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Simultaneous online monitoring of inorganic compounds in aerosols and gases in an industrialized area

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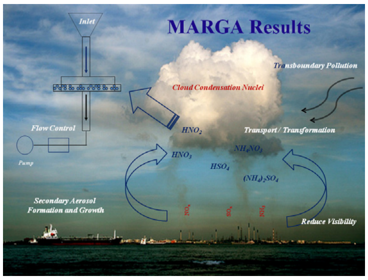
HIGHLIGHTS

- Online hourly measurement of ambient water-soluble gases and $PM_{2.5}$ aerosols.
- Higher concentrations of HNO_2 compared to HNO_3 were consistently recorded.
- NH_3 gas did not follow the expected diurnal trend in the high humidity environment.
- Sulfate levels were found to be very high at times of high biomass burning.

GRAPHICAL ABSTRACT



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ABSTRACT

The automatic MARGA (monitor for aerosols and gases in ambient air) sampling system was used to measure the inorganic ions Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} in the $PM_{2.5}$ aerosol phase and the corresponding inorganic gases HCl, HNO_2, SO_2, HNO_3 and NH_3 present in the gas phase. Samples were collected and analyzed hourly for 3 months between April and June, 2011, from a sampling site in Singapore close to a heavy industrial area containing extensive petrochemical refineries. The data (hourly and daily average) were analyzed, compared and discussed based on the ratios of HNO_2/HNO_3 and NH_3/NH_4^+, the levels of nitrate and sulfate, the total nitrogen, the distribution of particulate matter and gaseous compounds, and the acidity of the aerosols. SO_2 was the most abundant gas that appeared in an order of magnitude higher concentration than the other trace gases, and correspondingly SO_4^{2-} was found to be at least 3–10 times higher than other anionic aerosol species. The concentration of major ions in aerosol samples and the related gaseous compounds followed the order of: $SO_4^{2-} > NH_4^+ > NO_3^- > K^+ > Na^+ > Cl^- > Ca^{2+} > Mg^{2+}$ and $SO_2 > NH_3 > HNO_2 > HNO_3$, respectively. The maximum values for many of the target analytes occurred during the hazy period in May when there was significant contamination from regional fires. The elevated levels of HNO_2 compared to HNO_3 and high levels of HNO_3 were rationalized based on artifacts in the denuder sampling methodology.

1. Introduction

The most commonly used procedures for collecting aerosols are filter-based methods. Filter measurements may have become

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routine but because of their low accuracy it is not simple to quantify ambient aerosols (Appel, 1993; Chang et al., 2001). Furthermore, the atmospheric evaporation of semi-volatile aerosol species and the possible loss of some compounds due to surface reactions due to long time-scale sampling periods have been reported (Appel and Tokiwa, 1981; Appel et al., 1981; Chang et al., 2001; Perrino et al., 1988). It has been estimated that 50% of particulate nitrate (on average) is lost due to volatilization during sampling by Teflon filters (Chang et al., 2001). The combination of denuder systems with filters and impactors have been developed to solve the problems related to filter-base methods (Acker et al., 2005). The denuder is placed after the impactor and filter, and removes semi-volatile gases collected in the impactor (ten Brink et al., 2009).

Dry-coated diffusion denuders were the first generation of denuders with consistent results, but were tedious and provided only long time-average concentration measurements (Bai et al., 2003; Dasgupta, 1993). To overcome these drawbacks, other researchers have developed wet effluent diffusion denuders (Simon and Dasgupta, 1993; Simon et al., 1991), parallel-plate denuders (Simon and Dasgupta, 1995), thermo-denuders (Keuken et al., 1989) and wet-annular denuders (Keuken et al., 1988).

The replacement of filter-based methods by denuder techniques was a milestone in method development, although the denuder technique has been afflicted with blank problems and restricted to single measurements (gas or aerosol) (Bai et al., 2003). The desire to find a reliable collection and measurement system with good gas/particle separation, high time resolution and low detection limits for aerosols has encouraged researchers to develop better methodologies such as steam jet aerosol collectors (SJAC) (Khlystov et al., 1995; Wyers et al., 1993), which add steam to sampled air generating condensation droplets (Simon and Dasgupta, 1995; Zellweger et al., 1999). The combination of SJAC with denuder techniques is now the preferred approach for the simultaneous collection of aerosol species and related trace gases. Usually, these collection methods are followed by online analysis of the resulting aqueous solutions.

