Levels and variability of gaseous acidic compounds in the atmosphere of Athens

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Abstract: Acidic gaseous compounds such as nitric acid, hydrochloric acid and sulfur dioxide (HNO_3, HCl and SO_2 respectively) comprise important atmospheric constituents, with impacts on air quality, human health and acidity of the atmosphere. Despite these effects and with the exception of SO_2, the rest, namely HNO_3 and HCl, are not considered as national priority pollutants and published works in the past concern short term low resolution measurements. This work concerns the levels and the variability of these three acidic compounds at the urban background atmospheric monitoring station of the National Observatory of Athens at Thissio. A high resolution automatic Wet Annular Denuder Ion Chromatography technique is operated providing time resolved hourly averaged data for the period of December 2014 to February 2015, June to October 2015 and February to March 2016. Their diurnal and seasonal variability is investigated and compared to the past works. The role of winter time biomass burning, been reflected on the night-time levels, is also assessed. Emphasis is given on SO_2 since its levels have greatly been limited over the last two decades in Athens, Greece, as a consequence of the de-industrialization of the area, the implementation of antipollution measures and the reduction of emissions due to the financial recession period arising at 2008.

1 Introduction

Nitric acid, hydrochloric acid and sulfur dioxide (HNO_3, HCl and SO_2 respectively) comprise major atmospheric acidic trace gases. Their production pathways and the depletion by reactive species such as the hydroxyl radicals (OH), affect the air quality and oxidative capacity of the atmosphere. HNO_3 is mainly produced during day by the reaction of nitrogen dioxide (NO_2) with OH radicals. Its night-time formation includes reaction of nitrate radicals (NO_3) with organic compounds and the heterogeneous hydrolysis of nitrogen pentoxide (N_2O_5) (Atkinson et al. 2004), whereas the heterogeneous reactions of NO_3 on particles are not that important (Heintz et al. 1996). HNO_3 formation is also involved in ozone (O_3) production, serving thus as nitrogen oxides (NO_x) sink. SO_2 is one of the major products of fossil fuel combustion (e.g. traffic and industry), which is oxidized into sulfuric acid (H_2SO_4) in the atmosphere. It can also be released by volcanoes or as byproduct of the natural metabolism of the dimethyl sulfide (DMS) in marine environments (Berresheim and Jaeschke 1983). The emission of HCl is related to combustion of chloride-containing fuels (e.g. waste incineration), volcanic emissions, water treatment and emissions during manufacturing processes, whereas it is also produced by the secondary reactions of sea-salt dechlorination (Crisp et al. 2014 and references therein). The acidic compounds react with alkaline compounds either in gaseous with ammonia (NH_3) or particulate form (salts such as $CaCO_3$ and/or NaCl). Precisely, NH_3 selectively reacts first with the H_2SO_4; and the excess of ammonia is then available for the neutralization of HNO_3 and HCl, towards the formation of semivolatile salts (Seinfeld and Pandis 1997, Tsimpidi et al. 2007).

The ammonia induced acidity of the produced aerosol regulates the partitioning of the components into the gaseous and particulate phase. Therefore, the levels of the fine particulate matter (PM) in the atmosphere can also be affected by these secondary processes, highlighting thus the role of the gaseous acidic compounds on the control of the PM levels in the atmosphere. Apart from the health impacts, the acidification of the precipitation has adverse effects on ecosystems and the building materials of monuments. Nevertheless, the majority of the published works focuses on the particulate ionic components. Despite the fact that SO_2 is considered as typical regulatory compound, the reactive HNO_3 and HCl are not considered as priority pollutants.

The limited past publications on national level concern short-term measurements of low resolution techniques, not allowing thus the study on intraday basis. In addition, in recent years the atmospheric composition has been differentiated due to changes in the intensity of the emission sources, e.g. improvement of the air quality due to the application of anti-pollution techniques versus degradation due to biomass combustion in domestic heating systems. Therefore,

changes might have also occurred on the levels of the gaseous acidic compounds relative to the past records. The current work aims to (i) provide information on the levels and the seasonal variability of the acidic gases under the current atmospheric conditions using high resolution data that further facilitate the investigation of the diurnal pattern, (ii) assess the current levels of SO_2 taking into account the historical data in Attica basin and (iii) investigate the role of the residential wood burning on the emission of the acidic gases.

