An ion chromatographic analysis of water-soluble, short-chain organic acids in ambient particulate matter

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Recent studies have shown that the inclusion of water-soluble short-chain (WSSC) organic acids in source apportionment using positive matrix factorization (PMF) resulted in an improvement in the model's ability to resolve sources, and in understanding secondary particle formation. In the United States, numerous network samplers are operational. Quartz-fibre filters for thermal optical carbon analysis have been collected over a period of years as a part of these sampling campaigns on a routine basis. However, only a small portion of these filters are used for the carbon analysis. Thus, there is the potential to utilize these samples to enhance organic speciation for subsequent use in source apportionment. In this work, an ion-chromatographic method was developed to identify and quantify the WSSC organic acids present in fine particulate matter ($PM_{2.5}$). Samples collected to measure the concentrations of particles ($PM_{2.5}$) in south-western (Stockton) and northern (Potsdam) New York, USA from November 2002 to June 2004 were used in this study. Acetic, formic, propionic, oxalic, and malonic acids were successfully identified. The identified species accounted for 5–15% of the organic matter mass and thus enhance the knowledge of atmospheric organic-matter constituents. Oxalic acid was the most abundant species at Potsdam and Stockton with median concentrations of $17.71\,\mathrm{ng\,m^{-3}}$ and $92\,\mathrm{ng\,m^{-3}}$, respectively. Acetic and formic acids were present in Potsdam at median concentrations of $12.54\,\mathrm{ng\,m^{-3}}$ and $14.48\,\mathrm{ng\,m^{-3}}$, while at Stockton they were present at $57.58\,\mathrm{ng\,m^{-3}}$ and $51.54\,\mathrm{ng\,m^{-3}}$, respectively. The median concentration values for all acids at Stockton were higher than Potsdam. These observations are consistent with a study conducted in a semi-urban location, Schenectady, New York. At both sites, propionic and malonic acids were found in much lower concentrations when compared with the other acids. The concentration time series of various acids and seasonal variations in individual acids are discussed. The co-variance of acetic and formic acids is also outlined.

Keywords: Fine particles; Ion chromatography; Organic acids; Seasonal trends; Potsdam, NY; Stockton, NY

1. Introduction

Organic compounds constitute a significant portion of the fine particulate matter in the lower troposphere. It is believed that organic PM consists of a variety of compounds

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covering a wide range of carbon numbers, functional groups, and solubility in extraction media [1]. The sources of these compounds can be biogenic or anthropogenic. They can also be formed through chemical transformations of biogenic and anthropogenic emissions [2]. Carboxylic acids are found to be ubiquitous components in the tropospheric aerosol and are also believed to be chiefly secondary in origin [3, 4].

Recently, it has been shown that the identification and inclusion of WSSC organic acids proved beneficial in improving the source resolution of an advanced factor analysis, namely, Positive Matrix Factorization (PMF) [5]. The study was performed on the Toronto aerosol. In the Toronto aerosol study, formate, malic acid, malonate, oxalate, and succinate were used. The inclusion of WSSC organic acids led to the identification of secondary organic aerosol portion of the particulate matter. In the absence of WSSC acids, the model associated the secondary aerosol portion with secondary coal resulting in an unrealistic coal combustion source profile. The inclusion of WSSC acids in the model also provided insights into the nature and origin of these acids, and significance of interaction between secondary organic and inorganic aerosols.

A variety of methods are used to characterize WSSC organic particulate material. Analytical methods can either attempt speciation of individual compounds or determine functional groups of the organic molecules. Popular techniques include Fourier-transformed infrared spectroscopy (FTIR) [6–8] to provide information on the functional loading of an average molecule and gas chromatography (GC/MS) [9–11], capillary electrophoresis (CE) [5,12] and ion chromatography (IC) [13–15] to characterize organic compounds.