Advancements in aerosol measurement systems and modeling capabilities provide an opportunity to investigate the impact of anthropogenic activities on air quality. An online analyzer for monitoring for aerosols and gases (MARGA) is one of the latest measurement systems for semi-continuous analysis of gases and soluble ions in aerosols. The accuracy and performance of two MARGA systems are currently being evaluated by the United States Environmental Protection Agency. Between November 2012 and February 2013 it was found that the slopes of regression between the two instruments was within ±12% for particulate NO_3^- and within ±6% for gaseous SO_2 and NH_3 and particulate SO_4^{2-} and NH_4^+ (www.epa.gov). The data from the instruments was also compared with results from the weekly Clean Air Status and Trends Network (CASTNET) filter in 2011 (Cowen et al., 2011) and recently in April 2013 (www.epa.gov).

MARGA has been used for several short term studies in the Netherlands (ten Brink et al., 2007, 2009), in China (Du et al., 2011) and in Finland (Makkonen et al., 2012). Although it is not currently a common measurement method within aerosol measurement networks (EANET,[1] UKEAP,[2] EMEP[3]), it does offer great potential for rapid online automated measurements and is increasing in importance. Therefore, it is highly desirable to have data collected under a range of conditions from different sites in order compare trends in data and to identify possible errors in the measurement of different species.

2. Experimental

2.1. MARGA instrument

A model ADI 2080 monitor for aerosols and gases in ambient air (MARGA, Applikon Analytical B.V., the Netherlands) with a Teflon coated $PM_{2.5}$ sampling inlet was used to measure the inorganic composition of gases and aerosols in air at an hourly temporal resolution. The MARGA utilizes a Wet Rotating Denuder (WRD) to collect gases, while aerosols are collected by a Steam Jet Aerosol Collector (SJAC). Both the WRD and the SJAC produce aqueous sample streams, which are analyzed by online ion chromatography for anions and cations.

A detailed description of the WRD/SJAC and the analytical procedures is given by Wyers et al. (1993) and Slanina et al. (1992, 2001). The rotating denuder and steam jet aerosol collector, which are responsible for absorbing gases and collecting aerosols, are located in the sampling box. The air sample passes through the impactor and then enters a horizontally aligned WRD that scavenges soluble gaseous species. Water soluble gases are quantitatively (more than 99.7%) (Kim et al., 2011; Li et al., 2010) absorbed in the WRD. According to the difference in diffusion velocity of aerosols and gases, the aerosols pass the WRD and are trapped in the SJAC.

An online Metrohm ion chromatograph was used with two separation columns, Asupp10–75 × 4 mm and C4–100 × 4 mm for anions and cations respectively, the system was equipped with suppressed conductivity detection. Samples were injected *via* loops into 7 mM Na_2CO_3/8 mM $NaHCO_3$ eluent for anions and 3.2 mM HNO_3 eluent for cations. Changes in retention time and detector response were checked and controlled with internal bromide standard addition for anion chromatograph and internal lithium standard addition for cation chromatograph, for each sample during the sampling period.

2.2. Sampling site

Aerosol sampling was conducted at Nanyang Technological University in on the rooftop of the School of Physical and Mathematical Sciences (SPMS) approximately 15 m above the ground and 67 m above sea level between April 2nd and June 26th 2011 (close to 3 months continuously).

This sampling site is situated in the western part of Singapore and is influenced by emissions from major power plants, a plastic and paper incinerator, chemical industries and petroleum refineries located in Jurong Island, Tuas and Jurong Industrial Estate, in addition to heavy vehicular traffic from the Pan Island Expressway (PIE) motorway. Singapore also experiences transboundary haze pollution due to biomass burning in nearby Indonesia, which was particularly severe during 10th–19th May 2011. Table S1 in Supporting Information has summarized detailed information of meteorological conditions experienced during the sampling period.

3. Result and discussion

Measurements of 13 different compounds were performed in the present study which resulted in the collection of approximately 10,000 data points over 3 months. SO_2 was found to be the most abundant gas with an order of magnitude higher concentration than other inorganic trace gases, and reached a maximum value of 331 $\mu g\ m^{-3}$ on 11th May at 14:00 pm. Correspondingly, SO_4^{2-} was also found to be at least 3–10 times higher than other anionic

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[1] Acid Deposition and Monitoring Network in East Asia (EANET).

[2] United Kingdom Eutrophying and Acidifying Pollutants (UKEAP).

[3] European Monitoring and Evaluation Programme (EMEP).