2 Data and Methodology

2.1 Sampling site

The measurements were conducted at the air-quality monitoring station of the National Observatory of Athens at Thissio, Athens (37.97° N, 23.72° E). The sampling site located at the top of the Hill of Nymphs, is ideal for the characterization of the urban background air pollution conditions (Grivas et al. 2019), as the station overlooks the city center and serves as receptor point, through dispersion and circulation, of aerosols from different potential sources. The monitoring of the gaseous acidic compounds took place from December 2014 to March 2016, over selected periods representative of cold and warm conditions, as well as during the transition seasons, given the fact each one reflects contrasted air pollution profiles in terms of dominant emission sources and atmospheric processes.

2.2 Methodology

Real-time measurements of SO_2, HCl and HNO_3 were determined using a Wet Annular Denuder combined with an Ion Chromatograph (WAD-IC). The air was drawn at approximately 10 L min^{-1} through the WAD system and sequentially analysis of the samples was carried out by ion chromatography (IC) using a Metrohm 761 compact Ion Chromatograph, providing results in 20 min basis. Reported concentrations were blank corrected and averaged on hourly level. Black carbon levels were measured with Magee Scientific 7-λ aethalometers and the meteorological data were obtained by NOA's automatic meteorological station at Thissio. All the ancillary data were also hourly averaged to facilitate the study.

3 Results

The levels of the acidic gases were semi-continuously measured at Thissio, during December 2014 to February 2015, June to October 2015 and February to March 2016. The hourly concentrations of HNO_3 varied from 0.1 μg m^{-3} to more than 5 μg m^{-3} with a mean of 0.70.6 μg m^{-3}. These values are lower by almost 50% relative to the mean levels of 1.20.77 μg m^{-3} that have been observed in Finokalia Crete on 1996-1999 (Kouvarakis et al. 2001), whereas fall partially within the range of 1.6-4.2 μg m^{-3} reported by Danalatos and Glavas (1999) for the observations at Patras also 20 years ago, despite the lower levels encountered during our study in Athens. Furthermore, past levels obtained by short term late summer measurements in Athens (Eleftheriadis et al. 1998, Tzanis et al. 2009) exhibited also higher values relative to the current ones. HCl measurements are scarce in Athens, with the past late summer time levels of 0.5 μg m^{-3}(adopted by Eleftheriadis et al. 1998) ranging at the same levels as our measurements (0.50.3 μg m^{-3}).

The SO_2 measurements were as high as 44 μg m^{-3} and a mean value of 3.34.8 μg m^{-3} was obtained. Opposite to the other two compounds, SO_2 has gained the scientific interest over the years and it is included in the national reports for the major gaseous pollutants. A sharp decrease on the SO_2 levels was observed on the climatological analysis of Kalabokas et al. (1999) conducted for the central most polluted urban stations in Athens over the period 1987-1997. Precisely, a decrease of 52% was found for the Patision traffic station (located at one of the most congested streets of Attica) between the 1988-1990 and 1995-1997 levels (83±4 μg m^{-3} and 40±4 μg m^{-3} respectively), attributed to the application of abatement measures over the period 1991-1994. The mean annual roadside levels of SO_2 were further decreased to about 14 μg m^{-3} in 2009 (Henschel et al. 2013) and 8 μg m^{-3} in 2019 (annual report of the Greek national network for monitoring air pollution, Ministry of Environment, 2019). The mean level of 3±5 μg m^{-3} observed at Thissio on 2015 fall within the range of the mean annual levels of 4-11 μg m^{-3} reported for the stations of the network in Attica for the respective time period. The overall reduction of SO_2 levels over the years is attributed to the deindustrialization of Athens, application of abatement measures and the reduction of emissions after 2008 due to the financial recession (Vrekoussis et al. 2013).