In the United States, the Speciation Trends Network (STN) programme, includes 54 trends national air monitoring station (NAMS) network sites and up to 200 non-routine state and local air monitoring station (SLAMS) sampling sites. In addition, the Interagency Monitoring of Protected Visual Environments (IMPROVE) programme currently includes 143 monitoring stations. These programmes collect 24 h integrated samples every third day using samplers that operate at flow rates between $7.3 \, \mathrm{L \, min^{-1}}$ and $23 \, \mathrm{L \, min^{-1}}$. Routine sampling on quartz-fibre filters for organic and elemental carbon (OC and EC) analysis are performed as a part of these programmes.

Thus, the purpose of this paper is to present a relatively simple ion-chromatographic method developed for the detection and quantitation of 10 WSSC organic acids that could be present in the ambient aerosol. The method permits taking advantage of the samples already collected in order to extract additional information. The developed method adequately addresses the problems associated with co-elution of fluoride and acetic acid, and sulphate and oxalic acid. It also affords the simultaneous detection and quantitation of organic acids and common inorganic anions, if desired. Further, an eluent generator (EG-50) was used to produce ultrapure eluent, resulting in a stable baseline, increased retention time stability, enhanced resolution, and improved repeatability. A continuously regenerating anion trap column (CR-ATC), which continuously removes impurities from the eluent ensuring low baseline shifts during the gradient operations, was used with the EG-50. These improvements in the instrument features compared with previous studies enabled the development of a suitable gradient separation method.

2. Experimental

2.1 *Sampling sites*

Sampling was carried out at Potsdam and Stockton, NY. The Potsdam site (latitude 44° 40′ 20″ N, longitude 74° 59′ 16″ W) is located in St. Lawrence County in the northern region of NY near the Canadian border. The site is located near a very small airport, 400 m north-west of the runway and about 1 km from the main road. Considering the prevailing westerly winds, and very few landings at the airport, this site was chosen because it is not significantly impacted by local sources [16]. The Stockton site (latitude 42° 17′ 59″ N, longitude 79° 23′ 42″ W) is situated in Chautauqua County, approximately 20 km south of Fredonia, NY and approximately 10 km from the eastern shore of Lake Erie. This site is located in a remote rural area, on top of a ridge with an elevation of 488 m. This site was chosen because it is situated away from metropolitan areas; Erie, PA is 80 km south-west and Buffalo, NY is 88 km north-east. Further, it is well situated to sample the prevailing southwesterly winds from the Midwestern region of the United States entering New York State [16].

2.2 *Sampling methods*

Samples collected every third day, for a 24 h period from November 2002 to June 2004 at Potsdam and Stockton, NY, were used in this study. The samples were collected, at both sites, by exposing a single 47 mm quartz-fibre filter (prefired at 550°C for 16 h and further at 800°C for 1.5 h) in an Andersen Reference Ambient Air Sampler (RAAS) $PM_{2.5}$ speciation network sampler. The system consists of critical orifices for proper flow. The flow rate was set at 7.3 L min^{-1}. At Potsdam, the total volume of air sampled was 11.12 m^3 on average, with a standard deviation of 0.18 m^3 during the entire sampling period, while at Stockton it was 10.4 m^3 and 0.4 m^3, respectively.

The sampling was not planned to permit extensive organic speciation. A Hi-Vol sampler or a sampling arrangement to denude gas-phase organics followed by filters for particulate matter collection are more appropriate to collect samples for organic acids analysis. However, as mentioned elsewhere, a suitable method to utilize the extensive routine samples already collected using speciation samplers nationwide, to detect organic acids, is very valuable.

Samples collected from November 2002 were retrospectively analysed from April 2004 onwards. The samples were stored in clean, sealed Petri dishes and refrigerated prior to analysis. Punches of the quartz filter were analysed for OC and EC, and the remaining filter was leached with water and used for the WSSC organic acids analysis. Suitable correction was made during the quantitation of the acids, to account for the filter area used in the OC/EC analysis.

