preliminary information from laboratory experiments. The regression model, which is the empirical approach, is by design constructed to return an expected value for its predictions. The regression model suffers from the inherent assumption that the relationship derived between OC/EC and  $H^+$  is causal; there may be confounding factors that cause these two variables to show a link that may not exist directly. Therefore, the model cannot tell us that reducing  $H^+$  will actually reduce the OC concentration. However, if the link is indeed causal, then the expected reduction in OC might be less than 6%, assuming the values of other variables remain unaltered. The second approach is based on laboratory measurements, as the magnitude of SOA enhancement was obtained from laboratory studies examining the effect of inorganic acid aerosols on increases in SOA formation. The second approach returns a more conservative estimate as we chose an upper bound on acid-SOA enhancement observed in the laboratory to calculate the effect of  $H^+$  reduction on OC. However, the functional dependence of SOA enhancement on acidity had to be assumed, as the actual relationship is not well-known. Furthermore, the SOA estimates used for the calculations have high uncertainty, as a constant OC/EC ratio for primary emissions during all periods was assumed for its calculation (23). However, the methods by which we calculated the response of OC to  $H^+$  are rather conservative; despite the high uncertainties in our estimates, the benefit of reducing the inorganic acidity entirely appears to be a reduction in OC concentrations by less than 10%. Recently, Jang et al. (43) have developed more sophisticated models that predict aerosol yields as a result of interaction of carbonyls and free hydrogen, but their model requires carbonyl-specific parameters—in contrast, our calculation is kept sufficiently simple and not specific to any compound such that an estimate of the upper bound for the acid-catalysis effect is captured.

FTIR and mass spectrometry data indicate that polymeric products in atmospheric aerosols appear to be more ubiquitous than initially speculated (3, 15), even under the absence of inorganic acidity (15, 16). However, Gao et al. (42) also found that increasing seed aerosol acidity results in more rapid polymerization, which may lead to higher SOA yields during certain periods. Thus, how changes in the inorganic aerosol acidity will affect OC concentrations remains an important question. We have shown that for Pittsburgh, this effect may be small, but such conclusions are dependent on the availability of atmospheric acidity and also the contribution of SOA to the total organic aerosol in each location. For the Pittsburgh region, SOA contributes to  $\sim 35\%$  (to a maximum of 50%) of organic aerosol (23); Lim and Turpin (47) found that SOA can account for  $\sim 46\%$  of OC in Atlanta, with contributions as high as 88% during certain periods. As such, the effect of perturbing inorganic acidity may have comparable or larger effects on the OC concentrations in Atlanta. On the other hand, Strader et al. (48) reported that most of the OC in San Joaquin Valley is primary (SOA  $< 20\%$  of OC), so reducing the occurrence of acid-catalyzed SOA is likely to have a smaller effect on PM concentrations in that region. Furthermore, the source contribution of inorganic aerosol acidity is different according to region and season. For instance, in the eastern U.S. [where the highest con-

centrations of aerosol acidity are found (8), sulfate is regionally distributed and is the primary source of inorganic acidity during the summer, with increasing contributions from local production of  $\text{HNO}_3$  approaching winter. The inorganic acidity in urban regions in southern California, however, originates mainly from vehicular emissions that result in the production of  $\text{HNO}_3$ , but  $\text{NH}_3$  is also available in sufficient quantities such that much of the acidity is neutralized. As such, the implications of the interaction between inorganic and organic components of the atmospheric aerosol should be evaluated separately for each location.

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