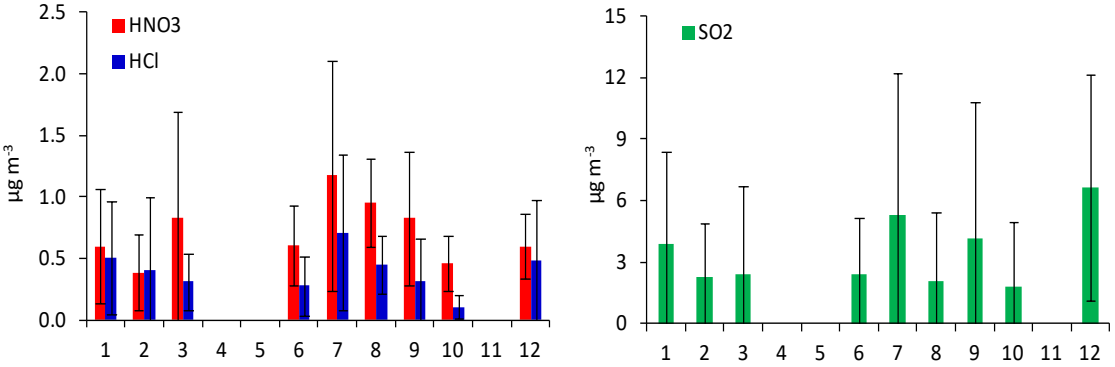

Fig. 1. Mean seasonal variability of HNO_3, HCl and SO_2 in Athens, Greece over the period 2014-2016.

A pronounced seasonal pattern results for HNO_3 (Figure 1), with high concentrations during summer and lower during the remaining months as reported in previous works for Greece (Danalatos and Glavas 1999). The average summer concentration was 70% higher than the winter one. The seasonal pattern for HNO_3 can be attributed to the reaction of NO_2 with OH radicals, with the later been enhanced during summer, as well as the absence of precipitation given its high solubility in water. The high levels during the warm period could also be attributed to the increased volatility of the particulate NH_4NO_3 under high temperatures that favors the presence of the gaseous HNO_3. The HCl seasonal profile follows that of HNO_3 depicting thus a summer-time peak, which could be linked with its production by the reaction of HNO_3 with sea salt the absence of precipitation and the volatilization of NH_4Cl. SO_2 demonstrated higher mean levels in winter relative to summer by almost 30%, whereas an average background of about 2 μg m^{-3} was maintained at the city. In general terms, the regional character of SO_2 was reported since the 1970s (e.g. OECD 1977; Eliassen and Saltbones 1983), establishing thus the trans-boundary transport as key process determining its atmospheric concentration. The increased SO2 levels in summer are attributed to absence of rain and enhanced transport from the N and NE sector which is typical for this period of the year. The winter maximum could be related to the increase of emissions by heating in combination with the lower mixing layer (Alexiou et al. 2018) relative to the summer.

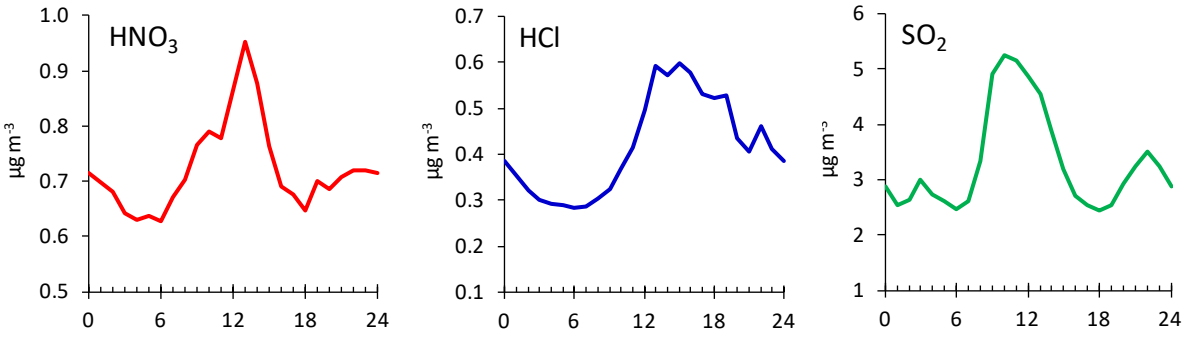

Fig. 2. Mean diurnal variability of HNO_3, HCl and SO_2 in Athens, Greece over the period 2014-2016.