2.3 *Sampling artefacts*

The effects of adsorption and volatilization sampling artefacts are of concern in this study. Studies show that under typical sampling conditions, adsorption is the dominant artefact in the sampling of organic aerosol [17]. Further, the mono-carboxylic acids are quite volatile and tend to partition almost entirely into the gas phase. Hence, one would

also expect volatilization losses of these acids from the particle phase. Given that the sampling period is 24 h, it is assumed that there is sufficient time for the gas-particle equilibrium to be achieved. It is hard to estimate the relative strengths of positive and negative artefacts, and it is assumed that the overall effect on particle phase WSSC organic acid concentrations is not significant.

This assumption seems reasonable, given that as a consequence of the long sampling time, the contribution of organic compounds adsorbed on the filter is not significant [17]. Further, this type of sampling for collection of particulate matter has been used in several studies reporting the concentrations of ambient particle phase organic acids [18–21].

2.4 *Instrumentation*

The analyses were performed on a Dionex DX500 ion-chromatography system consisting of a gradient pump (GP-50), an eluent generator (EG-50) with a KOH cartridge, a continuously regenerating anion trap column (CR-ATC), an auto sampler (AS-50), and a conductivity detector (ED-40). The instrument was equipped with an ASRS-Ultra II suppressor (4 mm). Separation was performed on an Ionpac AS17 analytical column (4 mm) with Ionpac AG17 guard column (4 mm).

2.5 *Chemicals*

All standards were prepared from reagent-grade chemicals and deionized water. Stock solutions of individual standards (acetic, propionic, formic, glutaric, adipic, succinic, malic, malonic, maleic, and oxalic acids) were prepared at a concentration of $100 \, mg \, L^{-1}$ and stored in a refrigerator for up to 2 months, with the exception of acetic, propionic, and formic acids, which were prepared fresh for each experiment due to the limited stability of the solutions. The stability of the stock solutions were verified by preparing standards using the stock solutions once a week and subjecting the standards to chromatographic analysis. Mixtures containing equal amounts of each acid, with the exception of oxalic acid (whose concentration was five times that of each of the other acids in the mixture, owing to a lower detection limit of the instrument as compared with the other acids), were prepared. Seven standard mixture solutions in the concentration range from 0.0833 to $0.833 \, mg \, L^{-1}$ of each acid ($0.4165–4.165 \, mg \, L^{-1}$ of oxalic acid) were prepared by dilution of stock solutions with deionized water.

2.6 *Sample preparation*

The quartz-fibre filter samples were placed in a 20 mL centrifuge tube with snap caps. They were leached with 10 mL of organic free de-ionized water at room temperature by ultrasonication for 60 min, followed by mechanical shaking for 60 min. The samples were then centrifuged for 20 min at 6500 rpm and stored in a freezer until analysis, with a maximum storage time of 2 days. The leachate was filtered through 0.22 μm-pore-size membrane filters (Millipore, IC Millex- LG) prior to IC analysis.

2.7 *Analytical procedure*

The samples were analysed using the gradient programme shown in table 1, and chromatograms of a standard (top) and a sample (bottom) are shown in figure 1. The standard shown in figure 1 has a concentration of $0.1666 \, mg \, L^{-1}$ of each acid and $0.833 \, mg \, L^{-1}$ of oxalic acid. A sample injection volume of $100 \, \mu L$ was used. The eluent (KOH) flow rate was maintained at $0.8 \, mL \, min^{-1}$. Other gradient programmes were implemented by varying the run time and the eluent concentration. It was found that a decrease in the eluent concentration and a consequent increase in the run time resulted in a better resolution of glutaric, succinic, malic, maleic, and malonic acids. Depending on the number of species present in a sample, such a programme may be used when a better separation is desired.

In this work, the programme shown in table 1 was used throughout the study. A typical batch consisted of two samples of ultrapure water, the full calibration curve, two samples chosen at random from a previous batch, 40 samples, a standard in the mid-concentration range every fifth sample, and a spiked sample every tenth sample. Four samples in the batch at random were analysed in duplicate. The calibration curves were linear, and the obtained r^2 for each species of interest was 0.995 or higher. The recovery for standards and spikes ranged between 95 and 107%. The relative standard deviation for duplicate samples was within 10%.

