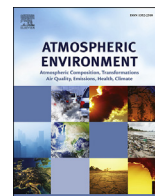




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Sulphuric acid and aerosol particle production in the vicinity of an oil refinery



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HIGHLIGHTS

- One month in-situ measurements were conducted close to a large oil refinery.
- We observed elevated concentrations of H₂SO₄ and nano-particles from oil refinery.
- SO₂, H₂SO₄ and particle concentrations showed source dependent behaviour.
- Large fraction of the particle growth could be accounted to sulphuric acid.

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ABSTRACT

In this paper we introduce in-situ observations of trace gases, aerosol particles and their precursors in the vicinity of an oil refinery and industrial area in Kilpilahti, Southern Finland. We conducted a one-month measurement campaign near the oil refinery during summertime when the sulphur dioxide concentrations at the site are typically the highest. The source areas around the measurement location were divided into three sectors: oil refinery area, industrial area and non-industrial area. The atmospheric concentrations of aerosols and trace gases showed a large temporal variability, when exposed to the different source areas. The median sulphur dioxide concentrations for the oil refinery, industrial and non-industrial area were 1.88 ppbv, 0.75 ppbv and 0.38 ppbv, respectively, and the corresponding sulphuric acid concentrations were 11.5×10^6 molecules/cm³, 4.4×10^6 molecules/cm³ and 1.3×10^6 molecules/cm³. The observed concentrations were similar to what have been measured in urban or industrial sites. The ratio between sulphuric acid and sulphur dioxide was the highest when the air mass was coming from the oil refinery. The correlation between the sulphuric acid and 1–2 nm particle concentrations was significant, but the composition of the particles remained unknown as no neutral sulphuric acid clusters were detected with the mass spectrometer. Only a few new particle formation events were observed during the measurement period, and during these events a large fraction of the particle growth could be explained by sulphuric acid condensation.

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1. Introduction

Atmospheric sulphur dioxide is connected to several important

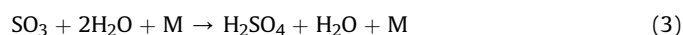
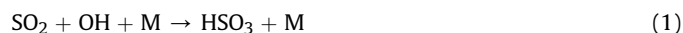
atmospheric phenomena: global warming, air pollution and acid precipitation. Sulphur dioxide has both natural and anthropogenic sources. The anthropogenic emissions have increased dramatically after the industrialization since the main source of sulphur dioxide is the combustion of fossil fuels. Over the past thirty years the emissions of sulphur dioxide have decreased significantly in Europe due to adaptation of new technologies and stricter regulations

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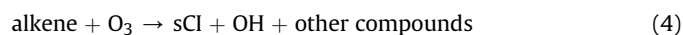
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(Stern, 2005; Smith et al., 2001). In Finland the emissions have been relatively low compared to other parts of Europe but still a clear decrease in the atmospheric concentrations have been observed (Anttila and Tuominen, 2010; Kyrö et al., 2014; Nieminen et al., 2014). The emissions of sulphur dioxide in Finland reached their maxima in 1980s when the total emissions were 600 kilo tons (Estlander, 2002). Since then the emissions have decreased significantly and the total emission of sulphur dioxide have dropped to 100 kilo tons.

Sulphur dioxide oxidizes to sulphuric acid in the atmosphere when an oxidant, for example hydroxyl radical (OH), is present (Eqs. (1)–(3)).



The hydroxyl radical is produced by photolysis of ozone or HONO and in the reaction between HO₂ and NO, so its concentration is dependent on the amount of sunlight. During the recent years, the role of stabilized Criegee Intermediates (sCI) in sulphuric acid production has been under discussion (Mauldin et al., 2012; Berndt et al., 2012; Boy et al., 2013). Stabilized Criegee Intermediates are formed in a reaction between alkenes and ozone (Eq. (4)), so they are abundant, for example, in a boreal forest environment where monoterpenes are present (Hakola et al., 2012).



Stabilized Criegee intermediates can oxidize SO₂ to SO₃ which can undergo reaction 3 if water is present. The reaction with water vapour compete with Eq. (5) and the predominant pathway depends on the composition of sCI (Berndt et al., 2014), so the importance of sCI as an oxidizer depends strongly on the precursors of sCI and the atmospheric conditions. In the reaction of ozone and alkenes also OH radicals are produced so not all of its production is depend on sunlight (Atkinson et al., 1992).