In daily level, the mean annual cycles depict a bimodal distribution with a major morning-noon and a secondary late evening to night maximum, with significant differences for each species (Figure 2). The average ratio of the daytime to nighttime peak concentrations measured for HNO_3 was above unit (~1.3), highlighting thus its photochemical production and the volatilization of NH_4NO_3 during the warm hours of the day, in accordance with the observations of the seasonal trend. The diurnal variability of HCl is driven by the presence of HNO_3, depicting thus similar pattern, characterized though by less late afternoon variability. Concerning SO_2 and taking into account its regional origin, the late morning maximum (~1.5 relative to the night one) is linked with the development of the boundary layer and the intrusion of the long range transported air masses. During winter enhancement is expected on the nigh-time levels of SO_2 due to the shallow boundary layer. On the other hand the photochemically produced HNO_3 as well as HCl are expected to present higher noon maxima during summer. Furthermore, SO_2 is not expected to present important difference on the diurnal pattern between weekdays and weekends due to its regional character. The same trend is expected for HCl, whereas HNO_3 levels should be decreased during the weekends at noon due to limited precursors availability namely NOx from vehicular emissions.

Table 1. Mean levels of the acidic gases on winter night-time depending on the presence of smog events.

Acidic gases	Total	SP	nSP
HNO_3 (μg m^{-3})	0.6	0.7	0.4
HCl (μg m^{-3})	0.5	0.3	0.7
SO_2 (μg m^{-3})	4.1	6.0	2.1

To assess the possible impact of heating and especially of wood burning that has an impact on Athens atmosphere during night over the last years (Liakakou et al. 2020), Table 1 presents the levels of the acidic compounds during night-time (22:00 – 2:00) in winter. Additionally, the night-time data of HNO_3, HCl and SO_2 obtained on winter 2014-2015, were classified in smog and non-smog periods (SP and nSP, respectively), taking into account the combination of low wind speed and the absence of precipitation (Fourtziou et al. 2017) conditions that enhance the accumulation of all pollutants. The selected time frame corresponds to the peak time of BC_{bb}. The role of the combustion processes during the enhancement of biomass burning is obvious on the SO_2 levels with an increase by almost 3 times relative to the non smog periods. Less significant is the impact on the HNO_3 night time concentrations by almost 50%, but still important. HCl present an opposite trend with higher levels during the non smog periods, supporting production by heterogeneous reactions of gaseous HNO_3 with sodium chloride (NaCl) of transported sea salt particles (Mihalopoulos et al. 1997) under favoring conditions, i.e. dominance of marine originated air masses and wind speed > 3msec^{-1}. The stagnant conditions of the smog periods are poor in precursors, leading thus in lower concentrations for the HCl.

4 Conclusions

The current work reports the levels of HNO_3, HCl and SO_2 in Athens, Greece over the period 2014-2016, using high resolution data obtained at the urban background station of the National Observatory of Athens at Thissio. Reduction on the mean levels of HNO_3 and SO_2 was observed compared to past works, whereas HCl is maintained at approximately the same levels, considering also the limited monitoring of the later. Furthermore, the proximity of the mean annual value of 3±5 μg m^{-3} SO_2 observed at Thissio on 2015 relative to the levels reported for the Attica by the national network for monitoring of air pollution, reflects the regional profile of the pollutant. The photoxidation reactions of NO_2 with OH radicals and the volatilization of the particulate NH_4NO_3, seem to drive the production of HNO_3 on both diurnal and seasonal basis, leading to maximum values during the warm period of the day and the year by almost 30% and 70% respectively. Similar variability was observed for the HCL, driven by the reaction of HNO_3 with sea salt. The absence of sea salt under the stagnant conditions that favors the smog events during winter nights in the urban environment of Athens can be considered as the regulating factor of the limited impact of the heating activities on the nocturnal levels of HNO_3. On the contrary, SO2 was linked to combustion processes during winter, whereas the summer time enhancement was attributed to absence of rainfall and regional transport as well.

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