3. Results and discussion

3.1 *Data analysis*

Even though a method has been developed to identify 10 acids, only five acids were present above detection limits in the samples from both sites. The discussion that follows is confined to these five WSSC organic acids, acetic, propionic, formic, malonic, and oxalic acids, that were successfully detected and quantified in most of the samples collected at both sites. In general, propionic and malonic acids were found in much lower concentrations than acetic, formic, and oxalic acids at both sites. The median concentration values for all acids at the Stockton were much higher than those for Potsdam. The key statistical details of the analyses are shown in table 2, where MDL is the method detection limit. The MDL for target analytes was determined in accordance with United States Code of Federal Regulations (CFR) Title 40, Part 136, Appendix B [22]. A minimum volume of 10 mL leachate was essential to ensure that the filter was completely wetted in order to permit satisfactory leaching of the acids. Thus, the detection limits could not be improved beyond that obtained by lowering the leachate volume.

At both sites, among the mono-carboxylic acids, acetic acid had the highest maximum concentration, followed by formic acid. Mono-carboxylic acids are

Table 1. Gradient programme.

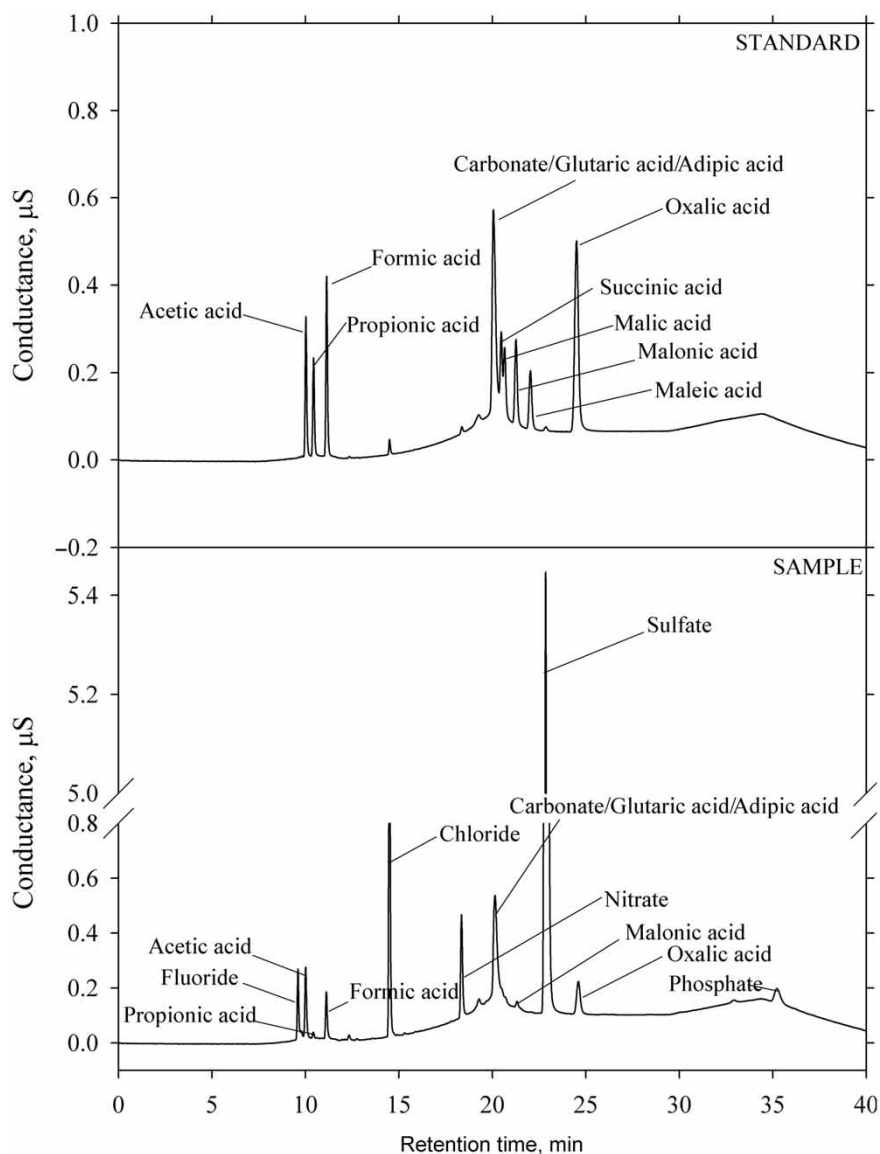| Time (min)	0.0	3.0	5.0	7.0	8.5	9.5	6.0	26.0	31.0	41.0
KOH (mM)	0.2	0.2	0.9	1.4	2.0	3.0	15.0	15.0	20.0	0.2