Atmospheric sulphuric acid has an important role in the initial steps of new particle formation (Sipilä et al., 2010; Kerminen et al., 2010; Kulmala et al., 2013). In a boreal forest environment, sulphuric acid has been estimated to be responsible for about 1–15% of the 3–25 nm particle growth (Nieminen et al., 2014). Atmospheric aerosol particles have a net cooling effect on the climate. As the sulphate aerosol concentrations have decreased significantly, the global warming is enhanced (Shindell and Faluvegi, 2009).

Air quality in the vicinity of Kilpilahti industrial area in Southern Finland has been regularly monitored since 1970s, and since 1990s the total sulphur dioxide emissions have been around 5 kilo tons per year. In this study, we examined the variability of sulphur dioxide and sulphuric acid concentration at the site. We studied how the sulphur dioxide emissions are reflected in sulphuric acid concentrations and thereby in the atmospheric sub-micron aerosol population. We divided the surroundings of the measurement station into different sectors to see how the source area of the air mass affects the concentrations. The aim of the study was to get information on the concentrations and behaviour of sulphuric acid and nano-particles in the vicinity of an oil refinery and to get insight into the formation of sulphuric acid and nano-particles close to the emission source.

2. Methods

2.1. Site description

The Kilpilahti industrial area in Porvoo, Southern Finland, is the largest centre of oil refinery and chemical industry in the Nordic countries. The industrial area covers 13 square kilometres and consists of Finland's largest harbour, road distribution terminal, railway unload terminal, technology research centre and ten different companies that are involved in a whole production chain from raw oil to plastics. Total emissions of the industrial area in 2012 were 2890 tons of nitrogen oxides, 5320 tons of sulphur dioxide, 138 tons of particulate matter and 4060 tons of volatile organic compounds. The largest sources of sulphur dioxide are industrial processes that cause 78% of the emissions. Energy production is also an important source, causing 21% of the sulphur dioxide emissions. Harbour activity, oil heating and road traffic are minor sulphur dioxide sources in the area.

We conducted one month (from June 7th to July 5th 2012) measurement campaign in Nyby measurement station which is located 1.5 km from the oil refinery (Fig. 1). Neste Oil performs there continuous sulphur dioxide measurements (Thermo Scientific™ Model 43i SO₂ Analyser, detection limit 1 µg/m²) that we utilized in this study.

2.2. Campaign instrumentation

Oxidized vapours, such as sulphuric acid (Eisele and Tanner, 1993; Petäjä et al., 2009) and Extremely Low Volatility Organic Compounds (ELVOC, Ehn et al., 2014), were measured with a Chemical Ionization Atmospheric Pressure interface Time-Of-Flight mass spectrometer (CI-API-TOF, Jokinen et al., 2012) that used nitrate ion as reagent ion. The instrument consists of an API-TOF (Tofwerk AG, Thun, Switzerland and Aerodyne Research Inc., USA, Junninen et al., 2010) and an inlet with ²⁴¹Am radioactive ion source. In the measurements 20 lpm of sheath gas (filtered air) is mixed with 5 mlpm nitric acid flow. The sheath gas is first guided through the ionizer and then guided with voltages to meet the sample flow (10 lpm). An ion filter was used to ensure that ambient ions do not contribute to the measured concentrations. With this method sulphuric acid is detected as a bisulphate ion HSO₄⁻ and as its cluster with nitric acid HNO₃HSO₄⁻. All the ELVOCs are detected as clusters with the nitrate ion. The concentration of trace gases is calculated by dividing the signals in question by the signals of reagent ions (NO₃⁻, HNO₃NO₃⁻ and (HNO₃)₂NO₃⁻) and multiplying it with a calibration coefficient (Jokinen et al., 2012). The CI-API-TOF was functioning on the site from June 7th to 18th and from June 25th to July 7th.

A Particle Size Magnifier (PSM, Vanhanen et al., 2010) and a Differential Mobility Particle Sizer (DMPS, Aalto et al., 2001) were used to detect particle size distributions. The PSM was used in scanning mode, which means that the supersaturation is changed by altering the saturator flow rate to give size information of 1–2 nm particles (Lehtipalo et al., 2014). The measurement cycle was 2 min. The PSM was operating on the site from June 11th to 13th and from June 27th until July 5th. A Differential Mobility Particle Sizer (DMPS) was used to measure particles from 6 to 1000 nm. In order to measure this size range, two flow rates were used. The particles with mobility diameter of 6–200 nm were measured with a flow rate of 4 lpm and particles in the diameter range 200–1000 nm were measured with a flow rate of 1 lpm. The time resolution of these measurements was 10 min. The DMPS was operating throughout the campaign from June 7th to July 5th 2012.

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