Figure 1.   Sample chromatograms of a standard (top) and a sample (bottom).

predominantly present in the gas phase, and the abundances of acetic and formic acids observed in this study are consistent with the results in the literature [3]. At a study conducted in Schenectady, NY, a semi-urban site, particle-phase acetic and formic acids concentrations ranged from 87 to $328\,ng\,m^{-3}$ and 89 to $245\,ng\,m^{-3}$, respectively, on a single day [14]. In another study conducted in the Los Angeles area, formic and acetic acids were found in measurable concentrations in the particle phase [23, 24]. The literature on particle phase mono-carboxylic WSSC organic acids quantitation is somewhat limited, and propionic acid concentrations are not discussed in most of the studies. The sampling sites are located in remote rural areas with considerable

Table 2.   Summary statistics for WSSC organic acids at Potsdam and Stockton sites for samples collected from November 2002 to June 2004.

	Species			Concentration (ng m^{-3})	
	Maximum	Minimum	Median	MDL (ng m^{-3})	BDL (%)
Potsdam (N = 183)					
Acetic	101.6	BDL	12.5	0.5	10.2
Propionic	8.9	BDL	1.9	0.4	67.2
Formic	74.5	BDL	14.5	1.6	9.7
Oxalic	150.3	BDL	17.7	3.6	9.1
Malonic	29.9	BDL	4.8	0.2	37.6
Stockton (N = 120)					
Acetic	91.0	BDL	57.8	0.5	1.7
Propionic	16.3	BDL	14.3	0.4	45.0
Formic	72.9	BDL	51.5	1.6	1.7
Oxalic	162.3	BDL	92.0	3.6	1.7
Malonic	28.1	BDL	18.9	0.2	34.2

vegetation, and vegetative emissions of acetic and formic acids may be fairly significant [3]. Although mono-carboxylic acids may also be present in the particle phase due to reactions with neutralizing salts such as calcium carbonate, the PM$_{2.5}$ being examined in this study is more likely to be acidic than basic, and thus this mechanism is unlikely to add to the concentrations of particulate acids. Thus, a possible explanation for low propionic acid concentrations is the preferential vegetative emissions of acetic and formic acids over propionic acid.

Among the di-carboxylic acids, only oxalic and malonic acids were detected. Oxalic acid concentrations are much higher than malonic acid at both sites. Oxalic acid is the most abundant WSSC organic acid species in Potsdam and Stockton. This observation is consistent with the literature. In most studies, oxalic acid was found to be present in the highest concentration, followed by malonic or succinic acids [10, 14, 25]. Preferential production of oxalic acid seems likely. It is the smallest di-acid and can potentially be produced from many precursor compounds containing carbon numbers > C$_2$. It is also likely that oxalic acid is an end product of photochemical oxidation reactions and can accumulate in the atmosphere.

3.2 *Individual acids concentration time series*

The concentration time series for all acids at Potsdam and Stockton were plotted for the monthly average concentrations. Figure 2 (top) shows the monthly average concentration time series for WSSC organic acids at Potsdam. The error bars represent one standard deviation in the measured values. Acetic, propionic, formic, and oxalic acids follow a similar trend. A slightly different trend is observed for malonic acid.

Figure 2 (bottom) shows the monthly average concentration time series for the WSSC organic acids at Stockton. The predominant feature in this plot is a significant rise in oxalic acid concentration between January and June in 2003 as well as in 2004. The other observations are similar to those seen at the Potsdam. However, the propionic acid concentration profile shows more variation at Stockton than at Potsdam.
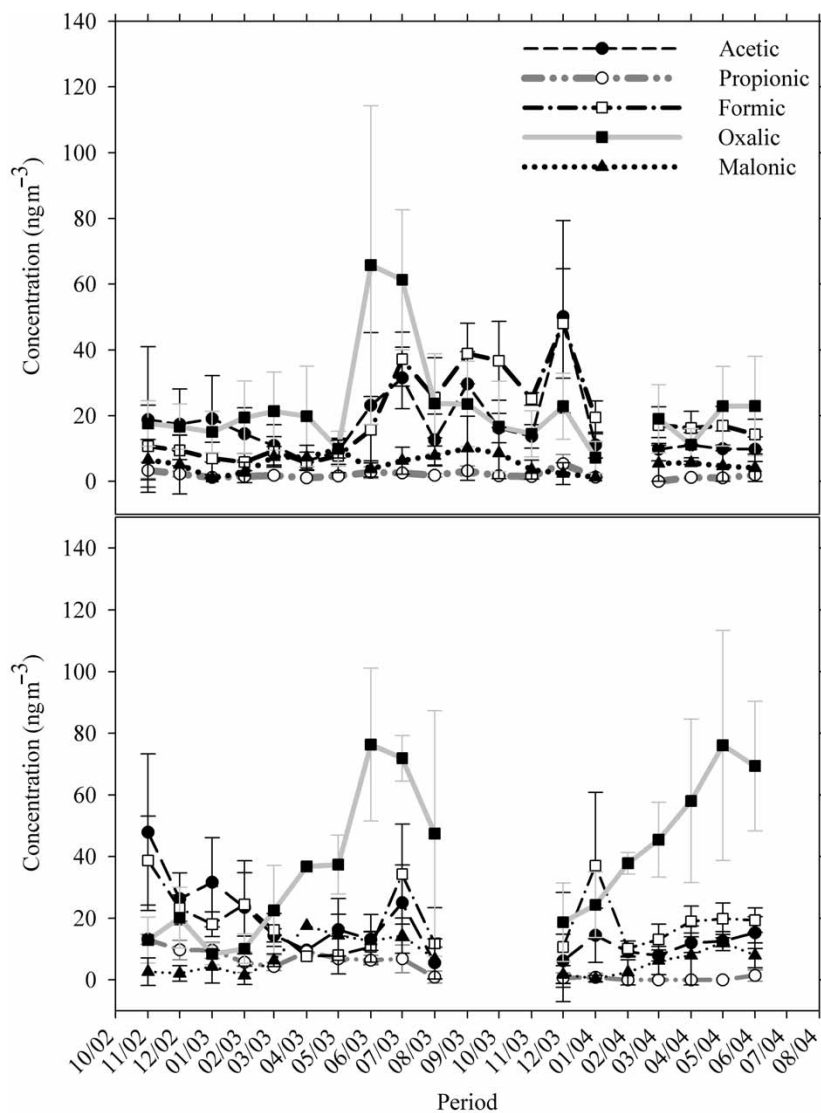
Figure 2. WSSC organic acids time series monthly concentration averages at Potsdam (top) and at Stockton (bottom).

3.3 *Seasonal variation in individual acid concentration*

For our study, winter was defined as the period from the beginning of November through the end of the following February, and summer as the period from beginning of May through the end of August. Figure 3 shows the seasonal variation in concentrations of acetic, propionic, formic, oxalic and malonic acids at both sites. The 5th and 95th percentile outliers as well as the median (solid line), mean (dotted line), and error bars are shown in all plots.

Oxalic acid and malonic acids showed an increase in concentration during the summer as compared with the winters at both sites. This pattern is consistent with
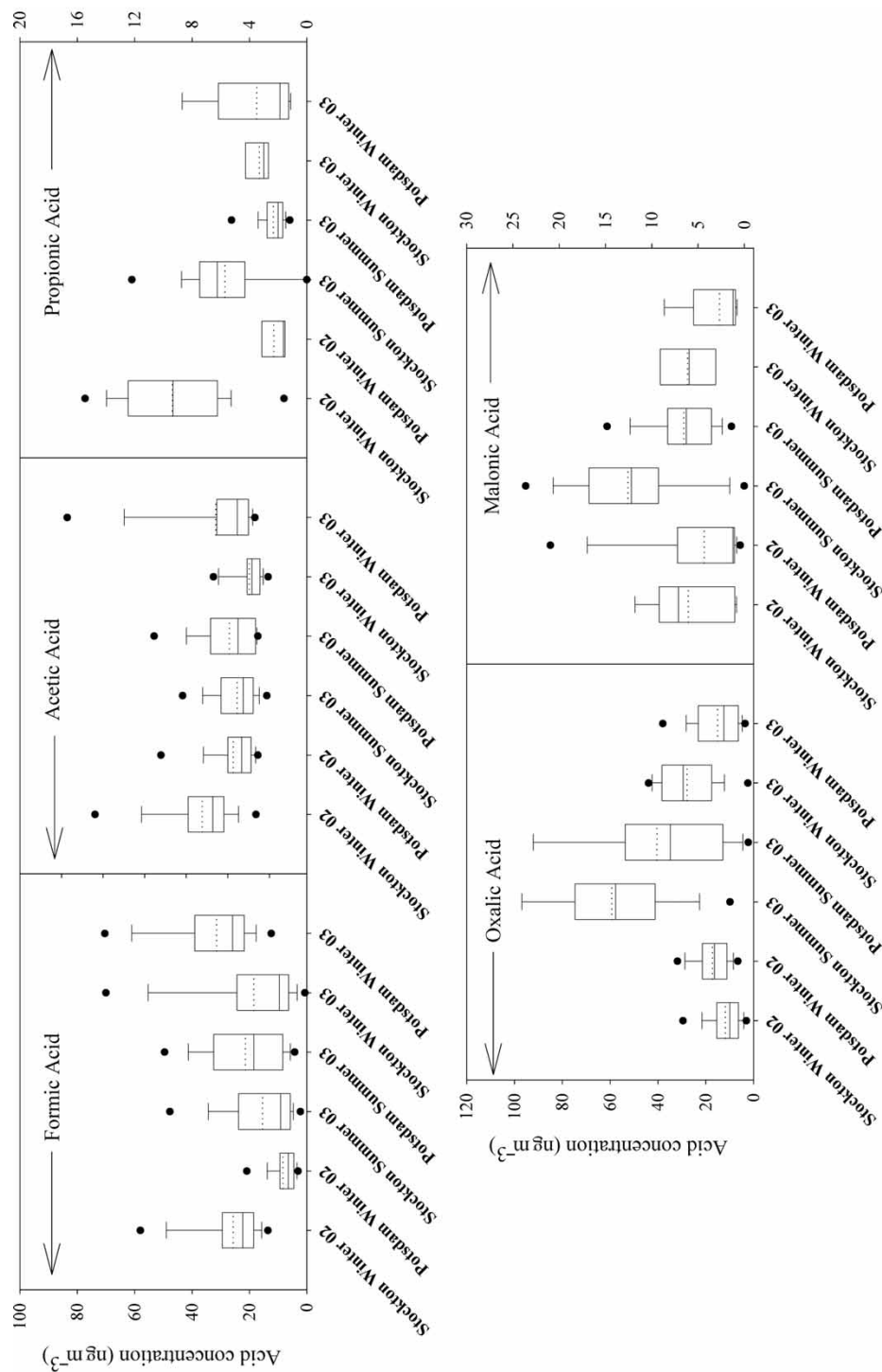
Figure 3. Box and whisker plot showing the seasonal variation at Potsdam and Stockton for (*a*) acetic acid; (*b*) propionic acid; (*c*) formic acid; (*d*) oxalic acid; and (*e*) malonic acid.
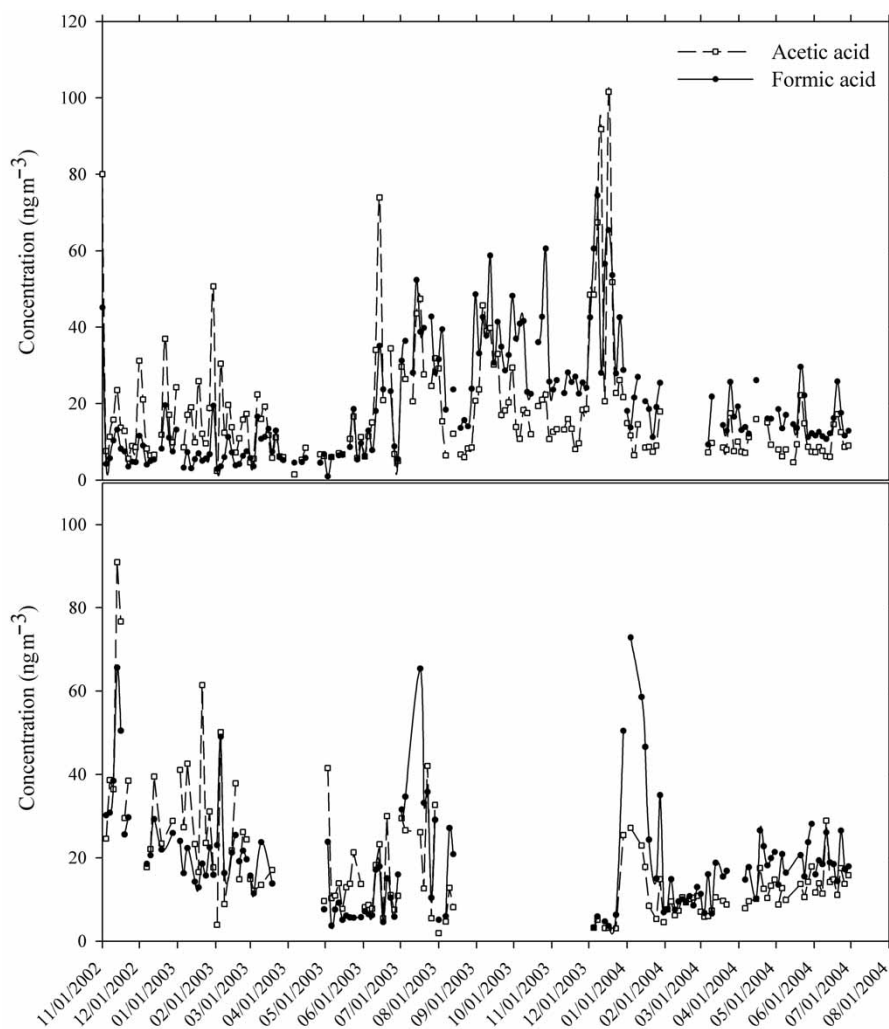
Figure 4.   Plot of acetic and formic acids at Potsdam (top) and at Stockton (bottom).

the expectation that summertime active photochemistry results in the secondary formation of these acids. No clear patterns in seasonal variations were observed for the mono-carboxylic acids. As far as the mono-carboxylic acids are concerned, even though one would expect a higher concentration of the acids in summer, vapour pressure changes with increasing temperature and may result in increased volatilization losses. Further, the strength of direct emissions when compared with secondary organic compound formation is also an important factor in establishing seasonal trends.

3.4 *Co-variance of acetic acid and formic acids*

The usefulness of the relationship between formic and acetic acids to identify the nature of the sources of these acids and their strengths has been examined in several studies.

Figure 4 (top) shows the co-variance of acetic and formic acids at Potsdam, while figure 4 (bottom) shows the same relationship at Stockton. Both plots indicate that acetic and formic acids co-vary at both locations. Natural biogenic emissions, biomass combustion, and gas-to-particle conversions have been proposed to explain the relationship between formic and acetic acids [26]. However, at both sites, the correlation coefficient was poor. Thus, no inference about the commonality in sources for these acids could be made.

Acknowledgement

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